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**INVESTIGATION OF ADHESION OCCURRING BETWEEN  
POLYURETHANE SUBSTRATES AND POLYURETHANE SURFACE COATINGS**

by

**KHOSROW BIDARI**

A Doctoral Thesis submitted in partial fulfilment  
of the requirements for the award of  
Doctor of Philosophy  
of the  
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Supervisor: R J. Heath, PhD

Institute of Polymer Technology and  
Materials Engineering

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This thesis is dedicated to my dear parents and my  
darling wife, Parvaneh.

\* \* \* \* \*



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## ERRATA

<u>Page No</u>	<u>Line No</u>	
3	5	'will remain' for 'remains'
4	Table 1.1	add 'foam' after 'rigid'
6	10	insert full stop after 'involved' - insert 'these' before 'can'
7	15	insert 'are' after 'thinners'
25	12	'neutralisation of' for 'neutralising'
27	15	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si} - \text{O}- \text{ for } (\text{CH}_3)_2 \text{SiO}^- \\   \\ \text{CH}_3 \end{array}$
27	16	insert 'it' after 'using' - delete 'it' after 'alone'
40	8	'made' for 'being' - delete 'the'
50	17	'swelling' for 'intumescing'
80	10	'observed' for 'real'
82	2	'adsorption' for 'adhesion'
83	16	'the' for 'both'
98	25	'confined' for 'combined'
99	9	'molecular layer' for 'lattice'

NB: All line numbers refer to text only; headings, diagrams and equations not being counted.

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## ABSTRACT

In the last two decades a substantial amount of research has been carried out on the physico-chemical aspects of adhesion. However, this phenomenon when related to organic coatings on polymeric substrates has undergone only limited study.

This research primarily studies the adhesion properties of polyurethane (PU) paint materials applied to a range of different PU substrate materials. Some PU coated polyester substrates are also used to provide a more complete understanding of interfaces produced. The coating of substrates has been by the traditional technique of post-mould coating (PMC) and a relatively new technique of in-mould coating (IMC).

This thesis gives a review of the chemistry of polyurethane and related materials, the surface coating of plastics with special emphasis on the need for protection of PU products, the theories of adhesion and the concepts of wetting and surface thermodynamics. The materials, equipment and techniques used for the preparation of IMC and PMC mouldings are also described.

A number of physical and chemical surface analysis techniques are carried out on original and coated substrates to determine the thermodynamic properties of solid surfaces.

Various mechanical tests are employed to measure the strength of adhesion in coated substrates and to evaluate the modes of failure, including tensile adhesion pull-off, instrumented falling weight impact and hardness. The feasibility of thermal analysis techniques is examined and the results of differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) reported. The nature of surface topography is examined using electron microscopy and X-ray microanalysis.

It is concluded that mechanisms promoting interfacial bonding of IMC and PMC systems are based on a combination of adhesion theories. For IMC systems some potential for chemisorptive bonding may be expected if free isocyanate and hydroxyl are present on both surfaces. For PMC systems considerable potential for dispersive and polar forces may exist.

It is argued that interfacial interaction between PU or a polyester substrate and a PU based coating depend on processing conditions. However, to optimise adhesive bonding the physical and chemical activity of surfaces must be maximised during processing. The overall results indicate that IMC mouldings are generally superior in terms of their interfacial and adhesion properties to PMCs.

## TABLE OF CONTENTS

	<u>Page No</u>
Acknowledgements . . . . .	i
Abstract . . . . .	ii
Table of Contents . . . . .	iv
List of Figures . . . . .	xii
List of Tables . . . . .	xvii
 CHAPTER 1: INTRODUCTION . . . . .	 1
 CHAPTER 2: POLYURETHANE CHEMISTRY AND ITS RELATED MATERIALS . . . . .	 10
2.1 Introduction . . . . .	10
2.2 Polyurethanes: A Chemical Review . . . . .	10
2.2.1 Addition Polymerisation of Isocya- nates with Active Hydrogen Containing Compounds . . . . .	13
2.2.2 Self-addition Oligomerisation of Isocyanates . . . . .	15
2.3 Materials for Conversion into PU Coatings and Substrates . . . . .	16
2.3.1 Isocyanates . . . . .	17
2.3.2 Polyols and Diols . . . . .	18
2.3.3 Catalysts . . . . .	22
2.3.4 Chain Extenders and Crosslinking Agents . . . . .	23
2.3.5 Blowing Agents . . . . .	24
2.3.6 Release Agents . . . . .	26
2.4 Polyurethanes as Substrates . . . . .	28
2.4.1 Polyurethane Foams . . . . .	29
2.4.2 Polyurethane Elastomers . . . . .	30
2.4.3 Polyurethane Reaction Injection Moulding . . . . .	30
2.4.3.1 Why RIM-PU? . . . . .	32

	<u>Page No</u>
2.5 Polyurethanes as Surface Coatings . . . . .	34
2.5.1 Commercial Types of PU Surface Coatings . . . . .	34
2.5.1.1 One- and two-pack PU surface coatings . . . . .	35
A) General properties of one- and two-pack PU coatings . . . . .	40
2.5.1.2 Powder Coatings . . . . .	40
2.5.1.3 100% Solid Coatings . . . . .	41
2.5.2 The Advantages of Polyurethane Surface Coatings . . . . .	41
2.6 Other Materials Used for PU Coatings . . . . .	41
2.6.1 Thinners . . . . .	42
2.6.2 Pigments . . . . .	43
2.6.3 Flow Agent . . . . .	45
2.6.4 Bodying Agent . . . . .	45
2.6.5 Flattening Agent . . . . .	45
2.6.6 Anti-foaming Agent . . . . .	46
<b>CHAPTER 3: SURFACE COATING OF PLASTICS . . . . .</b>	<b>47</b>
3.1 A Review . . . . .	47
3.2 Reasons for Coating Plastic Substrates . . . . .	49
3.2.1 Coated Polyurethane Products and Reasons for Protection . . . . .	51
3.2.2 Ultraviolet (UV) Stability of Aromatic Isocyanates Based PU Mouldings . . . . .	52
3.3 Surface Coatings of PU Substrates: Application and Method . . . . .	54
3.3.1 Painting Techniques . . . . .	54
3.3.1.1 Paint spraying application equipment . . . . .	56

	<u>Page No</u>
3.3.2 Printing Techniques . . . . .	57
3.4 Common Process Methods for Coating PU Substrates . . . . .	58
3.4.1 Post-Mould Coating (PMC) . . . . .	58
3.4.1.1 Weatherproof coating of spray applied PU foams . . . . .	63
3.4.2 In-Mould Coating (IMC) . . . . .	65
3.4.2.1 Barrier release coats (BRC) . . . . .	68
3.4.3 General Properties of IMC and PMC . . . . .	71
3.5 Alternatives to Surface Coating . . . . .	71
 <b>CHAPTER 4: ADHESION AND INTERFACIAL BONDING . . . . .</b>	 <b>74</b>
4.1 Adhesion: Introduction . . . . .	74
4.2 Theories of Adhesion . . . . .	75
4.2.1 Adsorptive Effect . . . . .	76
4.2.2 Electrical Double Layer (EDL) Theory . . . . .	81
4.2.3 Mechanical Interlocking and Related Surface Topography Theories . . . . .	84
4.2.4 Diffusion Theory . . . . .	88
4.2.5 Weak Boundary Layer (WBL) Effects . . . . .	93
4.3 Interfacial Bonding . . . . .	97
4.3.1 The Interface: Observations . . . . .	97
4.3.2 Interfacial Properties . . . . .	100
4.4 Interfacial and Adhesion Properties of Polymeric Systems . . . . .	102
4.5 Factors Affecting the Adhesion . . . . .	103
4.5.1 The Effect of Contact Time on Adhesion . . . . .	103
4.5.2 The Effect of Pressure on Adhesion . . . . .	105
4.5.3 The Effect of Temperature on Adhesion . . . . .	105



	<u>Page No</u>
<b>CHAPTER 5: THERMODYNAMICS OF ADHESION . . . . .</b>	<b>107</b>
5.1 An Introduction to Wetting and Adhesion . .	107
5.2 Work of Adhesion and Cohesion . . . . .	108
5.3 The Equilibrium Spreading Pressure, $\Pi_e$ . .	110
5.4 The Spreading Coefficient, $S_C$ . . . . .	112
5.5 The Surface Energy (Tension) of Liquids and Solids . . . . .	116
5.6 Surface Tension of Low and High Energy Solid Surfaces, $\gamma_S$ . . . . .	117
5.7 Surface Tension of Solids: Methods of Measurement . . . . .	121
5.7.1 Indirect Methods of Measurement for $\gamma_S$ . . . . .	121
5.7.1.1 Contact angle . . . . .	122
5.7.1.2 Critical surface tension, $\gamma_C$ . . . . .	127
5.7.1.3 Application of acid-base theory . . . . .	130
5.7.1.4 The harmonic mean method . . . . .	133
5.7.1.5 The geometric mean method . . . . .	134
5.7.1.6 The equation of state method . . . . .	135
<b>CHAPTER 6: RESEARCH PROJECT: AIMS AND OBJECTIVES . . .</b>	<b>137</b>
6.1 Project Aims and Objectives . . . . .	137
<b>CHAPTER 7: MATERIALS, EQUIPMENT AND SAMPLE PREPARATION</b>	<b>141</b>
7.1 Introduction . . . . .	141
7.2 Materials and Equipment . . . . .	143
7.2.1 Coating Materials . . . . .	143
7.2.2 Materials and Formulations for PU-RIM Moulding . . . . .	143
7.2.3 Materials for PU Foams Processing . . . . .	144
7.2.4 Polyester Materials . . . . .	145

	<u>Page No</u>
7.2.5 Materials for Coated PU Spray Foam Production . . . . .	146
7.2.6 Mould Release Agent . . . . .	147
7.2.7 Spraying Equipment . . . . .	148
7.2.8 Health and Safety Considerations . .	150
7.3 Sample Preparation . . . . .	150
7.3.1 PU-RIM Processing and Sample Preparation . . . . .	150
7.3.2 PU Foams Sample Preparation . . . . .	152
7.3.3 Polyesters Formulations and Sample Preparation . . . . .	153
7.3.4 Coated PU Spray Foam Preparation . .	155
<b>CHAPTER 8: SURFACE ANALYSIS TECHNIQUES . . . . .</b>	<b>157</b>
8.1 Introduction . . . . .	157
8.2 Surface Analysis: Physical Techniques . . .	157
8.2.1 Methods of Measurement of Contact Angle ( $\theta$ ) . . . . .	158
8.2.2 Experimental Procedure . . . . .	158
8.2.3 Initial Investigation . . . . .	160
8.2.4 Contact Angle and Wettability Results	162
8.2.5 The Relationship Between Work of Adhesion, $W_A$ , Spreading Coefficient, $S_C$ and the Surface Tension of Testing Liquids, $\gamma_{LV}$ . . . . .	169
8.2.6 Surface Tension, $\gamma_S$ , of Polyurethane and Polyester Substrates . . . . .	171
8.2.7 Modification and Simplification of Some Thermodynamic Relationships . .	183
8.2.7.1 Results and discussion . .	184
8.2.8 Wettability of Polyurethane Sub- strates . . . . .	188
8.2.9 Wettability of Polyester Substrates .	189
8.3 Surface analysis: Chemical Techniques . . .	190

	<u>Page No</u>
8.3.1 Applications and Limitations . . . . .	190
8.3.2 Results and Discussion . . . . .	193
<b>CHAPTER 9: MECHANICAL TESTING TECHNIQUES . . . . .</b>	<b>197</b>
9.1 Introduction . . . . .	197
9.2 Tensile Adhesion Pull-Off: Measurements, Results and Discussion . . . . .	197
9.2.1 Introduction . . . . .	197
9.2.2 The Choice of Test Method . . . . .	198
9.2.3 Expected Modes of Failure . . . . .	200
9.2.4 Experimental Procedure . . . . .	202
9.2.5 Results and Discussion . . . . .	206
9.3 Impact Properties: Measurements, Results and Discussion . . . . .	225
9.3.1 Introduction . . . . .	225
9.3.2 Impact Properties of Coated Plastics . . . . .	225
9.3.3 Experimental Procedure . . . . .	227
9.3.4 Results and Discussion . . . . .	231
9.4 Non-Quantitative Adhesion Tests: Measure- ments, Results and Discussion . . . . .	243
9.4.1 Introduction . . . . .	243
9.4.2 Cross-Cut Hardness Test . . . . .	243
9.4.2.1 Experimental procedure . . . . .	244
9.4.2.2 Results and discussion . . . . .	245
9.4.3 Scratch Hardness Test . . . . .	249
9.4.3.1 Experimental procedure . . . . .	250
9.4.3.2 Results and discussion . . . . .	250
<b>CHAPTER 10: THERMAL ANALYSIS TECHNIQUES . . . . .</b>	<b>256</b>
10.1 Introduction . . . . .	256
10.2 Differential Scanning Calorimetry (DSC) . . . . .	256
10.2.1 Theory of DSC . . . . .	257
10.2.2 DSC: Experimental Procedure . . . . .	260

	<u>Page No</u>
10.2.3 DSC: Results and Discussion . . . .	261
10.3 Dynamic Mechanical Thermal Analysis (DMTA) .	276
10.3.1 Theory of DMTA . . . . .	278
10.3.2 DMTA: Experimental Procedure . . . .	280
10.3.3 DMTA: Results and Discussion . . . .	281
<b>CHAPTER 11: SCANNING ELECTRON MICROSCOPY (SEM) AND X-RAY MICROANALYSIS . . . . .</b>	<b>287</b>
11.1 Introduction . . . . .	287
11.2 SEM and EDX Techniques . . . . .	288
11.3 Coating Process . . . . .	290
11.4 Experimental Procedure . . . . .	291
11.5 Results and Discussion . . . . .	292
<b>CHAPTER 12: DISCUSSION . . . . .</b>	<b>315</b>
12.1 Introduction . . . . .	315
12.2 Discussion . . . . .	315
12.2.1 General Discussion on IMC and PMC Performances . . . . .	315
12.2.2 Discussion on Thermodynamic Properties of Coated Samples . . . . .	325
12.2.3 Discussion on Mechanical Properties of Coated Samples . . . . .	331
12.2.4 Discussion on Thermal Properties of Coated Samples . . . . .	345
12.2.5 Discussion on SEM and EDX Studies of Coated Samples . . . . .	347
12.3 Proposed Scenarios for Change in State of Interfaces . . . . .	351
<b>CHAPTER 13: CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK</b>	<b>354</b>
13.1 Introduction . . . . .	354
13.2 Conclusions . . . . .	354
13.3 Suggestions for Further Work . . . . .	356

	<u>Page No</u>
APPENDICES . . . . .	358
REFERENCES . . . . .	361
PUBLISHED WORKS . . . . .	390

## LIST OF FIGURES

<u>Figure No</u>		<u>Page No</u>
1.1	Property Matrix of Polyurethanes . . . . .	2
1.2	European and World PU Markets . . . . .	3
1.3	Comparison of Curing Energy Requirements . .	6
2.1	Different Techniques for Polyurethane Synthesis . . . . .	11
2.2	Prepolymer Route for the Production of Polyurethanes . . . . .	12
2.3	Growth in Total PU Use 1980-1989 . . . . .	28
2.4	Material Energy Requirements . . . . .	33
3.1	Proportion (%) of Different Materials in Cars	47
3.2	Cross-Section of a Silicone Mould During the PU Curing Stage . . . . .	69
4.1	Molecular Attraction . . . . .	75
4.2	Potential Energy Curves of Various Bonding Forces . . . . .	80
4.3	The Effect of Surface Roughness . . . . .	85
4.4	Surface Coating of a Substrate . . . . .	88
4.5	Relation Between Measured Peeling Energy, $P_D$ , and Contact Time for the Autohesion of Polyisobutylenes of Various Molecular Weights	91
4.6	Dependence of Adhesion $Ad$ , of Copolymer SKN-40 to Cellophane on Time, $T$ , Elapsed from the Moment of Preparing the Bonded Specimen to the Moment of Testing . . . . .	104
4.7	Dependence of Adhesion, $Ad$ , of Copolymer SKN- 40 to Cellophane on the Temperature, $t$ , of Heating the Bonded Specimen . . . . .	106
5.1	Possible Actions of A Droplet of Liquid Contacting a Solid Surface . . . . .	107

5.2	The Mechanical Equilibrium of a Drop Resting on a Plane Solid Surface Under the Action of Three Surface Tensions . . . . .	108
5.3	Schematic Illustrating the Work of Adhesion in Separating a Liquid from a Solid's Surface . .	109
5.4	Schematic Illustrating the Work of Cohesion in Separating a Liquid or Solid into Two Parts .	110
5.5	Surface Tension vs Spreading Coefficient of Some Liquids on Fluorinated Polymers . . . . .	114
5.6	Schematic Diagram Illustrating Test Method Used to Measure Spreading Coefficient of a Liquid on a Solid . . . . .	115
5.7	Liquid Surface Tension vs Cosine for Four Series of Liquids on PTFE at 20°C . . . . .	123
5.8	Liquid Surface Tension vs Cosine of the Contact Angle for Several Liquids on Surfaces of High Polymers Studied . . . . .	126
5.9	Critical Surface Tension, $\gamma_C$ . . . . .	127
5.10	Zisman Plots for Polytetrafluoroethylene (PTFE) Using n-alkanes as the Testing Liquids, and for Polyethylene (PE) Using Various Testing Liquids . . . . .	129
5.11	Wettability of Polyvinyl Chloride, Polyvinylidene Chloride, and a Close-Packed Monolayer of Perchloropentadienoic Acid on Platinum, by Various Liquids . . . . .	129
5.12	Zisman Plot for Polytetrafluoroethylene Using Various Testing Liquids . . . . .	129
5.13	Equation of State Plots for Some Polymers at 20°C . . . . .	136
7.1	The Sprite Airbrush . . . . .	149
7.2	Spraying Action . . . . .	150
7.3	Schematic Diagram of RIM Machine . . . . .	151

8.1	$\cos\theta$ v $\gamma_{LV}$ for PE and PTFE Substrates . . . . .	163
8.2	$\cos\theta$ v $\gamma_{LV}$ for PE Substrates . . . . .	163
8.3	$\cos\theta$ v $\gamma_{LV}$ for PTFE Substrates . . . . .	164
8.4	Comparison of Wettability Results for PE and PTFE Substrates Using Various Data . . . . .	164
8.5	$\cos\theta$ v $\gamma_{LV}$ for PU Substrates . . . . .	167
8.6	$\cos\theta$ v $\gamma_{LV}$ for Polyester Substrates . . . . .	168
8.7	$W_A$ and $S_C$ Relationships for PU Substrates . .	174
8.8	$W_A$ and $S_C$ Relationships for Polyester Substrates . . . . .	174
8.9	Equation of State Plots for PU Substrates . .	182
8.10	Equation of State Plots for Polyester Substrates . . . . .	182
8.11	A Schematic Diagram Representing the Modified Thermodynamic Model . . . . .	185
8.12	$\cos^2 \theta/2$ v $\gamma_{LV}$ for PU Substrates . . . . .	186
8.13	$\cos^2 \theta/2$ v $\gamma_{LV}$ for Polyester Substrates . . .	186
8.14	$\cos\theta$ and $\cos^2 \theta/2\gamma_{LV}$ for PE Substrates Using Various Data . . . . .	187
8.15	$\cos\theta$ and $\cos^2 \theta/2\gamma_{LV}$ for PTFE Substrates Using Various Data . . . . .	187
8.16	Schematic Representation of Surface Analysis Methods . . . . .	192
8.17	IR Results for Some Substrate and Coating Materials . . . . .	194
8.18	FT-IR Results for X-226/C2885 and MRC (600) Coatings at Different Time Intervals . . . . .	195
9.1	Schematic Drawing of the Direct and the Sandwich Methods of Tensile Pull-off Test . .	198
9.2	Schematic Drawing of Lines of Force Existing During Pull-Off Test . . . . .	199



9.3	Isochromatic and Isopachic Pattern Representing Stress Distribution in a Sandwich and in a Direct Method of Pull-Off Test Assembly . . . . .	200
9.4	Modes of Failure of Adhesion Pull-Off Samples	201
9.5	Schematic Drawing of Specimens Preparation for Sandwich Pull-Off Test . . . . .	203
9.6	Bond Failure Load for IMC and PMC PU Substrates (kg) . . . . .	214
9.7	Mean Failure Stress for IMC and PMC PU Substrates ( $\text{MNm}^{-2}$ ) . . . . .	215
9.8	Bond Failure for IMC and PMC Polyester Substrates (kg) . . . . .	216
9.9	Mean Failure Stress for IMC and PMC Polyester Substrates ( $\text{MNm}^{-2}$ ) . . . . .	217
9.10	Bond Failure Load for Coated PU Spray Foam Substrates (kg) . . . . .	218
9.11	Mean Failure Stress for Coated PU Spray Foam Substrates ( $\text{MNm}^{-2}$ ) . . . . .	218
9.12	(a) Impact Failure of Coated Plastics; (b) Effect of Primer Flexibility on Crack Propagation; (c) Effect of Coating Flexibility on Impact Properties of ABS Specimens . . . . .	228
9.13	Instrumented Falling Weight Impact Tester . .	228
9.14	Impact Force-Deformation Trace . . . . .	229
9.15	Different Types of Impact Failure . . . . .	232
9.16	Average Peak Energy for IMC and PMC PU Substrates (J/mm) . . . . .	236
9.17	Average Peak Energy for IMC and PMC Polyester Substrates (J/mm) . . . . .	237
9.18	Average Peak Energy for Coated Spray Foam Substrates (J/mm) . . . . .	238

<u>Figure No</u>		<u>Page No</u>
9.19	Cross-Cut Hardness Classification for IMC and PMC PU Substrates . . . . .	247
9.20	Cross-Cut Hardness Classification for IMC and PMC Polyester Substrates . . . . .	247
9.21	Scratch Hardness Classification for IMC and PMC PU Substrates . . . . .	252
9.22	Scratch Hardness Classification for IMC and PMC Polyester Substrates . . . . .	253
10.1	Schematic Diagram of a Typical Differential Thermal Analyser System . . . . .	258
10.2	An Ideal Representation of Major Processes Observable in DSC . . . . .	258
10.3	DSC Cell Cross Section . . . . .	260
10.4	DSC Scans of Various One and Two Pack PU Coatings . . . . .	262
10.5	DSC Scans of Coated Semi-Flexible PU Foam Substrates . . . . .	263
10.6	DSC Scans of Coated Rigid PU Foam Substrates .	264
10.7	DSC Scans of Coated PU-RIM Substrates . . . .	265
10.8	DSC Scans of Coated C <sub>196</sub> Polyester Substrates	266
10.9	DSC Scans of Coated C <sub>198</sub> Polyester Substrates	267
10.10	DSC Scans of Coated C <sub>199</sub> Polyester Substrates	268
10.11	DSC Scans of Coated PU Spray Foam Substrates	269
10.12	Argand Diagram Showing Dynamic Storage E' and Loss E'' Module and Tan $\delta$ Under Sinusoidal Loading . . . . .	279
10.13	A Schematic Representation of Temperature on Storage Modulus and Tan $\delta$ . . . . .	279
10.14	The Effect of Frequency Multiplexing on Storage Modulus and Tan $\delta$ . . . . .	280
10.15	(a) A Schematic Diagram of the Mechanical Head of PL-DMTA; (b) A Typical Dual Cantilever Clamping Device Used in the Bending Mode . .	280

<u>Figure No</u>		<u>Page No</u>
10.16	DMTA Scans of IMC and PMC RU-RIM Substrates .	282
10.17	DMTA Scans of Coated Semi-Flexible PU Foam Substrates . . . . .	283
10.18	DMTA Scans of Coated PU Spray Foam Substrate	283
10.19	DMTA Scans of Coating, Substrate and Coated PU Spray Foam Substrates . . . . .	284
11.1	Schematic of a Scanning Electron Microscope (SEM) Equipped with Energy Dispersive X-ray Analysis (EDX) . . . . .	289
11.2	SEM Micrographs of Coated Semi-Flexible PU Foam Substrate . . . . .	294
11.3	SEM Micrographs of Coated Semi-Flexible PU Foam Substrate . . . . .	295
11.4	SEM Micrographs of Coated Rigid PU Foam Substrate . . . . .	296
11.5	SEM Micrographs of Coated Rigid PU Foam Substrate . . . . .	297
11.6	SEM Micrographs of Coated PU-RIM Substrate . .	299
11.7	SEM Micrographs of Coated PU-RIM Substrate . .	300
11.8	SEM Micrographs of Coated C <sub>196</sub> Polyester Substrate . . . . .	303
11.9	SEM Micrographs of Coated C <sub>198</sub> Polyester Substrate . . . . .	304
11.10	SEM Micrographs of Coated C <sub>199</sub> Polyester Substrate . . . . .	305
11.11	SEM Micrographs of Coated Polyester Substrates After Adhesion Pull-Off Test . . . . .	306
11.12	SEM Micrographs of Coated PU Spray Foam Substrate at Various Coating Conditions (x50)	308
11.13	SEM Micrographs of Coated PU Spray Foam Substrate at Various Coating Conditions (x50)	309

11.14	EDX Elemental Analysis of In-Mould Coated Semi-Flexible PU Foam Substrate with 2 Pack MRC (200) Coating . . . . .	311
11.15	EDX Elemental Analysis of In-Mould Coated Semi-Flexible PU Foam Substrate with 1 Pack MRC (600) Coating . . . . .	312
11.16	EDX Elemental Analysis of In-Mould Coating RIM-PU Substrate with 2 Pack (X-220/C075/C770) Coating . . . . .	313
12.1	The Relationship Between Max $W_A$ , $\gamma_S$ , $\gamma_S^D$ and $\gamma_S^d$ for PU&Polyester Substrates . . . . .	328
12.2	The Overall Effect of Substrates, Coatings, Coating Processes on Mean Failure Stress of Coated PU and Polyester Substrates . . . . .	341
12.3	The Overall Effect of Substrates, Coatings and Coating Processes on Average Peak Energy of Coated PU and Polyester Substrates . . . . .	342
12.4	The Overall Effect of Substrates, Coatings, Coating Processes on Cross-Cut Hardness of Coated PU and Polyester Substrates . . . . .	343
12.5	The Overall Effect of Substrates, Coatings and Coating Processes on Scratch/Gouge Hardness of Coated PU and Polyester Substrates . . . . .	344

## LIST OF TABLES

<u>Table No</u>		<u>Page No</u>
1.1	European Polyurethane Markets by Product . . .	4
2.1	Diisocyanates . . . . .	18
2.2	Effect of Base Strength and Nitrogen Accessibility on Catalytic Activity of Tertiary Amines . . . . .	22
2.3	Cohesion Energies of Groups Common in Urethane Polymers . . . . .	31
2.4	Clamping Force, Tonnes . . . . .	33
2.5	ASTM Classification of Isocyanate Based Coatings . . . . .	36
2.6	Advantages and Disadvantages of One- and Two- Pack PU Coatings . . . . .	40
3.1	Estimated Consumption of Plastics in Western European Automotive Industry in 1990 . . . . .	48
3.2	Flow Diagram for Post Mould Surface Coating Process . . . . .	59
3.3	Flow Diagram for the Application of Rigid Polyurethane Foam Coated with a Weatherproofing Elastomer Film . . . . .	64
3.4	Flow Diagram for In-Mould Surface Coating Process . . . . .	66
3.5	Flow Diagram for In-Mould Barrier Release Surface Coating Process . . . . .	70
3.6	In-Mould and Post-Mould Coating of PU Materials	72
4.1	Bond Energies for Adsorption and Chemisorption Systems . . . . .	79
5.1	Equilibrium Spreading Pressure Obtained by Vapour Adsorption Measurement at 25°C . . . . .	111
5.2	Equilibrium Spreading Pressure Calculated from the Contact Angle at 20°C . . . . .	112

5.3	Surface Free Energy Components of Various Liquids $\text{mN.m}^{-1}$ . . . . .	116
5.4	Surface Tension of Some Low Energy Solid Surfaces . . . . .	117
5.5	Surface Tension of Some Metals and Metal Oxides . . . . .	118
5.6	Surface Tension Components for Low and High Energy Solid Surfaces . . . . .	119
5.7	Surface Energy and Contact Angle of Four Series of Liquids on Polytetrafluoroethylene at $20^{\circ}\text{C}$ . . . . .	124
5.8	Critical Surface Tension of Wetting of Some Solid Surfaces . . . . .	128
5.9	Critical Surface Tension of Wetting of Some Polymers . . . . .	131
5.10	Solvents Classification According to Acid-Base Theory . . . . .	131
5.11	Polymer Classification According to Acid-Base Theory . . . . .	132
7.1	Coating Materials . . . . .	141
7.2	PU-RIM Material and Processing Data . . . . .	143
7.3	PU Foam Materials and Specifications . . . . .	144
7.4	Typical Properties of Liquid Crystic Polyester Resins . . . . .	145
7.5	Typical Properties of ISOFOAM Substrate Materials . . . . .	146
7.6	Typical Properties of FUTURA-THANE 5000 Coating . . . . .	147
7.7	Mould Release Agents Specifications . . . . .	148
7.8	The Effect of Accelerator E on Gel Time of Resins . . . . .	154
7.9	Various Coated PU Spray Foam Combinations . . . . .	156
8.1	Contact Angle Measurements for PE and PTFE Substrates . . . . .	161
8.2	A Comparison of Various Contact Angle Results for PE and PTFE Surfaces . . . . .	161

8.3	Contact Angle Measurements for Polyurethane Substrates . . . . .	165
8.4	Contact Angle Measurements for Polyester Substrates . . . . .	166
8.5	Wettability Equations and Critical Surface Tensions for Different Substrates . . . . .	172
8.6	Quadratic Equations for $W_A$ and $S_C$ for Different Substrates . . . . .	173
8.7	Maximum Values of $W_A$ and $S_C$ for Different Substrates . . . . .	172
8.8	Surface Tension, $\gamma_S$ ( $\text{mN.m}^{-1}$ ) Calculated From Harmonic and Geometric Methods for Semi-Flexible Polyurethane Substrate . . . . .	175
8.9	Surface Tension, $\gamma_S$ ( $\text{mN.m}^{-1}$ ) Calculated From Harmonic and Geometric Methods for Rigid Polyurethane Substrate . . . . .	176
8.10	Surface Tension, $\gamma_S$ ( $\text{mN.m}^{-1}$ ) Calculated From Harmonic and Geometric Methods for RIM Polyurethane Substrate . . . . .	177
8.11	Surface Tension, $\gamma_S$ ( $\text{mN.m}^{-1}$ ) Calculated From Harmonic and Geometric Methods for PU Foam Substrate . . . . .	178
8.12	Surface Tension, $\gamma_S$ ( $\text{mN.m}^{-1}$ ) Calculated From Harmonic and Geometric Methods for Polyester Substrates . . . . .	179
8.13	Surface Tension, $\gamma_S$ ( $\text{mN.m}^{-1}$ ), Calculated by Different Methods . . . . .	180
8.14	Critical Surface Tension, $\gamma_C$ ( $\text{mN.m}^{-1}$ ) of Different Substrates Calculated by Equation of State Method . . . . .	181
8.15	Wettability Equations and Critical Surface Tensions for Different Substrates . . . . .	187

8.16	Comparison of Primary Elemental Surface Characterisation Techniques to Determine Locus of Failure . . . . .	192
9.1	Typical Adhesives Used in Tensile Adhesion Pull-off Test . . . . .	205
9.2	Tensile Adhesion Results for IMC and PMC Semi-Flexible PU Substrate . . . . .	207
9.3	Tensile Adhesion Results for IMC and PMC Rigid PU Substrate . . . . .	208
9.4	Tensile Adhesion Results for IMC and PMC RIM-PU Substrate . . . . .	209
9.5	Tensile Adhesion Results for IMC and PMC C <sub>196</sub> Substrate . . . . .	210
9.6	Tensile Adhesion Results for IMC and PMC C <sub>198</sub> Substrate . . . . .	211
9.7	Tensile Adhesion Results for IMC and PMC C <sub>199</sub> Substrate . . . . .	212
9.8	Tensile Adhesion Results for Coated PU Spray Foam Substrate . . . . .	213
9.9	IFWI Determination of Ductile-Brittle Transition Temperatures (mc <sup>-1</sup> ) . . . . .	226
9.10	Sample Thickness from Impact Tests . . . . .	227
9.11	Impact Properties of Coated Polyurethane Substrates . . . . .	233
9.12	Impact Properties of Coated Polyester Substrates . . . . .	234
9.13	Impact Properties of Coated PU Spray Foam . . . . .	235
9.14	Cross-Cut Hardness Results for IMC and PMC Polyurethane Substrates . . . . .	246
9.15	Cross-Cut Hardness Results for IMC and PMC Polyester Substrates . . . . .	246
9.16	Scratch Hardness Results for IMC and PMC Polyurethane Substrates . . . . .	251
9.17	Scratch Hardness Results for IMC and PMC Polyester Substrates . . . . .	251



## CHAPTER 1

### INTRODUCTION

Although polyurethanes are of relatively recent origin as far as natural and synthetic polymers are concerned, the chemistry of organic isocyanates dates back more than 140 years. A. Wurtz synthesised an aliphatic isocyanate in 1849 and described several simple isocyanate reactions which are among the most important reactions used commercially to this day. Over the years several different methods for the synthesis of aliphatic and aromatic isocyanates have been developed and their reactions explored. However, it was not until 1937 that Professor Otto Bayer and co-workers in the laboratories of the German I.G. Farben Industrie, discovered the diisocyanate addition polymerisation reaction which resulted in world-wide interest in polyurethane and other isocyanate-based polymers. Ironically, it was the Bayer team's initial effort in a competitive response to the successful investigations by Carothers of Du Pont on polyamides, that had a considerable influence on the discovery of urethanes [1-3].

In ensuing years, polyurethanes have been constantly developed to meet the needs of the various industries throughout the world. These changes reflect the dynamic character of the whole polyurethane field because of its versatility which reflects innovations in raw materials, processes, technologies and applications.

The main types of polyurethane products positioned in a property matrix relating density and stiffness are shown in Figure 1.1.

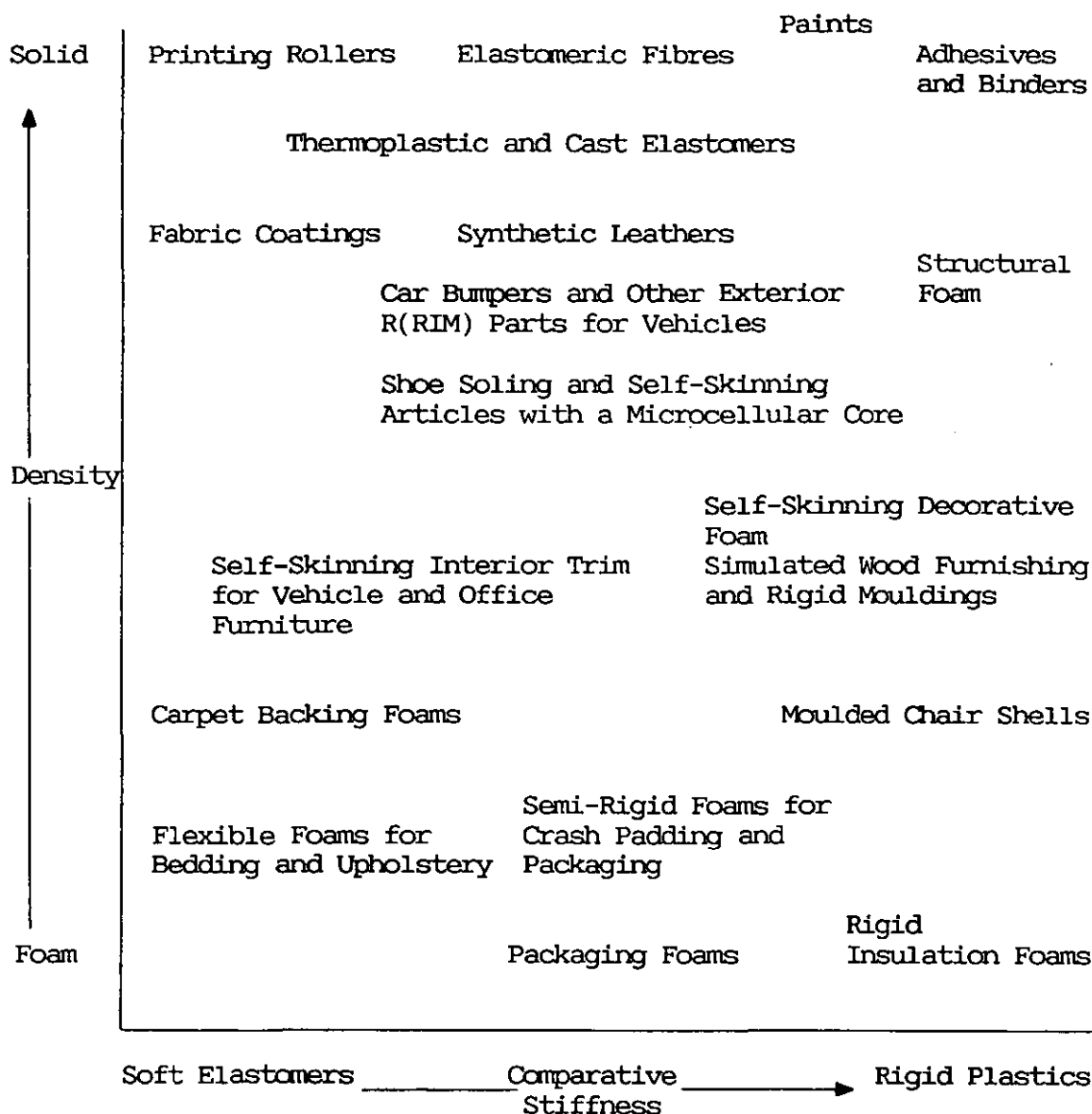


FIGURE 1.1: Property Matrix of Polyurethanes [4,5]

At the beginning of 1990, the world market for polyurethanes stood at 5 million tonnes with best estimates suggesting a steady climb to 6 million within the next five years. Europe's consumption accounts for around a third at 1.5 million tonnes, but is expected to reach over 1.6 million tonnes by 1993, showing an average growth of 2.7% Pa between 1988 and 1993 (the period of the report) [6]. The European

polyurethane market by end use and country for 1988 are shown in Figures 1.2a and 1.2b. The world PUs industry standing at the end of the 1980's is also shown in Figures 1.2c and 1.2d.

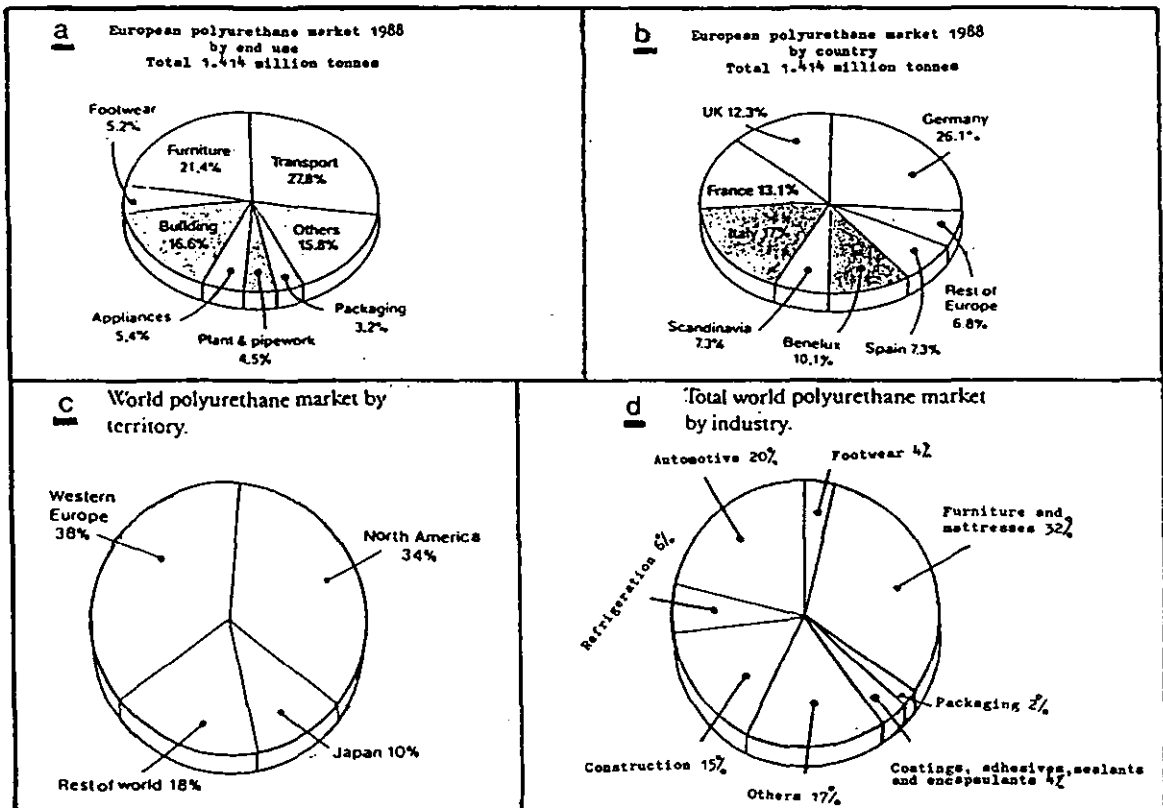


FIGURE 1.2(a to d): European and World PU Markets [6,7]

It is expected that flexible foam remains the largest single sector during the 1990s, although its importance is in decline. At the start of the 1980s, flexible foam accounted for over half of the total PU consumption, but that had slipped to under 40% at the beginning of the 1990s. Rigid foams are expected to increase their share of the European market by an average of 3% pa during the early 1990s, mainly through application in buildings and refrigerators.

Further growth is forecast for the RIM/RRIM (reinforced reaction injection moulding) polyurethane sector, at a rate of around 4% pa on average. In particular, there should be potential for still more RIM PU from bumper/fascias which account for up to half the market for automotive RIM in Europe. The European PU markets by product for 1988 and estimated values for 1993 are shown in Table 1.1:

Product	1988 (Kt)	Growth, %*	1993 (Kt)
Flexible foam	576	2	635
Rigid	375	3	435
Integral skin foam	34	0	34
RIM/RRIM	46	4.4	57
Adhesives	68.5	1	72
Sealants	15	5	19
Paints and Coatings	180	4.1	220
Elastomers	120	3.6	143
TOTAL:	1414.5	2.7	1615.0

\* Average annual rate, 1988-1993

TABLE 1.1: European Polyurethane Markets by Product [8]

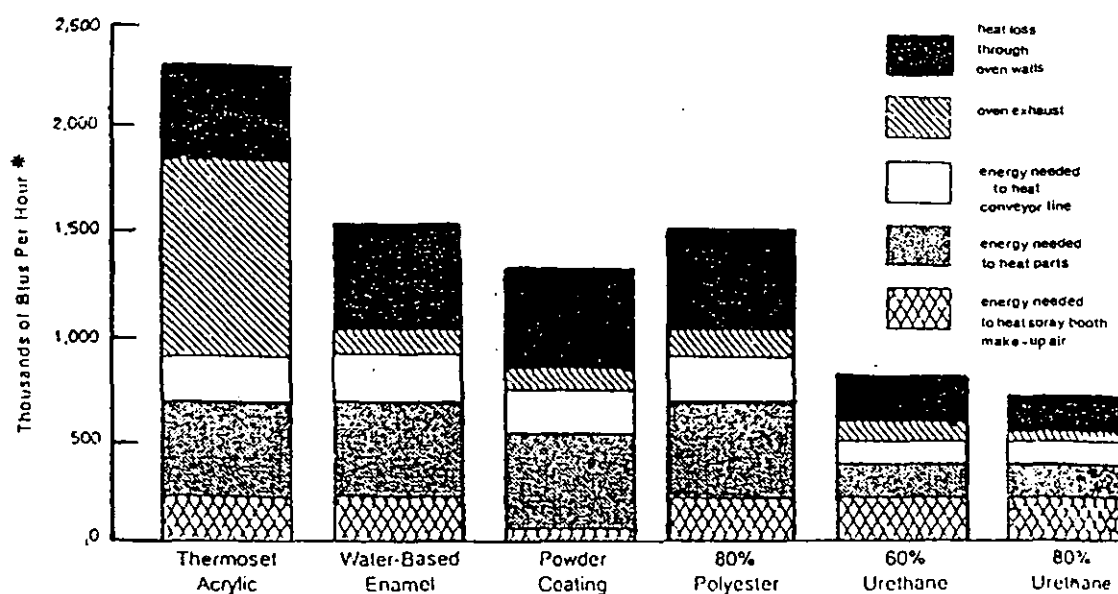
Polyurethane (PU) foam products are now manufactured to meet demanding end property requirements and to compete with other polymers. For external uses, common PUs, i.e. those based on aromatic isocyanates, are prone to environmental attack, promoted by ultra violet and oxidative degradation. Increased resistance can be protected by the

incorporation of anti-degradants but these have limitations. Equally the use of non-aromatic isocyanate based foams is commercially uneconomic [9]. Therefore protection is essential for PU foams for most applications and this is achieved by applying a stable surface coating. The surface coating also enhances the use of the substrate by widening the range of colours and shades, hiding moulding defects (e.g. striations) and generally improving the aesthetic appeal of the product.

The surface coating material instead of the substrate material must promote certain stability in the overall moulding. Generally the coating will supply the resistance to chemical degradation, the substrate supplying the physical properties. The surface coating of plastics is more fully reviewed in Chapter 3.

In the isocyanate contest, the trend towards MDI (4,4'-diphenylmethane diisocyanate) and away from TDI (toluene diisocyanate) is continuing in the 1990s [6]. MDI is forecast to put on 7% growth per annum against 2% per annum for TDI, suffering from concerns over its relative toxicity. However the biggest growth is reserved for aliphatic isocyanates at 10 to 20%, as the small sector expands, especially for coatings and paints.

Commercial success of polyurethane coatings has stemmed from outstanding long-term performance combined with low energy demand cure characteristics (see Section 2.5). Figure 1.3 illustrates that the energy requirements for high-solids PU coatings are much less than for water-based enamels, powder coatings and other high solid coatings [10].



\* 1KW = 3413 Btu/Hour

FIGURE 1.3: Comparison of Curing Energy Requirements [10]

The painting of plastics materials has attracted the imagination of coating technologists for a long time, with the variations in flexibility, plasticity and hardness that plastics offer, and the problems with solvent attack and ensuring good adhesion between coating and substrate [11].

Polymeric mouldings have been traditionally painted by the post-mould coating (PMC) technique (see Section 3.4.1). It has been shown that although acceptable results are provided in many cases, the technique requires more labour, time and energy due to the number of preparatory operations involved can make it uneconomical in certain instances. A

more serious drawback of PMCs from the point of view of aesthetic and performance in service is, however, related to the problems associated with their adhesion and the interfacial bonding formed between paint and substrate. Due to these disadvantages, many of the industrial practices evolved on a trial and error basis to improve the PMC technique have not always proved suitable. As a result, processes like in-mould coating (IMC) have been devised as a way round the problem for certain PU moulding processes. In-mould surface coating is a relatively new technique when applying thermosettable surface coatings (e.g. PUs, epoxides, unsaturated polyesters) to similar chemically based polymers. In the IMC process, a liquid paint system is sprayed by conventional paint-spray techniques into a clean, often released mould and then, while it is still only semi-cured (i.e. after the paint solvents or thinners allowed to flash off), the liquid substrate polymerisable ingredients are injected (see Section 3.4.2). Possibly the most sophisticated system is the application of aliphatic or alicyclic isocyanate based PU paint film onto an aromatic isocyanate based PU substrate. Generally IMCs appear to have superior adhesion properties (cf PMCs), although no adhesion studies had been carried out on the system.

It should be noted that facilities in a factory providing post-mould painted parts, cost far more in capital equipment, than incorporating in-mould spray facilities into the existing moulding line. Waddington [12] has estimated that for an uncoated PU part costing £9, IMC adds £2 to the manufacturing cost, compared with an additional £8 for PMC.

The phenomenon of adhesion has a very long history. In ancient times it was found that solids could be made to adhere strongly by solidification of liquids which had thoroughly wet two surfaces to be

joined. Over the centuries numerous explanations for adhesion have been put forward [13-15] (see Section 4.2).

The scientific literature from the 1920s to the 1960s demonstrates the quantity of theoretical papers which substantially advanced the science of adhesion. However, it has been the improvement of analytical techniques to adhesion testing over the last 15 years that has resulted in some outstanding scientific analysis.

The adhesion of a coating to its substrate is clearly of importance if the coating is to be retained under service conditions. This is thought to involve mechanical interlocking (especially with porous substrates), physically mixing (in the case of lacquers applied to plastics) or chemical bonding/molecular attraction (in the general case of organic coatings applied to metals). Nevertheless, despite the apparent advances in technology, the adhesion is rarely maximised in industrial applications.

Along with the concept of adhesion, wetting and interfacial bonding phenomena, developed in coated polymeric substrates and examined on the basis of currently accepted surface science and thermodynamic theories are of crucial importance (see Chapter 5).

As far as my literature search shows, little or no scientific study has been carried out to evaluate the bonding in IMC and PMC systems. Consequently with no full understanding of the bonding and adhesion phenomenon no optimisation of processing to give the best adhesion properties of coated systems has been possible.



This research primarily aims at studying the adhesion properties of a number of IMC and PMC polyurethane substrates. Some coated polyester substrates will also be used in order to provide a more complete picture of various types of interfaces produced. This research also aims at applying the theories of adhesion and the concepts of wetting and surface thermodynamics to some PU and polyester coated systems. This will help to provide more evidence of any possible relationship between the magnitude of the adhesion strength and the interfacial effect and of some means of understanding the interfacial bonds in adhesion joints.

## CHAPTER 2

### POLYURETHANE CHEMISTRY AND ITS RELATED MATERIALS

#### 2.1 INTRODUCTION

As discussed in Chapter 1, this thesis is concerned largely with the adhesion phenomena of PU paint materials applied to a range of different PU substrate materials. This Chapter will first discuss a chemical review of polyurethanes and the materials for conversion into PU substrates and coatings. It will then review PU materials in their forms of substrate and surface coating.

#### 2.2 POLYURETHANES: A CHEMICAL REVIEW

Polymers based on urethane repeat units  $[-\text{NH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-]$ , can be derived from any of a large number of reaction mechanisms [2,16-20]. Much of the chemistry of polyurethanes was described by Bayer et al in the 1930s. This provided a basis for the development of foams, elastomers and coatings materials.

Generally PU structures can be changed by varying the proportions and structure of the polyols, isocyanates, chain extenders, crosslinking agents and reaction routes to form a number of prepolymers and polymers.

The techniques commonly used in the synthesis of polyurethanes are prepolymer, semi- or quasi-prepolymer, and one-shot shown schematically in Figure 2.1.

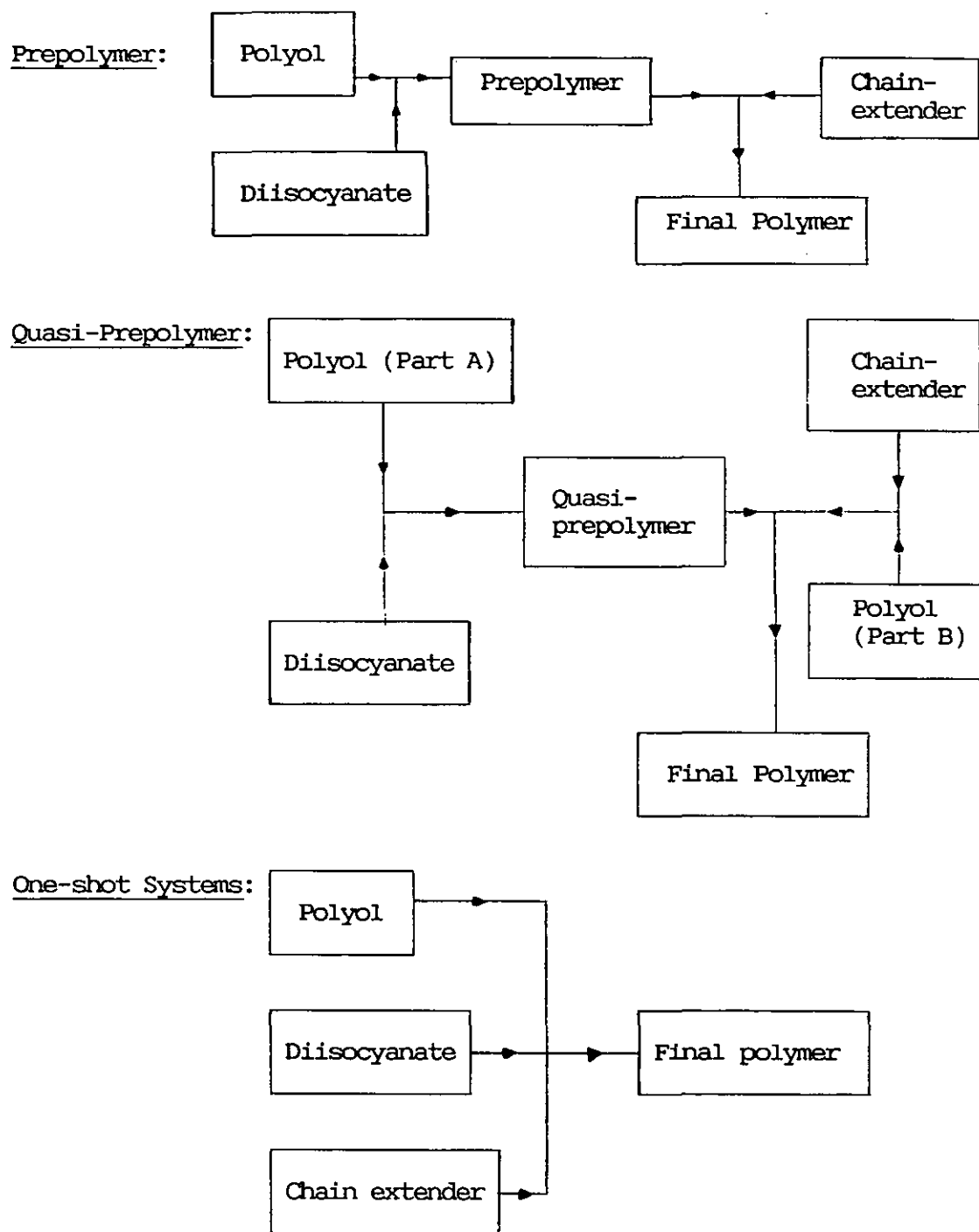


FIGURE 2.1: Different Techniques for Polyurethane Synthesis

The prepolymer route shown in Figure 2.2 is the most widely used method in the production of commercial solid PU systems, and in particular used for PU elastomers. Initially the polyol (polyester or polyether) with an excess of diisocyanate are reacted together to form an isocyanate-terminated polymer of moderate molecular weight which is called a 'prepolymer'. This prepolymer, normally a thick viscous liquid or low melting point solid of low or no strength, is then further reacted with a diol or diamine chain extender to give the high molecular weight polymer.

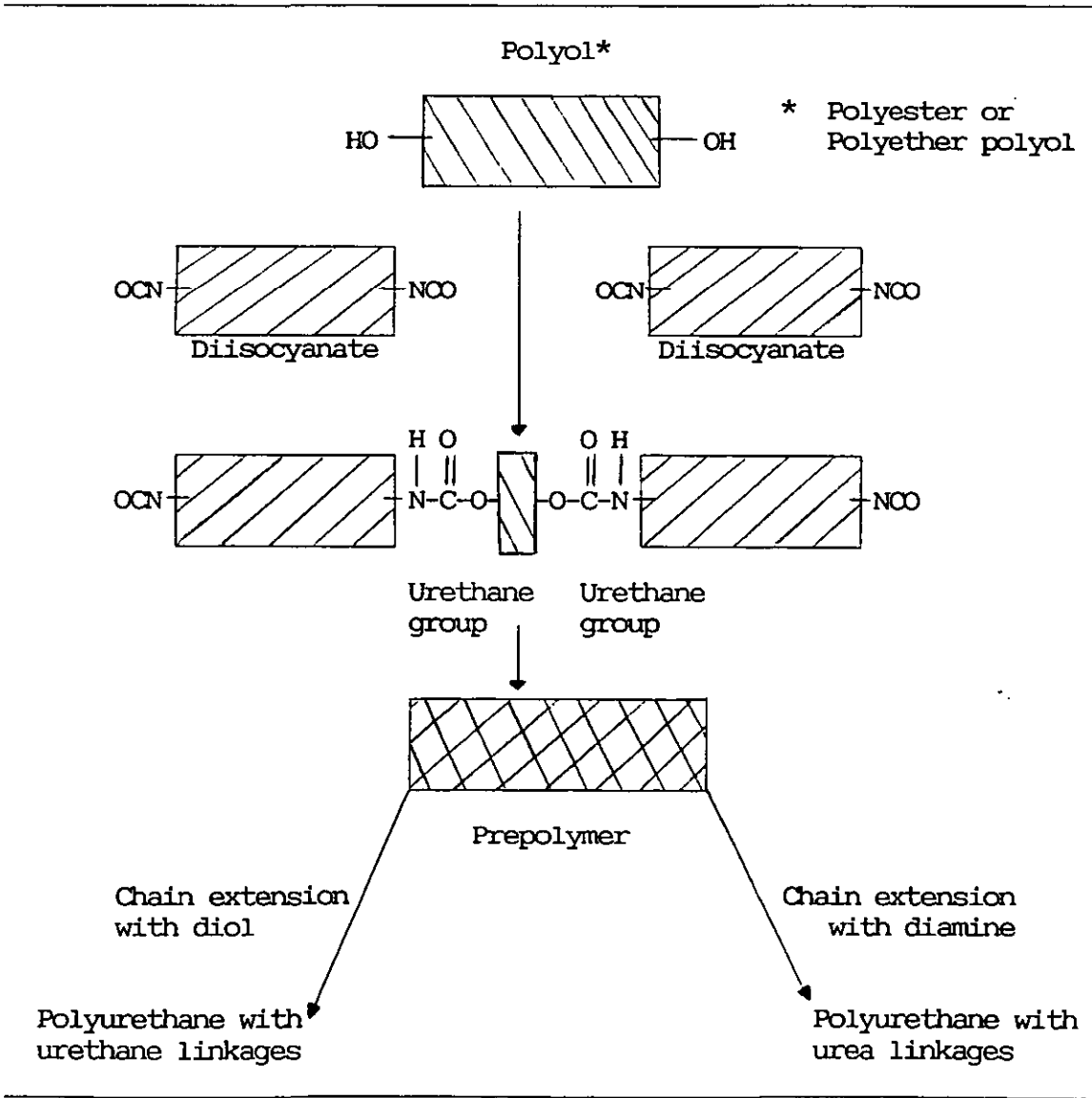


FIGURE 2.2: Prepolymer Route for the Production of Polyurethanes

With the quasi-prepolymer method initially only part of the polyol component is reacted with all the diisocyanate. The resultant partial (or quasi) prepolymer is then reacted with a mixture containing chain extender and the remainder of the polyol to give the final polymer.

The one-shot process is carried out by simultaneously mixing together diisocyanate, polyol, and the chain extender (in the presence of catalysts).

The most important reactions of isocyanates may be divided into two main types:

- i) functional group polymerisation of isocyanates with active hydrogen containing compounds;
- ii) oligomerisation of isocyanates.

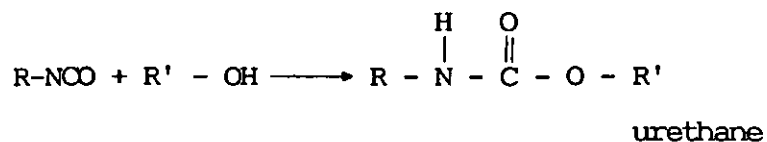
#### 2.2.1 Functional Group Polymerisation of Isocyanates with Active Hydrogen Containing Compounds

The isocyanate group will react with a number of compounds having an active hydrogen atom to result in functional group polymerisation. These reactions are either primary or secondary types.

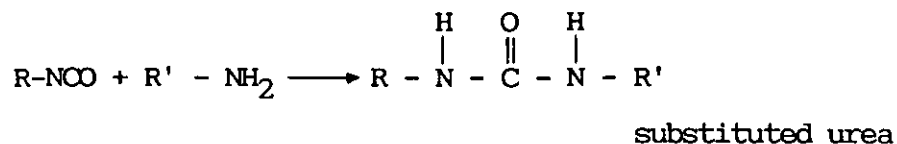
##### A. Primary Reactions of Isocyanates

In these reactions, no by-products are given off unless water or a carboxyl group is present, in which case carbon dioxide gas is given off [16,19,20].

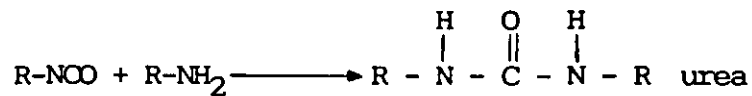
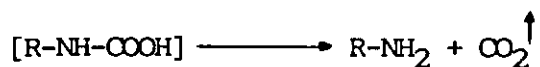
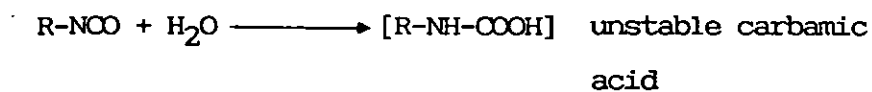
With alcohols:



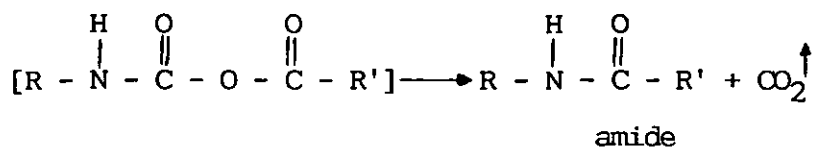
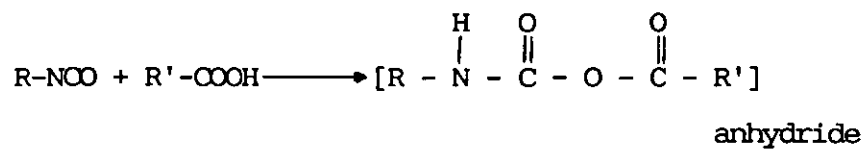
With amines:



With water:

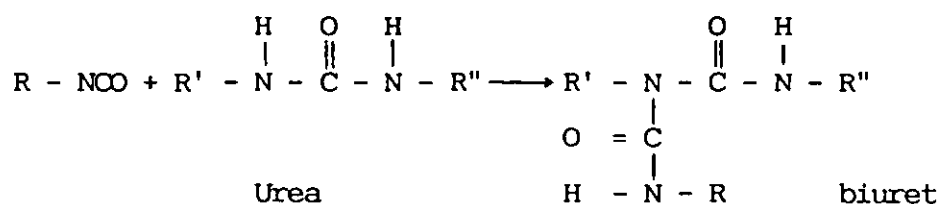
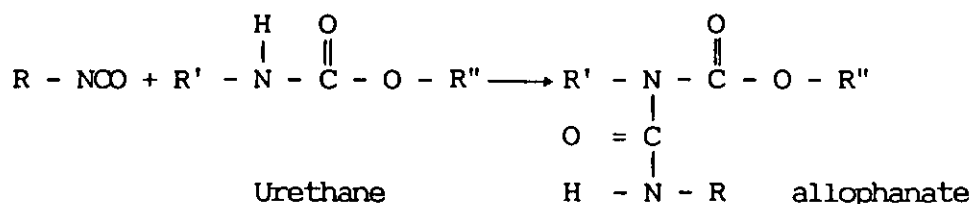


With carboxylic acid:



## B. Secondary Reactions of Isocyanates

The isocyanate group can react further with the active hydrogen atoms of the products of primary reactions either at higher temperatures or in the presence of suitable catalysts:

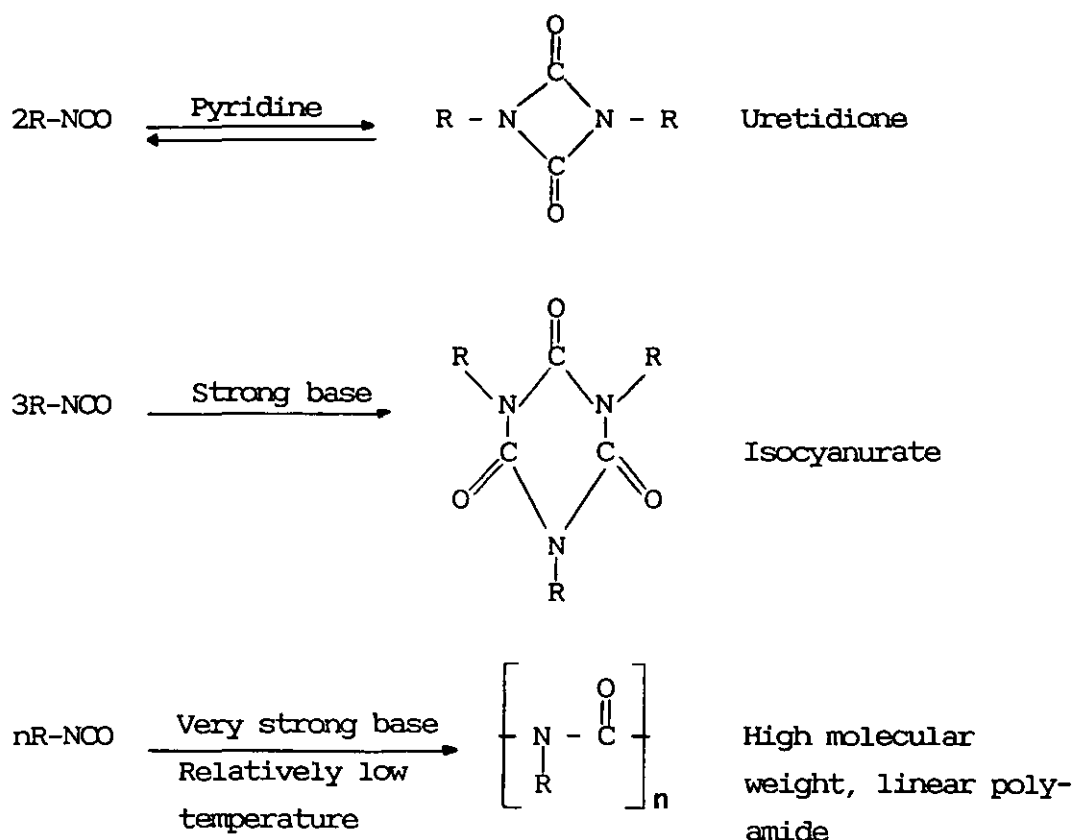


The conditions encouraging the formation of allophanates and biurets in reactions mean that crosslinks and branches are produced in the polymer, influencing the properties of polyurethanes.

### 2.2.2 Oligomerisation of Isocyanates

Isocyanates form oligomers, especially in the presence of basic catalysts, giving uretidione and isocyanurate. Oligomerisation can be used beneficially in order to:

- i) reduce volatility of monomeric isocyanates and therefore reduce the health risk from volatile isocyanates.
- ii) control the molecular structure and hence specific end properties.



### 2.3 MATERIALS FOR CONVERSION INTO PU COATINGS AND SUBSTRATES

The main components of urethane materials i.e. urethane coatings used as the resin or "carrier" in the liquid coating, and urethane substrate as foams, elastomers and microcellular reaction injection moulded are di- or polyisocyanates and di- or polyhydroxy compounds. Both crosslinking agents (e.g. diamines), and catalysts (e.g. tertiary amines and tin salts) are used to enhance properties and speed urethane and side reactions. Auxiliary chemicals such as thinners (normally organic solvents), flow aids, antioxidants, wetting agents and pigments are common and important additives used in many urethane coatings and substrate systems. Additives such as flow agents,



bodying agents, flattening agents and anti-foaming agents are used in many urethane coatings. The materials for conversion into PU substrates and coatings have been reviewed in many articles [18,21-25].

The common chemicals used in PU substrate and coating processing are discussed in this section. The additional materials used for PU coatings are dealt with in Section 2.4. Polyurethanes as substrates and as surface coatings are discussed in Sections 2.5 and 2.6 respectively.

### 2.3.1 Isocyanates

In general, aromatic isocyanates tend to be cheaper and have a slight edge in terms of health and safety. The purer grades of aromatic isocyanates are most commonly used, either the mixed 2,4, 2,6 isomers of toluene diisocyanate (TDI), or 4,4'-diphenylmethane diisocyanate (MDI), having the chemical structures shown in Table 2.1 [16,19, 26,27].

Non-aromatic isocyanates are preferred to impart UV and oxidative resistance particularly for external applications (see 3.2.1.1) but the disadvantages of their relative higher price, limited reactivity and increased health hazards must be considered.

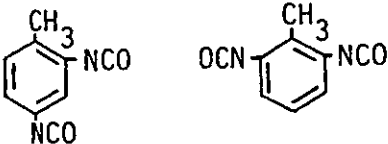
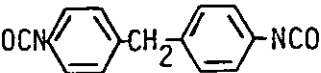
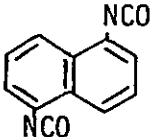
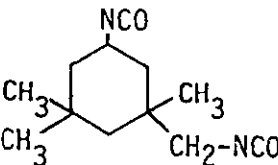
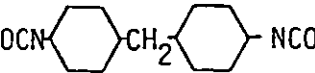
Chemical Name	Structure	Chemical Abbreviation
Toluene diisocyanate 2.4 and 2.6 isomers		TDI
4,4'-diphenylmethane-diisocyanate		MDI
Naphthylene 1,5-diisocyanate		NDI
Hexamethylene diisocyanate	$\text{OCN} - (\text{CH}_2)_6 - \text{NCO}$	HDI or HMDI
Isophorone diisocyanate		IPDI
Dicyclohexylmethane-4,4'-diisocyanate (hydrogenated MDI)		PIOM (H <sub>12</sub> MDI)

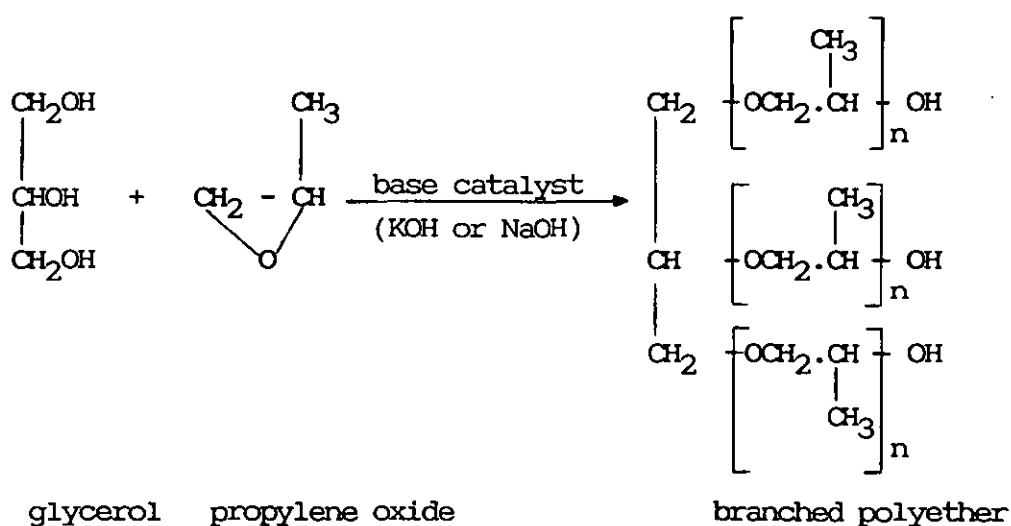
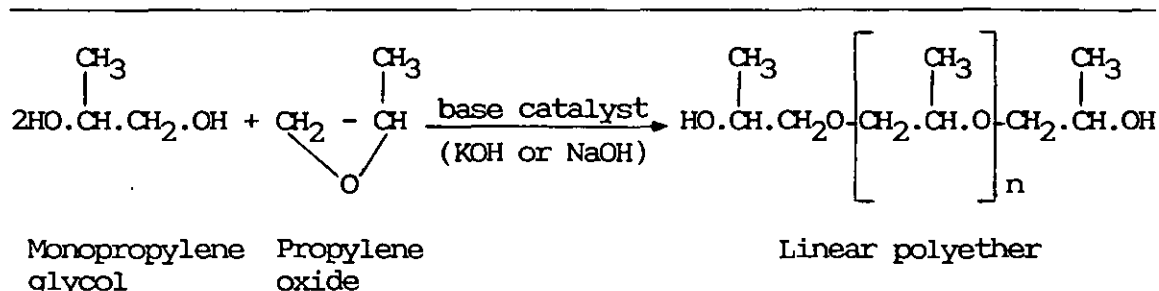
TABLE 2.1: Diisocyanates

### 2.3.2 Polyols and Diols

Oligomeric hydroxyl compounds such as polyester polyols or polyether polyols are largely used in the manufacture of polyurethane products [19,22,28].

The polyethers are used in about 90% of commercial polyurethanes [29]. They are most frequently manufactured by base-catalysed oligomerisation of propylene oxide. Linear and branched polyethers may be

prepared by using glycols e.g. polypropylene glycol and higher functionality polyols e.g. glycerol as their initiators respectively.



Amine-terminated polyethers where the hydroxyl end-groups of polyether polyols are converted to amino end-groups are normally used with conventional polyether polyols. This is because their direct use with isocyanates results in extremely fast reaction. During the last few years, however, the use of amine-terminated polyethers has increased rapidly due to their application together with hindered aromatic diamines as chain extenders in the polyurea RIM process.

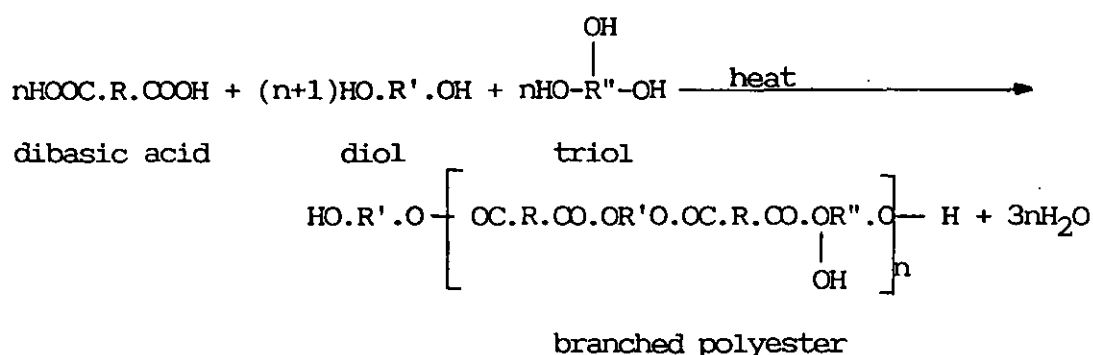
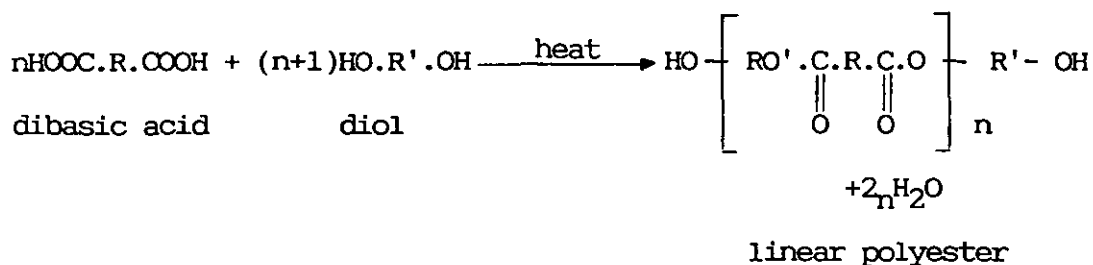
There are also three main types of modified polyether polyols used in the production of polyurethanes. These are: polymer polyols, polyurea-modified polyols, and pipa polyols.

Polymer polyols or polyvinyl-modified polyethers contain three types of polymer: unmodified polyether polyol, the vinyl polymer and some vinyl polymer grafted onto the polyether chains.

Polyurea-modified polyols are conventional polyether polyols containing up to 20% dispersed particles of polyurea formed from the reaction of TDI and a diamine. The dispersed polyureas may react with isocyanates during polyurethane manufacture to give increased crosslinking of the final polymer [30].

Pipa polyols (i.e. polyisocyanate poly addition) are basically similar in concept to polyurea-modified polyols but they contain dispersed particles of polyurethanes formed by the reaction, in-situ, of an isocyanate and an alkanolamine.

The polyesters have been largely replaced by polyethers in the polyurethane foam production, but they are still used for elastomer and coating productions. The basic components are usually dibasic acids e.g. adipic and sebacic acid with glycols e.g. ethylene and diethylene glycols, for uncrosslinked linear polyesters, and triols e.g. glycerol and trimethylolpropane, in cases where branched or crosslinked polyesters are required [20,26].



However, the surface coatings used are based also on vinyl chloride monomers ( $\text{CH}_2=\text{CHCl}$ ), usually referred to as vinyl resins. The main vinyl resins used in coatings are the copolymers of vinyl chloride and vinyl acetate, but vinylidene chloride and vinyl-butyrac also are used [31]. Vinyl resins are often modified by hydroxyl groups in order to increase their compatibility with other types of film-forming materials such as: alkyd resins, urethane prepolymers, polyamides, acrylics, etc. Due to this compatibility, many types of surface coatings can be tailored to give improved properties for different applications.

### 2.3.3 Catalysts

Catalysts play a major part in the production of urethane polymers. Catalysts will not only control the rate of the chemical reactions responsible for chain propagation, extension, and crosslinking, but they also influence the ultimate properties of the resulting polymers. The number of catalyst systems for urethane products has increased over the last 30 years. They include basic catalysts, either inorganic bases such as sodium hydroxide or sodium acetate or, more commonly, tertiary amines and organo-metal compounds such as tin catalysts [26,28].

The efficiency of tertiary amine catalysts depends upon their chemical structure. The catalysts work by producing chemical rearrangements, this generally increases as the basicity of the amine and the accessibility of the nitrogen atom increases (Table 2.2).

Catalyst	Structure	Base Strength pKa	Relative Activity
Trimethylamine	$N(CH_3)_3$	9.9	2.2
Ethyldimethyl- amine	$N.C_2H_5(CH_3)_2$	10.2	1.6
Diethylmethyl- amine	$N.CH_3(C_2H_5)_2$	10.4	1.0
Triethylamine	$N.(C_2H_5)_3$	10.8	0.9
Triethylene- diamine, DABCO	$  \begin{array}{c}  CH_2 - CH_2 \\  \diagdown \quad \diagup \\  N - CH_2 - CH_2 - N \\  \diagup \quad \diagdown \\  CH_2 - CH_2  \end{array}  $	8.2	3.3

TABLE 2.2: Effect of Base Strength and Nitrogen Accessibility on Catalytic Activity of Tertiary Amines [32]

A number of metals in the form of organometallics are effective in the formation of the urethane linkage. Tin compounds such as dibutyltin dilaurate, stannous octoate and stannous oleate are particularly effective.

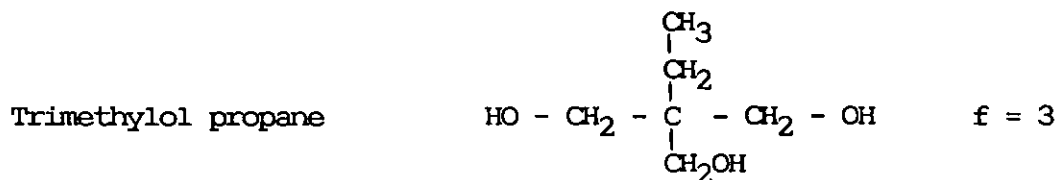
Combinations of tertiary amines and tin compounds are particularly used in the production of polyurethane foams, but coatings, adhesives, sealants and other urethane based materials may also use these catalysts in single or combined forms.

It must be noted that many of the catalysts lead to the degradation of the PU products [33]. Therefore, a control on the type, concentration, and amount of catalyst must be used in order to minimise its degradative effect. The degradation is more severe in cases where catalysts are unable to evaporate after production is completed. In fact, often the products of degradation e.g. acids, themselves have a degradative effect, i.e. autocatalysis, causing accelerated deterioration in a degradable environment. Some prepolymer systems for solid PU elastomers usually do not require catalysts [34], e.g. "Adiprene".

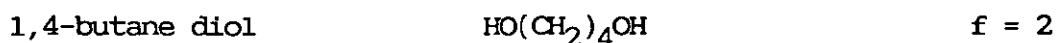
#### 2.3.4 Chain Extenders and Crosslinking Agents

In addition to two principal components i.e. isocyanates and polyols, a number of diols, triols or diamines are used in PU coatings and in curing the isocyanate terminated prepolymer in the mould by serving as chain extenders and crosslinking agents [18,23].

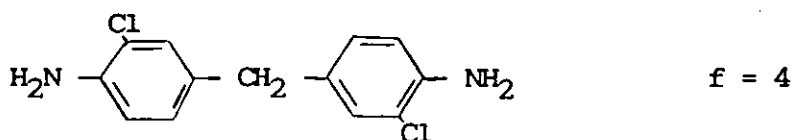
It has been argued [35] that only low molecular weight polyols with a minimum of three functionalities should be strictly called "crosslinking" agents e.g. glycerol or TMP i.e.



whereas low molecular polyols with two functionalities should be called "chain extender" agents e.g.



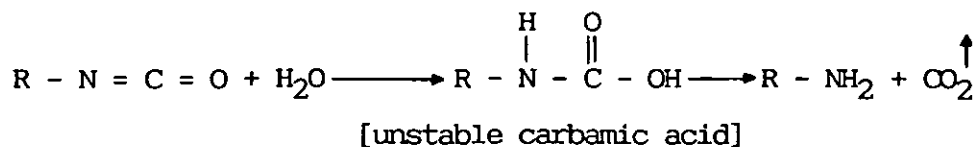
and 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA)



MOCA with  $f = 4$  though strictly a crosslinking agent is also referred to as a chain extender when there is an assumption that the active hydrogen groups have two different orders of reactivity and therefore  $f = 2$ .

### 2.3.5 Blowing Agents

The blowing or foaming agents are used to form the gases which will become trapped in the solid PU polymer, producing the cellular character of the foam. The simplest blowing agent is water, which reacts with isocyanate to form carbon dioxide, expanding the foam [36].





Although water is a satisfactory blowing agent for a wide range of foams, it has some disadvantages:

1. The use of large amounts of water to produce low density foams gives a very exothermic reaction, causing fire hazard problems for the manufacturer. Today with the use of modern catalysts this problem is almost overcome.
2. High water levels have a hardening effect on the foam due to the formation of substituted ureas and biurets.
3. For PU foam systems based on MDI, water consumes MDI at a rate of 16 parts MDI for each part of water and is therefore a costly blowing agent [37].
4. Hydrolysis and neutralising many metal salt catalysts.

In addition to water, low-boiling halogenated alkanes are used as blowing agents. Of these, monofluorotrichloromethane,  $\text{CCl}_3\text{F}$ , known as Refrigerant 11 or Arcton 11 (ex ICI), Freon 11 (ex Du Pont), a low viscosity inert liquid which is volatilised by the exothermic reaction to form gas bubbles is the most widely used. The problems associated with using water only may be overcome by using a combination of water and  $\text{CCl}_3\text{F}$ . Since  $\text{CCl}_3\text{F}$  expands the foam by vaporising under the heat of the urethane reactions, it reduces then increases the total heat of reaction, thus helping to reduce the fire risk in processing. Also, because it does not chemically react with the isocyanate it does not have a hardening effect on the foam.

There is a strong challenge facing the PU foam industry to eliminate CFC blowing agents because of the effect of CFC's on the earth's ozone layer. As a result, hydrogenated blowing agents (HCFC), are being developed as possible replacements. The alternative blowing agents (e.g. hydrocarbons) are inflammable and more difficult to use in normal PU processing. However, it seems inevitable that in the near future the PU industry would have to respond even further to its present environmental concerns. However, in the research work described below CFC blown PUs were used.

#### 2.3.6 Release Agents

During the formation of moulded PU products, high adhesive forces will arise between the mould surface and the reacting PU system. This is due to the reaction of any unreacted isocyanate groups with water or moisture, and also possible hydrogen bonding formed between the urea or urethane groups with any polar groups present. The reacting urethane system is low viscosity, very mobile, and has high surface energy. Therefore it will spread across and wet the mould surface and while being low viscosity and mobile can find holes, cracks, porosity etc in the mould. Therefore the release agents are used with most PU mouldings to serve a number of functions [38-40]:

- i) They must be strong enough to allow the continuous, smooth film to adhere to the mould surface
- ii) They should be weak (i.e. poor cohesive strength) to ease the removal of the PU moulded object
- iii) Hence as the result of (i) and (ii), the flexible release agent films must have adhesive and abhesive properties
- iv) They must also have a low degree of crystallisation, high chemical and oxidation resistance and be thermally stable.

The release agents are used either externally or internally to the polymer. External release agents normally sprayed as a light coating (i.e. ideally a few 10s of micron) into the mould open cavity for smooth, more even films, will act as a barrier between the PU foam and the mould surface. Internal release agents are compounds either part of the polyol or added to it prior to application and assumed to migrate to the surface of the moulding during the reaction. They are more effective with simple, less complex moulds, but find use with polyureas rather than PU systems.

Silicone and wax based release agents are the most frequent types used. Silicone materials are available either as waxy solids, i.e. silicone resins and silicone elastomers or as liquids i.e. silicone oils.

Silicone oils based mainly on polydimethylsiloxanes, having the structural unit  $(\text{CH}_3)_2\text{SiO}^-$  are used both alone and in combination with other silicone and wax based release agents. However using alone it has limited application due to its defoaming action with low density, hot-cured and high resilience foams. It is mainly used with microcellular and high-density integral foam systems. Silicone resins having  $\text{SiO}^-$  and  $\text{CH}_3\text{SiO}^-$  as base molecular components are brittle, crystalline materials which can be applied from organic solvents and form very tough, strongly adhesive films. However, they cannot be used as PU release agents because they do not yield a gliding film due to their brittle, crystalline character. Silicone elastomers also can be applied from organic solvents forming thin films. Due to its mainly amorphous character, elastic behaviour and ability to combine with silicone oils, silicone elastomers can yield a surface that has good gliding and release properties.

Waxes most widely used are polyethylene waxes having lower surface tension than PU liquid reactants and with a low tendency to crystallise. They are easier to degrease than silicone materials and contamination problems are reduced. Nevertheless due to their build up in the mould, regular cleaning is required. In response to many manufacturers demands for having moulds with (semi)-permanent release properties, a number of trials have been made with polytetrafluoroethylene (PTFE) coated moulds. Although PTFE coated surfaces show good release properties due to their low surface tension, their release effect diminishes considerably after 20 to 30 demouldings and the renewal of a PTFE layer is both costly and time consuming.

2.4 POLYURETHANES AS SUBSTRATES

Polyurethane substrates are unique in that variations in formulation and processing conditions enable the end product to range from soft foams to tough rigid materials. Growth of the PU use in the 1980s is illustrated in Figure 2.3. Polyurethane foams, elastomers and reaction injection moulded (RIM) types are reviewed here.

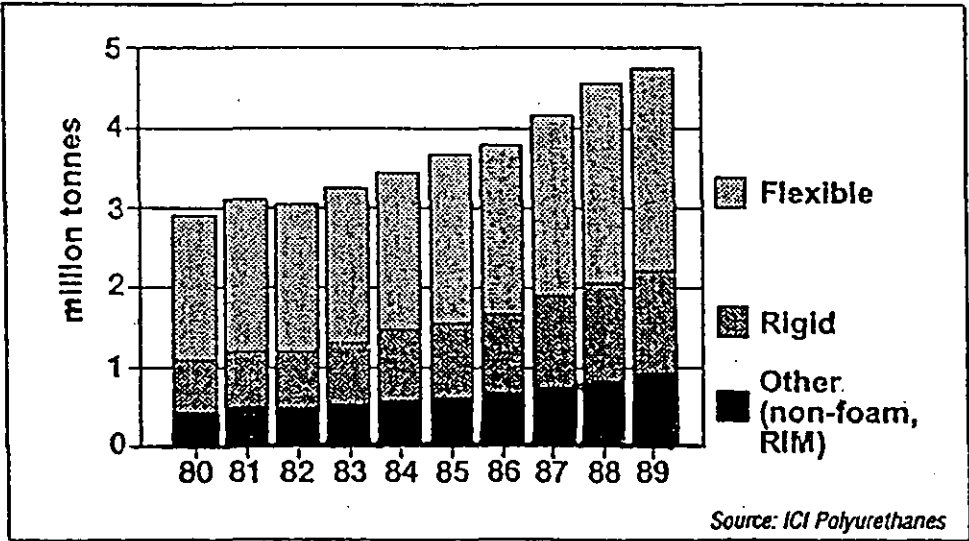


FIGURE 2.3: Growth in Total PU Use 1980-1989 [41]

#### 2.4.1 Polyurethane Foams

The chemistry of polyurethane foam formation is complex and the properties of the foam depend on the choice of polyol and its combination with a particular isocyanate. The amount of water or blowing agent, catalysts, and a balance of urethane and urea groups and of crosslinking groups represented by allophanate, biuret and isocyanurate linkages will affect the physical and chemical properties of the final PU foam [42,43].

The PU foam reaction is an exothermic type where some of the  $\text{CO}_2$  gas evolved due to blowing agent and isocyanate reaction is lost and some of it retained to produce the porous character of the substrate. The viscosity of the initial ingredients increase with the time of reaction. The reaction of isocyanate and hydroxyl both being difunctional produces linear polyurethanes. If the functionality of either is increased to three or more, then a crosslinked PU is produced. The more crosslinks the system possesses the harder the foam. The degree of crosslinking can also be influenced by using more or less than the stoichiometric isocyanate requirement [44] e.g. an index of 90 indicates a 10% isocyanate deficiency and an index of 105 a 5% excess over the stoichiometric requirement. The higher the index, the harder the foam. PU foams may be divided into flexible, semi-flexible and rigid types. Flexible PU foams have an open cell structure. Semi-flexible PU foams contain more than 90% open cells. Most rigid PU foams have a closed structure, however, open celled grades are also used for specific applications.

#### 2.4.2 Polyurethane Elastomers

Polyurethane elastomers are block copolymers, usually made by first forming a low molecular weight prepolymer, and then building the molecular weight with suitable chain-extending agents. Almost all PU elastomers have the general molecular structure,  $(AB)_n$ , with alternating soft and hard segments. The soft or flexible segments, so called because the molecular segments are flexible or soft at normal ambient temperatures, are due to polyether or polyester diols. The hard segments (i.e. rigid or hard at normal ambient temperatures) are composed of urethanes or urea linkages. The interactions between these polar groups are important in determining the properties of PUs of all types, and especially for the PU elastomers where local concentrations of polar groups occur together [19,27,45-47]. Table 2.3 shows an empirical estimate of the energies of interaction between some common groups.

A wide range of PU elastomers commercially available include thermoplastic elastomers, cast (liquid) elastomers, elastomeric fibres, one- and two-pack elastomeric coating systems, and millable rubbers.

#### 2.4.3 Polyurethane Reaction Injection Moulding

Reaction injection moulding, or RIM, is a relatively new high speed processing technique that has rapidly taken its place alongside the more established plastic processes [49-51]. The RIM concept was developed in the early 1960's, and was first introduced to the public by way of an all plastic car at the 1967 International Plastics Fair in Dusseldorf, West Germany [52].

TABLE 2.3: Cohesion Energies of Groups Common in Urethane Polymers  
[48]

Group		Cohesion Energy KJ mole <sup>-1</sup>	Volume* cm <sup>3</sup> mole <sup>-1</sup>
1. Urethane	$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad   \\ -\text{O}-\text{C}-\text{N}- \end{array}$	36.5	43.5
2. Urea	$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad   \\ -\text{C}-\text{N}- \end{array}$	35.5	36.2
3. Phenyl	$-\text{C}_6\text{H}_4-$	16.3	83.9
4. Methylene	$-\text{CH}_2-$	2.8	21.8
	$-\text{C}(\text{CH}_3)_2-$	7.9	65.4
5. Oxygen	$-\text{O}-$	4.2	7.3
6. Carboxyl	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{O}- \end{array}$	12.1	28.9
7. Ketone	$\begin{array}{c} \text{O} \\    \\ -\text{C}- \end{array}$	11.12	21.6

\* Based on small-molecule liquids. The corresponding figures for actual polymer specimens are less and the appropriate polymer cohesion energies greater than the quoted values for the small-molecule liquids.

RIM has been commercially used with urethanes since the early 1970's, and is the fastest growing segment of the urethane industry [41,53,54]. Its growth rate mainly depends upon the car manufacturer's acceptance of exterior body parts. Other important PU-RIM products include: insulation panels, shoe soles, ski boots, furniture parts, steering wheels, and housing for electrical and electronic devices.

The introduction of reinforcing fibres such as milled glass, and the addition of fillers and pigments to impart special properties that expand the engineering properties range and impart special finishes to the surface have widened the range of possible applications. Alongside urethanes, RIM has successfully been used to process epoxy, polyamides, polyurea, polyester, acrylates and other polymers.

#### 2.4.3.1 Why RIM-PU?

The production of polyurethane mouldings in the RIM process only covers a small part within the total aspect of plastic processing. Nevertheless, some fundamental reasons make the RIM of PU's to be of great importance [52,55-57]:

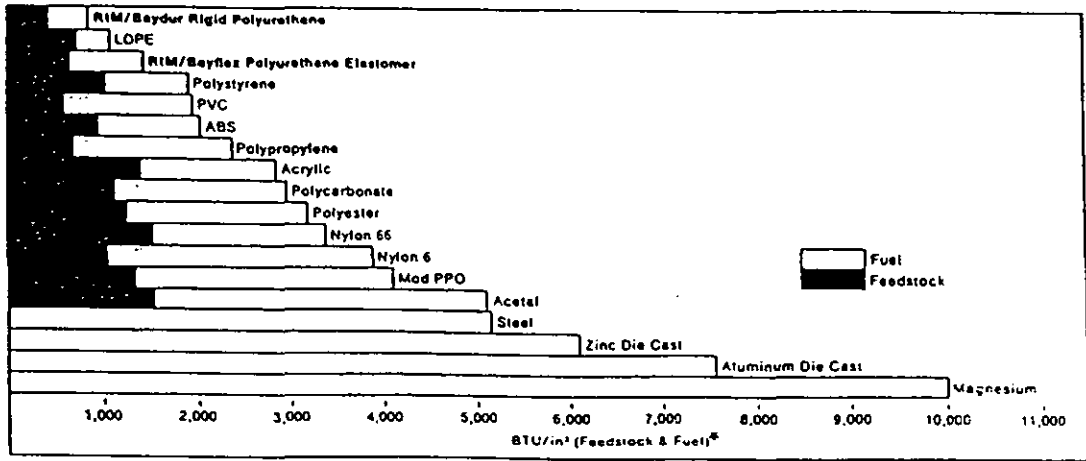
1. high reactive components catalysed for rapid polymerisation;
2. low processing and injection temperatures;
3. low injection pressures requiring considerably less mould clamping force than for other injection moulding processes (Table 2.4). A pressure no higher than a few bar is sufficient while conventional plastics require moulds able to withstand as much as 1400 bar [58];
4. wide formulating possibilities permitting tailor-made properties;
5. short demoulding times even for large parts resulting in high output rates;
6. relatively low tooling cost requiring less labour;
7. relatively inexpensive prototype moulds of reinforcing epoxy or sprayed metal;
8. excellent surface finish. This is possible with better tools and clamping facilities and closed loop RIM control, all of which tend to increase the price of RIM.



Projected Area in <sup>2</sup>	Injection Moulding	SMC	RIM
400	1000	400	10
800	2000	800	20
1500	3750	1500	37.5
3000	7500	3000	75
6000	15000	6000	150

TABLE 2.4: Clamping Force, Tonnes [59]

As a result of reasons 1 to 3 listed above, it is evident that PU-RIM needs very low energy (Figure 2.4), making it more favourable to manufacturers in the future as energy costs rise [60].



\* 1 Btu = 1054.8J

FIGURE 2.4: Material Energy Requirements [60]

## 2.5 POLYURETHANES AS SURFACE COATINGS

The wide use of polyurethane coating materials in the paint industry did not occur until the mid 1950's [61]. PU surface coatings are as diverse in chemical type and in end uses as any other PU material. As elsewhere, the ability of isocyanate material to react to form polymers with many types of functional groups, and also the ease of hydroxylation of many organic materials led to the vast number of surface coatings said to be urethane based i.e. acrylics, silicones, alkyds, epoxides, cellulose and others.

PU surface coatings properties are characterised by the urethane along with other functional groups in the main chain and crosslinks such as ester, ether, urea and amide. Their uses include [62]: paints, varnishes or lacquers, abrasion resist surfaces, leather-cloth, barrier coats, inks and sealants. Depending both on the finished product end-use and the type of PU, the thickness of a thin dry film of PU coating may range from microns to centimetres.

### 2.5.1 Commercial Types of PU Surface Coatings

The term "PU surface coating" covers such a vast variety of product types that a breakdown into different classifications is inevitable. ASTM D16-82a [63], lists five general types of PU surface coatings which in turn can be split into two groups, the one and two-pack or component systems (Table 2.5). Powder coatings and 100% solid coatings are also used in many applications. Fuller description of paint formulations and the coatings mechanisms have been reviewed elsewhere [18,21,62,64-68], however, some of the important features of these coatings are discussed here.

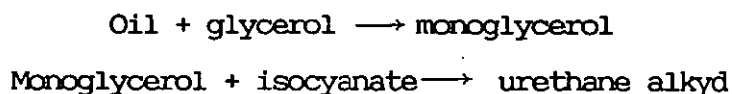
#### 2.5.1.1 One- and two-pack PU surface coatings

The one-pack PU coating may cure by air (oxidative drying), moisture and heat to form urethane films. Oil-modified, moisture-cured and blocked isocyanate types of one-pack PU coating are reviewed here.

The two-pack PU coatings consist of two reactive components. The A-component being a polyol or a prepolymer and the B-component being a chain extender or crosslinking agent [69]. Generally it is thought that two-pack coatings will give superior properties over one-pack systems, although both are greatly used in many applications. The conditions and properties of raw materials and the reactions involved for the processing of two-pack PU coatings are reported in literature [18,67,70,71], however, catalysed and polyol cured types are reported here.

##### a) One-pack oil modified PU coatings

They are prepared by a drying oil being hydrolysed with glycerol or penterithritol [21]. The di- or monoglyceride formed is refined and reacted with isocyanate to give a low molecular weight urethane alkyd, also known as "uralkyd".



The isocyanate content can be varied depending on process and end property requirements. By increasing the isocyanate content i.e. the shorter the oil length, the resulting film shows reduced flexibility and impact resistance, increased hardness and solvent resistance and shorter drying times [72]. Uralkyds are cured in the same manner as normal alkyds, i.e. through oxidative drying. Metallic

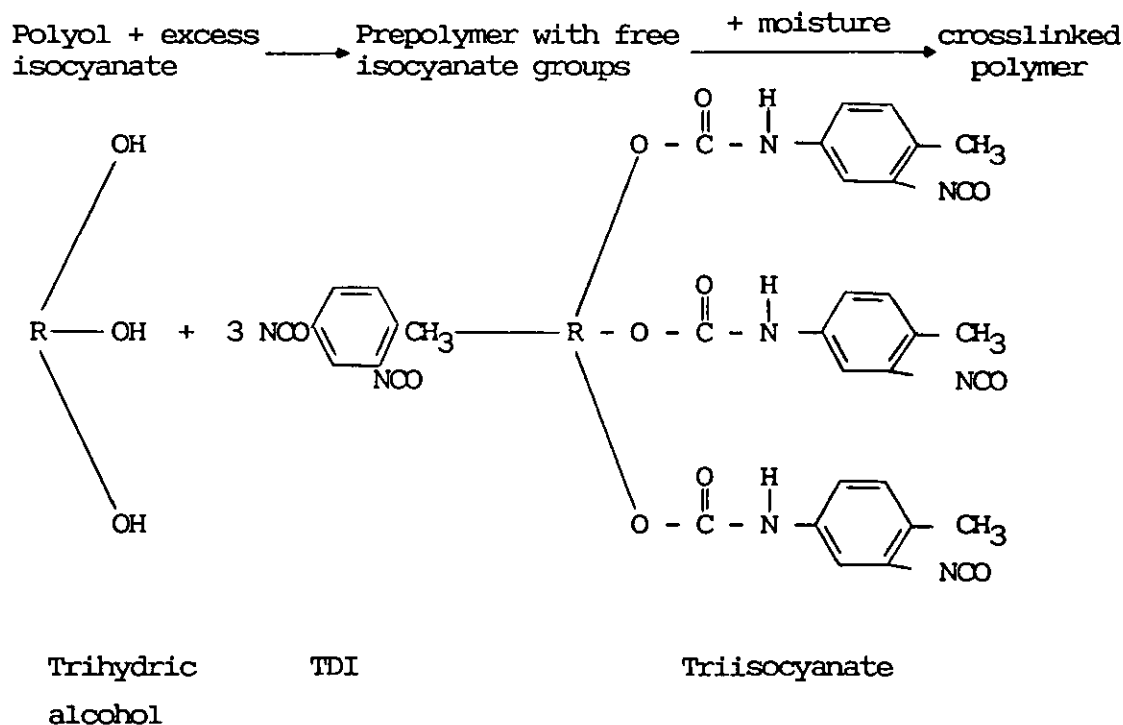
TABLE 2.5: ASTM Classification of Isocyanate Based Coatings [76]

ASTM Type	ONE-PACK			TWO-PACK	
	1	2	3	4	5
Description	Pre-reacted Urethane Oil Modified	Moisture Cured	Heat Cured	Catalysed	Polyol Cured
Cure Mechanism	Oxygen	$\text{NCO} + \text{H}_2\text{O}$	$\text{NCO} + \text{OH}$	$\text{NCO} + \text{H}_2\text{O}$	Polyol + NCO
Reactive	No	Yes	Yes	Yes	Yes
Polymer Type	Prereacted Isocyanate	Prepolymer	Capped Prepolymer + Polyol	Prepolymer + Catalyst	Prepolymer + Polyol
Pot Life	Unlimited	Extended	Unlimited	Limited	Limited
Pigmentation	Normal	Very Difficult	Normal	Difficult	Normal + Additives
Uses	Interior, Wood, Marine, Exterior Topcoats	Marine, Leather, Concrete, Maintenance	Wire Coatings	Leather, Wood	Maintenance, Wooden Furniture, Marine, Exterior
Chemical Resistance	Good	Very good	Excellent	Excellent	Excellent

catalysts may be used to accelerate the drying. If fillers are used, they should not contain stearate, which acts as a surfactant and can prevent good adhesion [73]. This type of coating has been fully reviewed in the literature [70,74,75].

b) One-pack moisture-cured PU coatings

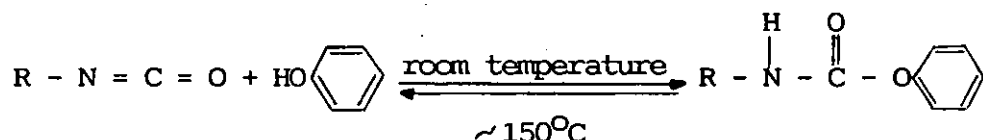
PU coatings belonging to this type are typically polyester polyols reacted with excess isocyanate, to produce low molecular weight urethane prepolymers with isocyanate-tipping. These will cure through the reaction of atmospheric moisture with the terminal isocyanate groups.



Due to their ease of cleaning and stain resistance, moisture-cured PU coatings have become popular in many aspects of floor coatings. A fuller description of this type of coating has been reviewed elsewhere [21,62,70].

c) One-pack blocked isocyanate PU coatings

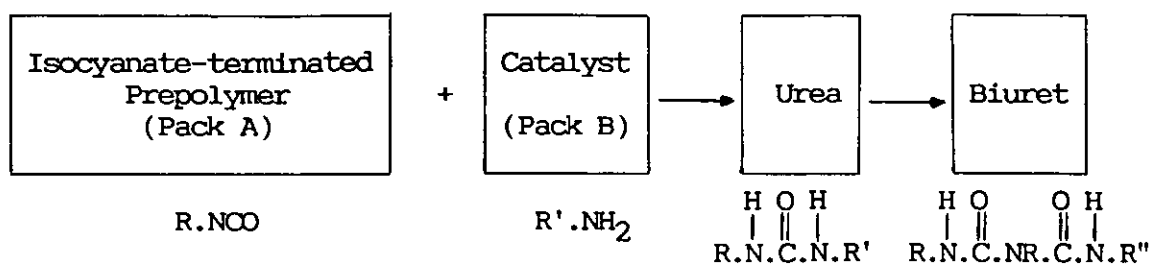
These coatings take advantage of the fact that the reaction between an isocyanate and a monofunctional hydroxyl compound, such as phenol, produces a 'blocked isocyanate' i.e. labile urethane linkage which is unstable at about 150°C [21,64].



The blocked isocyanate can be added safely to a paint formulation, i.e. containing free hydroxyl groups and other additives. When the coating is baked at about 150°C, or at lower temperatures in the presence of catalysts, the isocyanates become 'unblocked' and will react with the -OH groups to crosslink them, while the phenol volatilizes from the paint film. These coatings have good mechanical and electrical properties and are used as wire coating and powder coating, especially by electrostatic spraying.

d) Two-pack catalysed PU coatings

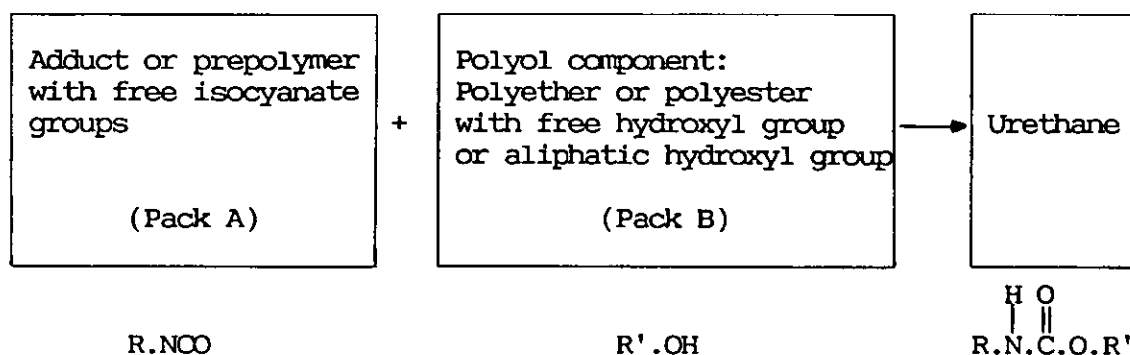
This type is very similar to one pack moisture cured PU coatings. The essential difference is that being a two-pack system, an isocyanate terminated prepolymer forms one pack and a catalyst the other. Both reactive catalysts containing hydroxyl groups such as alkanol amines and non-reactive catalysts such as tertiary amines and metal salts are used.



These coatings will show more reliable drying performance but at the expense of a limited pot-life.

e) Two-pack polyol cured PU coatings

In these coatings, one-pack contains isocyanate-tipped urethane prepolymer or isocyanate-tipped adduct and the second pack contains a blend of active hydrogen containing compounds such as polyols, hydroxyl-tipped urethane prepolymer or an aliphatic hydroxyl group.



The two-packs are mixed prior to application due to limited pot-life of the compounds and reactions take place normally at room temperature, although catalysts may be used to speed up the cure. Pack A will react with any water present in high humidity or if there is adsorbed water on the substrate, resulting in a softer film with some excess of Pack B. To overcome this problem, there is usually a slight excess of Pack A, ensuring that isocyanate to polyol ratio is not too high resulting in a brittle film.

#### 2.5.1.1A General properties of one- and two-pack PU coatings

The advantages and disadvantages of one and two-pack PU coatings are shown in Table 2.6.

	Advantages	Disadvantages
One-pack	Extremely fast drying, highly flexible systems, no problem with pot-life	Generally low solids, problems with pigmentation, limited solvency, only average chemical proper- ties, expensive in rela- tion to solid content
Two-pack	Higher solids, good chemical resistance, easy to pigment, more flexibility in formulating better adhesion	Limited pot-life, more problems with health and safety

TABLE 2.6: Advantages and Disadvantages of One- and Two-Pack PU Coatings

#### 2.5.1.2 Powder coatings

These are based on a number of pigmented powders such as polyethylene, polypropylene, polyamides, epoxies and polyurethanes [77]. PU powder is usually a mixture of a solid polyol and a solid blocked diisocyanate. Powder coatings are applied either using an electrostatic spray gun or by immersing the article to be coated in a fluidised bed of powder, i.e. powder being mobile by passing the air through it. The uniformly dispersed powder coating applied to the substrate's surface is then melted and crosslinked to produce a uniform protective film. Achieving a satisfactory thin film thickness is a problem, but thick, tough coatings, containing no solvent and very low wastages can be obtained by this technique.



### 2.5.1.3 100% solid coatings

High solid polyurethane coatings (essentially fast gelling two-pack solid elastomers) have mainly been developed to meet pollution regulations and to reduce energy costs by lowering the amount of solvents used in the formulation. Since many of the starting materials, i.e. polyols and isocyanates are low viscosity liquids, it is reasonable to think that non-solvent base coatings i.e. 100% solid coatings may be formed as a result. However, in practice, moisture contamination and the resultant escape of CO<sub>2</sub> gas from the thick wet films of such viscous coatings causes problems.

### 2.5.2 The Advantages of Polyurethane Surface Coatings

Many applications of PU surface coatings (PUC) have been reviewed in the related literature [18,64,73]. Some of the advantages of PUCs over other coating systems include the ability to tailor to:

- a) wide range of mechanical properties especially abrasion resistance;
- b) fast curing rate: "drying" often at low temperature of cure;
- c) excellent chemical and solvent resistance;
- d) good electrical properties, particularly for baked urethane systems;
- e) good adhesion to wide range of substrate materials.

## 2.6 OTHER MATERIALS USED FOR PU COATINGS

Fully reacted PUs and oligomeric curing agents may be solubilised, suspended or emulsified in a thinner material. This can be compounded with pigments, flow aids etc to give a surface coating [18,23,24].

### 2.6.1 Thinners

Thinners are a group of fluid components which will normally act as solvents to dissolve the hard resin in a PU paint formulation (i.e. one pack systems) and a suspension aid for solids, allowing the coating to be applied to the substrate as a wet low viscosity film. Solvent thinners can be used to reduce fluid resin viscosity. In addition thinners may be used with PU resins designed for emulsion, suspension etc. The solvent will also affect the wetting and spreading properties of the resin, i.e. reducing the surface tension of resin and allowing the resin to move into the interstices or porosity in the substrate's surface. The solvent may have some beneficial effects in the etching or solvation of the substrate. There is evidence that the solvent system should be selected to suit the substrate material type, depending for instance on the relative Lewis acid-base character [78] (see Section 5.7.1.3). There is the possibility that polarisation occurs preferentially between a polar solvent and the substrate, rather than the PU coating. After solvents have volatilised, a solid dry PU film will be left on the substrate.

Solvency, viscosity, evaporation rate and flash point of solvents being the most important properties for processing and application purposes. The formation of an impermeable skin on the drying paint must be avoided to permit complete solvent release. Flash-off should occur uniformly across the substrate's surface, by employing appropriate drying conditions, e.g. controlled temperature and air flow rates. Also, and particularly for PUs, toxicity, odour and cost are factors becoming more important in today's environment.

Except for urethane oil and alkyd finishes, all PUSCs require solvents that will not react with isocyanates, i.e. active hydrogen

and water contaminated materials cannot be employed [79]. For coating applications volatile, fast drying solvents such as methyl ethyl ketone (MEK) and ethyl acetate are used in spraying applications whereas for brushing, slower, less volatile solvents such as methyl isobutyl ketone (MIBK) and butyl acetate are more suited. In two-pack systems, chlorinated solvents, i.e. methylene chloride and 1.1.1 trichloroethane, giving a longer pot life are used.

### 2.6.2 Pigments

Pigments for PU coatings, either organic or inorganic, are mainly used to provide the desired colour to a paint, to improve the strength, adhesion and durability of paint film, and modify flow and application properties. The main pigment characteristics are light fastness, opacity, particle-size, refractive index, chemical resistance, dispersibility, migration resistance and permanence [80,81].

A suitable pigment for PU coatings is selected on the basis that it is free from moisture and reactive chemical groups. Moisture may be removed by adding the pigment to an appropriate component such as a polyol, a liquid epoxy, an alkyd resin, a neutral resin, and others followed by azeotropic distillation [82].

In order to achieve desired surface effects, pigments must be properly dispersed. Many problems caused by pigmentation can be overcome if flocculation, a condition in which loose aggregation of pigment particles formed into clusters, can be avoided [83]. Flocculation can be due to a number of physico-chemical effects: comments here are also relevant to pigmented PU RIM products. Flocculation may result from static effects caused by pigment particles in contact with one another (i.e. adsorption), density differential effects produced with pigment particles joined to other substances in the coating resin

(i.e. chemisorption), restricted flow paths for liquid moulding materials (i.e. filter plate problem), or differential foam formation.

Defects such as: poor gloss, inconsistent colour of coating, and separation of pigment particles on the surface, mostly attributed to flocculation, can be reduced by increasing the coating viscosity, proper evaporation rate of drying, and balanced pigment mobilities. Therefore wetting agents are used to improve the dispersion and its stabilisation especially where the hydrophility of the pigment reduces the ease of dispersibility in hydrophobic systems. Owing to storage and transport, humidity forms a thin water skin around inorganic compounds. The molecular structure of organic pigments causes them to be generally hydrophobic. However they have a large specific surface, and consequently absorb water, and they also change to a hydrophilic character. During dispersion with a wetting agent, the water skin is removed allowing the polar groups to react with the pigment surface; the hydrophobic 'tail' is compatible with the hydrophobic resin. Additives such as polycarboxylic acids, certain silicon compounds, and acid salts of long chain amines may be used to eliminate the flocculation problems [83-85].

Apart from the pigments used in the surface coating of PU products, mass pigmentation may be applied in order to colour the PU substrates. In general, pigments for plastic substrates are insoluble organic or inorganic compounds dispersed as discrete particles throughout a resin to achieve colour [86]. Examples of organic pigment compounds are: dioxazine, disazo and diarylide. Inorganic pigments include: iron oxide, zinc sulphide, chromates, titanium dioxide, and carbon black. The overall cost of pigmenting the PU substrate specially with a strong, expensive organic pigment must be considered and compared with the surface coating of that product, especially if the base PU is coloured.

### 2.6.3 Flow Agent

Regardless of the method of application i.e. brushing, spraying, etc, a PU coating should result in a smooth, level dry film without any undesirable effects such as "orange peel". Good levelling vehicles, specially treated pigments, and maintenance of low wet coating viscosity by slow evaporation of solvents may be used to improve the flow. However, in many cases, addition of a small amount of flow agent such as silicones, cellulose acetate butyrates and certain acrylic copolymers are used to improve the wetting and levelling. They can also be used to stop bubbling formation in the urethane coatings.

### 2.6.4 Bodying Agent

Bodying agents, also known as anti-settling or anti-sag agents, are mainly used to improve the stability of a urethane coating by raising its viscosity after solvent loss and hence increasing the sag resistance. They are also described as flow control thixotropes (i.e. when a fluid is stirred, brushed, or otherwise worked and becomes less viscous, it is referred to as thixotropic).

Bodying agents mainly used for urethanes and acting as a thixotrope are polyacrylic acids and polyacrylamides. Certain types of cellulose acetate butyrates or polyvinylbutyral may be used as well.

### 2.6.5 Flattening Agent

In order to reduce the high gloss of many urethane coatings and get a duller effect, some flattening agents may be used. Metallic stearates such as aluminium or zinc stearates, which are insoluble in cold solvents, will cause minor irregularities on the surface, thus increasing the diffuse reflection of light from that surface and improving the dullness. Amorphous silicas used in both solvent and aqueous coatings is another useful flattening agent, where the flattening efficiency will depend on the silica's particle size.

#### 2.6.6 Anti-Foaming Agent

In many PU paint systems, foaming refers to the condition where stable bubbles are produced at the air-paint interface due to agitation, boiling, turbulent pumping or any other processing conditions. Anti-foaming agents which act by reducing surface tension can be added to break any bubble formed and prevent any disruption in the manufacturing process. Normally low viscosity paints show a decrease in foam.

Anti-foaming agents should have a high spreading coefficient and their surface tension (see Chapter 5) must be lower than that of the foaming solution. They must be readily dispersed in the solution without reacting with it, and they must not leave odour or taste or any residue that is detrimental to the end product.

Anti-foaming agents mainly used are certain partially soluble solvents, silicone oil or hydrophobic silica based additives. Also, sonic devices may help breaking the foam and in some cases higher temperature is effective.

CHAPTER 3  
SURFACE COATING OF PLASTICS

**3.1 A REVIEW**

Many polymer systems can be moulded without the necessity for surface coating. Such self-colouration using pigments or dyes along with additives such as anti-oxidants, UV or heat stabilisers will provide finished products resistance to withstand most end-uses. Nevertheless, there has been a rapid shift towards the surface coating of plastics especially over the last decade. This has been due to some complications in terms of pigmentation (see 3.5) and also the need for many surface properties (see 3.2).

Plastics have replaced metals and wood in the manufacture of many types of components which often need to be surface coated. This in part is due to the demand for plastics in the automotive industry [9,87,88] (Figure 3.1). During the 1980s, such demand has particularly been for the production of various vehicles exterior and interior parts.

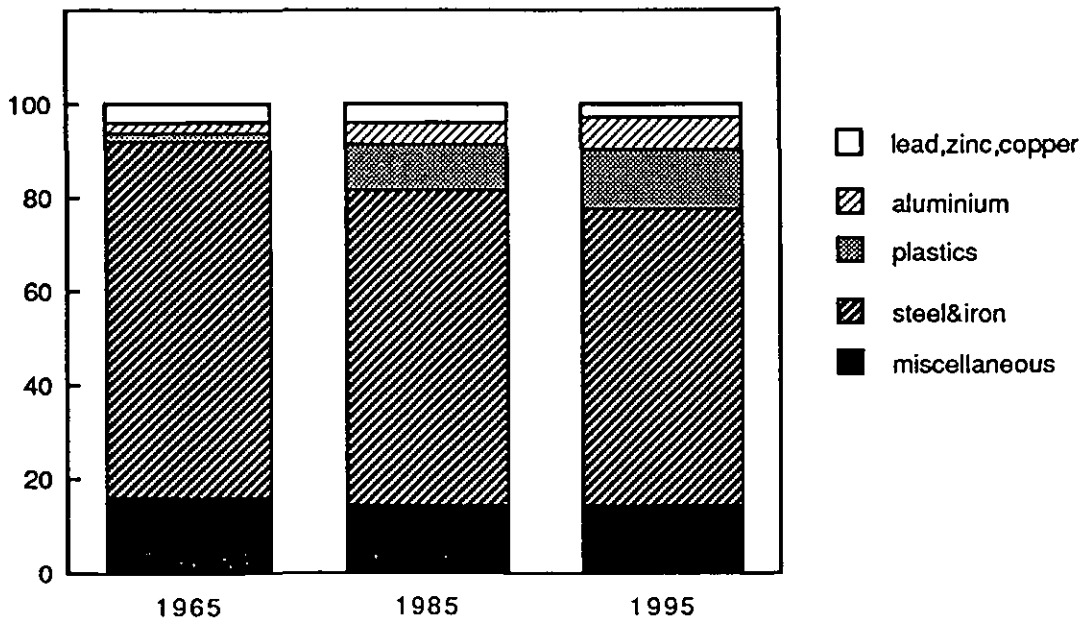


FIGURE 3.1: Proportion (%) of Different Materials in Cars [89]

It has been estimated that the consumption of plastics, per vehicle, in Western Europe in 1980 and 1985 was 60 kg and 100 to 150 kg respectively [87,90]. A forecast for 1990 is given in Table 3.1. The figures in Table 3.1, exclude surface protection, wire coverings and tyres. If these applications are included, the 1990 estimate for the consumption of plastics per vehicle can rise to 250 kg.

Type of Plastics	Private cars		Commercial vehicles		Total
	1000t	%	1000t	%	1000t
Polyurethane	290	22	25	15.5	315
Polyvinyl chloride	170	13	15	9.5	185
Polypropylene	310	23.5	25	15.5	335
ABS	85	7.5	8	5	93
Thermosetting polyesters	130	10	45	28	175
Polyamides	70	5.5	5	3	75
Polymethyl methacrylate	27	2	4	2.5	31
Phenolics	19	1.5	4	2.5	23
Others	219	16.5	29	18	248
Totals:	1320	100	160	100	1480

TABLE 3.1: Estimated Consumption of Plastics in Western European Automotive Industry in 1990 [91]

It must be noted that difficulties in reclaiming plastics materials from scrapped vehicles have, more recently, produced modified predictions that plastics use (especially of exterior panels) is unlikely to increase from the late 1980s content.



However, the consumption of surface coatings will undoubtedly increase with the growth of the plastics industry. Such consumption has been estimated at 46,000 tonnes in 1988 compared with 20,500 tonnes in 1980 for all Western Europe [92]. Of this total usage, the transport industry, mainly the automobile sector, dominates the demand utilising some 26,850 tonnes of coatings. Around 80% of this is for exterior components of vehicles and the remainder for interior items. Electrical appliances and electronic equipment are the other major usage sectors, accounting for around 16,525 tonnes in 1988. Other areas of use include furniture, packaging items, toys and leisure goods and various building components.

The consumption of surface coatings indicates an average growth rate of 10.6% yearly over the 1980 to 1988 period. On this basis, it has been anticipated that the West European market will reach a level of 120,000 tonnes by 1998 [92].

### 3.2 REASONS FOR COATING PLASTIC SUBSTRATES

Plastic substrates are coated for the following reasons [9]:

- a) To alter the appearance and particularly the aesthetic appeal of the substrate:

This can range from changing the colour to modifying the texture of the surface to simply hiding defects in the substrate. Coatings can be used to give change in texture, opalescence or metallic effects. Thus plastics mouldings which would otherwise have a solid plastic appearance can be completely changed to make them appear more like natural items such as wood, leather, stone or cork, etc. Often these effects rely both on the spray painter

and paint formulation. It may be argued that coating an object permits the use of a much greater number of colours compared with incorporating solid colouration to the object itself. However, a counter-argument suggests that the surface coating is "skin-deep" and therefore scratching through will reveal the substrate colour and permit ingress of external agencies.

b) To change the physico-chemistry of the surface:

The bulk mechanical properties of a plastics moulding should be at least adequate to give good performance during its working life. However, deterioration often is initiated at the moulding's surface due to attack by external agencies e.g. weathering (e.g. UV radiation, oxygen or ozone/thermal degradation), corrosive industrial or marine environments. Resultant weakening of the surface structure may have a dramatic effect on the bulk mechanical properties. Therefore use of a coating as a barrier will be beneficial. Coating can even be used to provide fire barrier by intumescing in heat.

c) To alter the mechanical properties of the surface:

Surface coatings can be formulated to enhance the surface mechanical properties of a plastics material. Examples include improvements to abrasion/marring resistance, alter electrical and friction properties, and improve impact resistance. Ideally the coating must have similar bulk properties as the substrate, e.g. same thermal expansion and same modulus (already greater flex has certain advantages).

In summary, the plastic materials are primarily coated in order to achieve better surface properties and appearance, while at the same time prolonging the useful life of the plastic substrate.

### 3.2.1 Coated Polyurethane Products and Reasons for Protection

Over the last two decades, both the development of higher pressure dispense equipment, e.g. as used in reaction injection moulding (RIM), and the advent of high performance grades of self-skinning PU foam, has broadened the end use of polyurethanes in moulded products [9]. To compete against the traditional materials such as timber and metal and other polymers, PU products must perform at least as well on a cost basis (i.e. RIM machinery and process costs).

The coating of PU products will give them greatly improved resistance to ultraviolet and oxidative attack (see 3.2.2), enhance their physico-chemical properties, hide their imperfections and improve their aesthetic appeal.

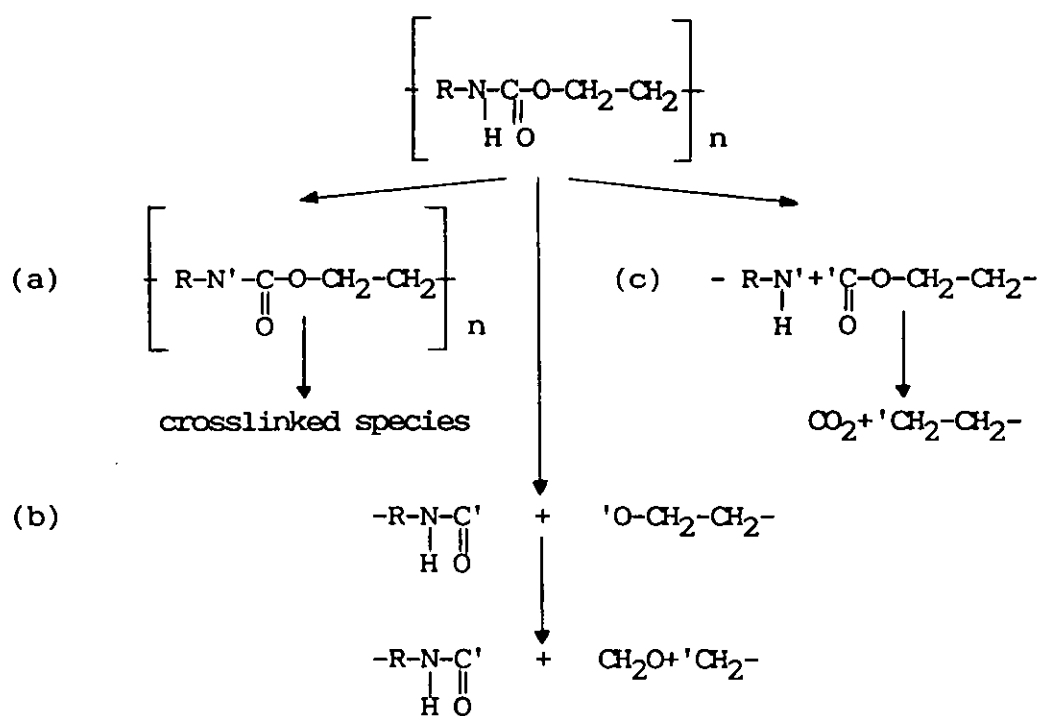
PU products, where surface coatings have been employed particularly to protect the substrate, include [9,93]:

- i) automotive uses (internal): steering wheels, head-restraints, armrests. Currently based on energy absorbing grades of semi-flexible self-skinning foam (pure MDI, modified polyether polyol blends,  $SG = 0.4 \pm 0.1$ ).
- ii) automotive uses (external): bumpers, vehicle panels, wheel-arch eyebrows, rear spoilers. These will be based on a range of urethane and urea systems of various moduli, self-skinned microcellular foamed and solid materials, some incorporating fibre reinforcement (pure MDI, modified polyether/polyester polyols, urethane/urea and ureas,  $SG = 0.4$  to  $1.1$ ).

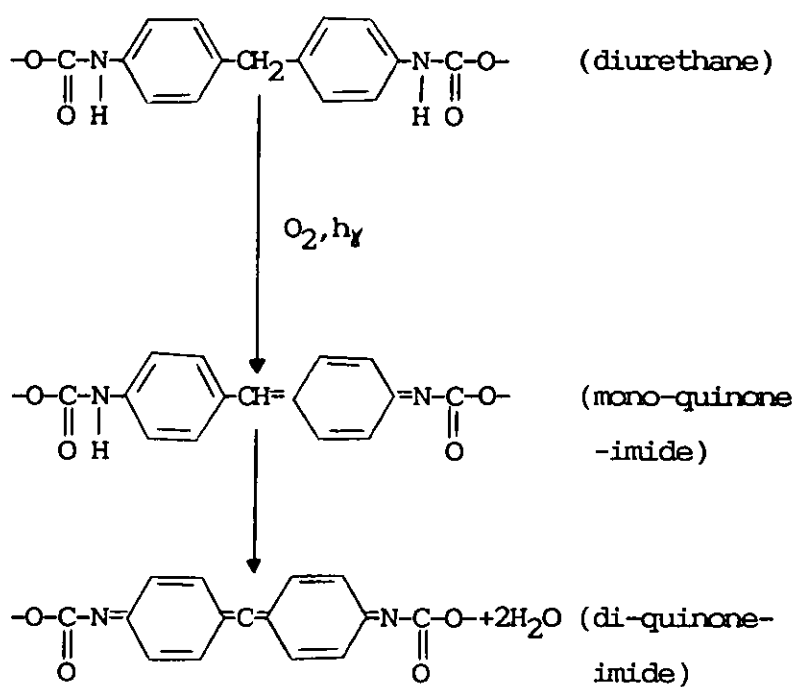
- iii) housing for electrical and electronic components, e.g. business machines, computer castings. These are based on rigid high density self-skinning foams (polymeric MDI, polyether polyols, triols, SG =  $0.5 \pm 0.2$ ).
- iv) insulation grades of spray foams used to clad the exterior of storage tanks, roof tops, etc. These will be based on rigid low density grades of either highly crosslinked PUs and/or polyisocyanurates foams.
- v) decorative panels, kitchen cabinet doors. These will be based on intermediate density rigid foam, normally self-skinned. Although strictly use of low pressure dispersive and simple tooling (G-clamped epoxy types) means that skin thickness may be minimal (cf RIM structural rigids).

### 3.2.2 Ultraviolet (UV) Stability of Aromatic Isocyanate Based PU Mouldings

Aromatic isocyanates tend to impart poor UV and oxidative resistance to a PU molecule. As a result, exposure to sunlight produces discolouration, surface cracking and a general loss of surface related properties [9]. A benzene ring structure in a polymer chain strongly absorbs radiation at 290 to 350 nm [94]. The resulting degradation species are coloured in visible light. The chromophores formed include the nitro, carbonyl and ethenyl radicals which are often attached to a benzene ring. The coloured molecules in turn can be further colour intensified by specific associated groups, known as auxochromes. These include the primary, secondary and tertiary amines, hydroxyl and methoxy radicals. Nevskii et al [95], suggested for a TDI based, triethylene glycol/PEG 600 PU, the following scission mechanisms might occur:



Schollenberger et al [96], suggested that di-urethane groupings subjected to UV and oxidative attack produced the chromophore di-quinone-imide, i.e.



With these changes in molecular structure and associated losses in hydrogen bonding between chains, physical and mechanical properties will be reduced. The surface of the degraded PU becomes friable and can then suffer abrasive losses, e.g. by wind borne dust. As a result new PU surfaces will be progressively exposed to continued attack.

### 3.3 SURFACE COATING OF PU SUBSTRATES: APPLICATION AND METHOD

Over the years, the areas and the types of applications in which PU surface coatings were traditionally used have extended. Consequently, the wide number of process parameters and end applications of urethane coatings mean that many application techniques can be employed. Methods of applying a coating material to a PU substrate may be split largely into painting and printing techniques.

#### 3.3.1 Painting Techniques

The methods of painting depend on both the coating and substrate materials. The size and geometry of the substrate along with its processing and surface conditions are all determining factors. Paint formulation and viscosity are among the coating conditions affecting the method of painting. Other factors such as the required quality, the type and cost of machinery and the numbers and cost of products also have a bearing on the method of painting being used [13,93,97]. Some of the most important methods applied to PU materials are as follows:

##### A. Brushing and rollering

Hand application using brush or roller is the simplest and cheapest method, but the quality and consistency of the finished product is dependent on the applicator and to a lesser extent, on the grade of

paint and type of tooling used and ambient conditions. Paint brushes are available in a wide variety of sizes and designs to suit various types of paints and surfaces. They can be used in areas where other application methods would be restricted. Paints and lacquers for brush application are normally fairly viscous and have a high solid content. By rollering a greater surface area can be treated but effects are limited to block colouring. One limitation of rollers is their inability to cut into corners or work into confined spaces and it is normally necessary to use a brush for finishing off in such cases. Both techniques are labour intensive.

#### B. Dip-coating

This technique used for three-dimensional shapes, relies on partial or total immersion of the component into a tank of the coating material, which is then allowed to drain to remove any excess. Careful formulation of the coating and control of the process will minimise loss of surface definition and slump marking at lower points of the drained component [93]. One of the limitations of this type of painting is the pigment settlement in the tank as the result of low viscosity of paint needed for good draining. Fire hazard due to storage of a large quantity of liquid paint in the tank is another serious problem.

#### C. Continuous-coating operations

Curtain coating is usually used with continuous and uniformly flat profile products. The film thickness is dependent on formulation, line speed and volumetric output from the coater. Consistent and low film thicknesses can be achieved on uniform profiles, using modified forms of printing and film lamination equipment such as reverse-roll, gravure, knife-over-roll and doctor blade coating.

#### D. Air-fed or airless spraying

Spray application using air-fed or airless units is the most widely practised method in the plastics industry. The benefits of spray painting lies in the speed of application, quality, economy and adaptability to almost any conditions, shape or size of article. The intervention of robotics and simpler forms of automation means there is less reliance on skilled and experienced manual sprayers. The main disadvantage associated with this system is the wastage of paint material due to overspray.

The overspray problem can be overcome by electrostatic spraying which can be used in both air-fed and airless spraying. In this type of spraying, paint is electrically charged either by a specially designed gun or by passing it through an electric field. The paint will then be attracted to a conductive substrate whereby the coated parts will become electrically insulated allowing further deposition to occur at uncoated parts.

##### 3.3.1.1 Paint spraying application equipment

Air-fed units rely on a suitable capacity air compressor to provide a supply of clean air free from dust, water and oil contamination. The compressed air and paint are then carried to the spray gun which, when triggered, allows the compressed air to force the paint to propel through a nozzle onto the substrate's surface. The nozzle will control the droplet size, the volume dispensed and the overall spray pattern. Paints made for application by air-fed spraying must be low viscosity and stable allowing break up into droplets [98,99].

Airless spraying relies on mechanical pumping to the spray head, the pump displacement having most control over the volume dispensed, the



nozzle setting controlling the final outlet. The very high pressure in the region of  $20 \text{ MNm}^{-2}$  used in the airless spray [100] will permit nearly all paints to be sprayed in their original unthinned state. With both airless and air-fed systems, the distance of any droplet propelled is dependent on the pump or air pressure. Airless spraying will give a smaller droplet size and a very wide spray pattern and, thus, it is ideally suited for the fast coverage of large areas with decreased paint wastage.

The basic spray equipment is not expensive although spray booths, handling systems and extraction systems will mean large capital investment and occupation of floor space. Automation is facilitated by conveyor systems and drying tunnels. Along with fume extraction, dust extraction is important. Drying ovens are used to speed cycles, depending on PU coating and its solvent, by decreasing cure times. High temperature stoving ovens are used to achieve high gloss and superior physical properties specially in automotive components. Spray operators have to be fully equipped with air-fed masks and protective clothing.

### 3.3.2 Printing Techniques

The more important techniques include [93,101,102]:

- a) letter press (ink transferred from a raised print image);
- b) lithography (ink transferred from a flat image);
- c) gravure (ink transferred from a depressed image);
- d) screen (ink passed through a series of holes forming a pattern);
- e) hot foil transfer;
- f) xerography.

Currently printing of PU substrates is comparatively restricted. Examples include leather clothes where perhaps a subtle image is required, printed using gravure or screening methods.

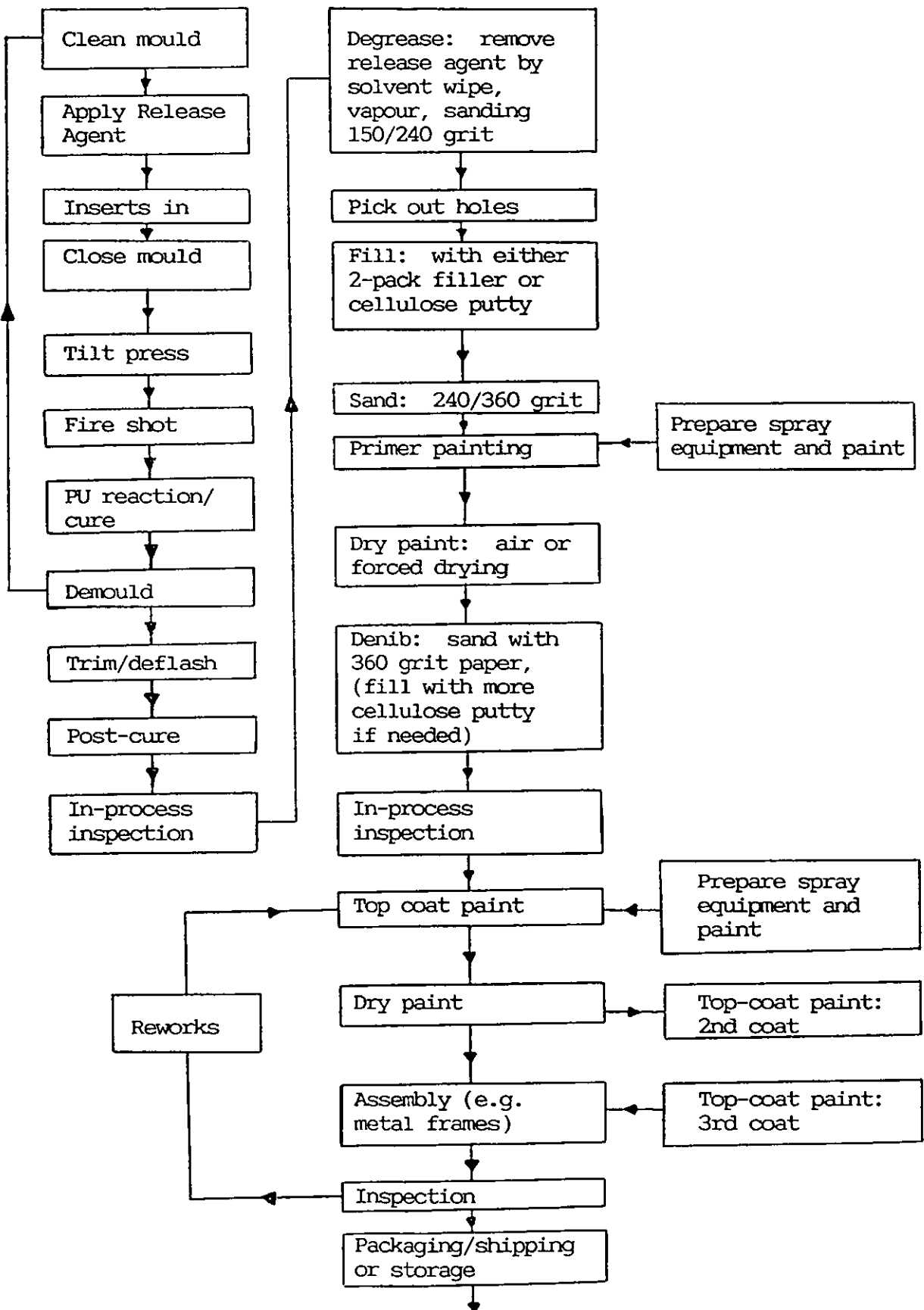
### 3.4 COMMON PROCESS METHODS FOR COATING PU SUBSTRATES

With a few notable exceptions, dealt with below, a manufacturer has no choice but to apply a surface coating to a ready formed plastics product. This series of process steps may be called post-mould coating (PMC). A specific example of PMC is weatherproof coating of spray applied PU foams. The exceptions to this rule have come about over the last 15 years or so, with the evolution of certain production techniques (especially with PU mouldings) and the need to cheapen the overall moulding/painting process. Such methods for PU/PU combinations detailed below include in-mould coating (IMC) and barrier release coats (BRC) where a coating is applied to the mould surface prior to filling with a reacting PU system. In addition, in-mould label (used with extrusion blow moulding) and in-mould foil transfer (used with thermoplastic injection moulding), are noted here but detailed elsewhere [103].

#### 3.4.1 Post-Mould Coating (PMC)

Most plastics to be painted will undergo PMC, with some minor variations. Table 3.2 illustrates a typical manufacturing process flow for PMC. The overall operation consists of making the PU moulding, preparing its surface, then a coating is applied. Both reaction injection moulding (RIM), and open and closed pour mouldings form low pressure dispense units, are used in the manufacture of moulded components. At this stage, proper moulding practices: good design in the feed system associated with sprue, runner and gate,

TABLE 3.2: Flow Diagram for Post-Mould Surface Coating Process [9]



accurate PU foam ingredients, adequate control of temperature, humidity and cleanliness, correct use of release agents and good deflashing and post-cure, results in higher perfect moulded components, saving time and cost in the operations to follow. In terms of the production rate, the painting stages are the most time consuming and costly operations (cf less than 10 minutes to mould and deflash, up to 2 hours to prepare and paint). This largely comes down to the extra steps in the preparatory stages to painting: release agent and contamination removal, repairing the moulding imperfections (hopefully of low numbers), primer, pre-top and top coating operations [9].

#### A. Release agent and other contamination removal

Several techniques are recommended and used to remove the residual release agent and other surface contaminations which might otherwise affect the adhesion between the PU substrate and the coating [38,69,104]. The excess release agent is usually removed at the same step when the deflashing and light surface abrasion is carried out. A vapour degrease bath using a chlorinated hydrocarbon, will effectively remove most release agents and waxes picked up in the process. The moulding must be free of degreasing fluid to prevent blistering of the subsequently applied and dried paint. There is some risk that the hot vapour may distort the thin sections of undercured mouldings. Any remaining release agents should then be dissolved into the paint's solvent during the early part of the painting stage. On the loss of the solvent it becomes part of the paint film without inhibiting the interfacial bonding or reducing the cohesive strength of the dry paint film [9].

Silicone based release agents are extremely efficient, have low surface energy values, and prove extremely difficult to degrease completely, which will tend to prevent subsequently applied liquid paint properly wetting out the substrate. Therefore they are not usually recommended if the PU moulding has to be painted.

Dust must be removed from the surface of the abraded moulding using anti-static cloths and "tac rags" to prevent paint defects. Care must be taken to avoid contamination from anti-static cloths getting into the moulding. Good extraction and satisfactory housekeeping helps this and also reduces the health hazard.

#### B. Repairing the moulding imperfections

If faults are found in a moulding, then they have to be rectified before surface coating can be carried out. The most common faults are: air traps, blisters, sink and surge marks, problems associated with integral skin thickness variations and defects due to inadequate use of release agents. Since most paint systems (as solvent thinned pigmented resins) will not impart a cosmetic effect that will hide such defects, special repair materials are used.

Repairing materials usually fast curing at room temperature are basically two-pack thermosetting polymers such as unsaturated polyesters, epoxides and polyurethanes [69]. The PU type repair fillers are mostly selected with PU substrates for best mechanical and chemical matching properties. It must be noted that good housekeeping, regular moulding process control and quality control will virtually eliminate many of the moulded imperfections.

### C. Primer surface coating

Prior to any coating, the surface should be as smooth as possible. To do this, correct grades of emery cloth or sandpaper should be used. Care must be taken not to cut deeply into the substrate and not to change the required geometry of the moulding.

Once the surface is ready for coating, most substrates must be primer coated. Several functions fulfilled by a primer coating are listed below:

- i) enhance the adhesion between the top coat and the substrate;
- ii) act as a coloured mask or "undercoat" to the substrate colour;
- iii) reinforce the strength of the top coat colour, so less need be used;
- iv) can be used as a 'stopper' or surface filler of minor surface faults.

The primer is normally heavily pigmented to mat down the surface and to promote extra mechanical keying by effectively increasing the real surface area of the substrate (see 4.2.3).

It is thought that because of the near identical chemistry of the PU surface coating to the PU substrate materials, that they offer the best combination of end properties, although epoxides, polyesters, acrylics and cellulosic coatings may also be used.

### D. Pre-top coating

After the primed substrate is dried a thorough inspection particularly for holes missed in the filling stage is carried out. In addition, moulding defects due to high temperature of drying or solvent stress

relaxation can be revealed at this stage. By rubbing down of the dried primed moulding to remove inherent roughness, relatively small defects such as 'fish eyes' (i.e. small depressions in the paint film exposing the substrate) can be found. All such defects should be filled and then rubbed down prior to the top coating.

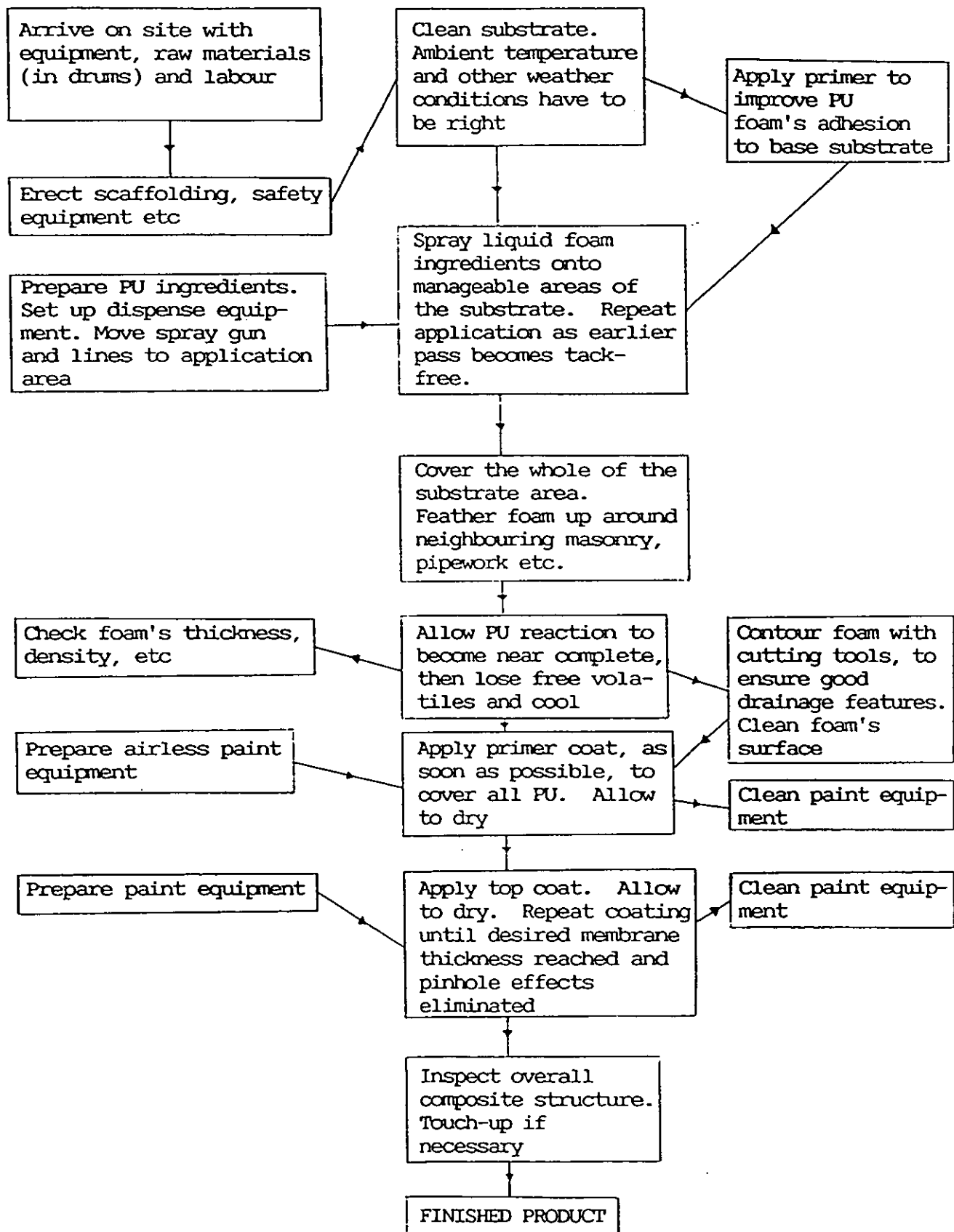
#### E. Top coating

The top coat will provide the surface that will be viewed in the finished product. Therefore it should be aesthetically pleasing as well as providing the surface properties necessary for a long service life. It must adhere well to the primer or in some instances to the bare substrate. The formulation and manufacture of the top coats are more critical than the primer, since colour and surface finish can be equally as important as the physical properties [9]. Top coating can be carried out in single or multiple operations depending on the quality of the dried film required.

##### 3.4.1.1 Weatherproof Coating of Spray Applied PU Foams

This type of coating is a specific example of PMC, where a thick layer of surface coating, usually a type of PU or acrylate elastomer, is sprayed onto a substrate normally based on PU rigid foam. Hence enhancing a number of properties of the substrate in external applications such as roofing and thermal insulation cladding of cooling and heating constructions. Table 3.3 shows the flow diagram for this system. Weatherproof coatings are excellent barriers for many mainly outdoor environmental effects such as UV/oxidative degradation, rain/water penetration and rupture and impact due to light traffic.

TABLE 3.3: Flow Diagram for the Application of Rigid Polyurethane Foam Coated with a Weatherproofing Elastomer Film [9]





### 3.4.2 In-Mould Coating (IMC)

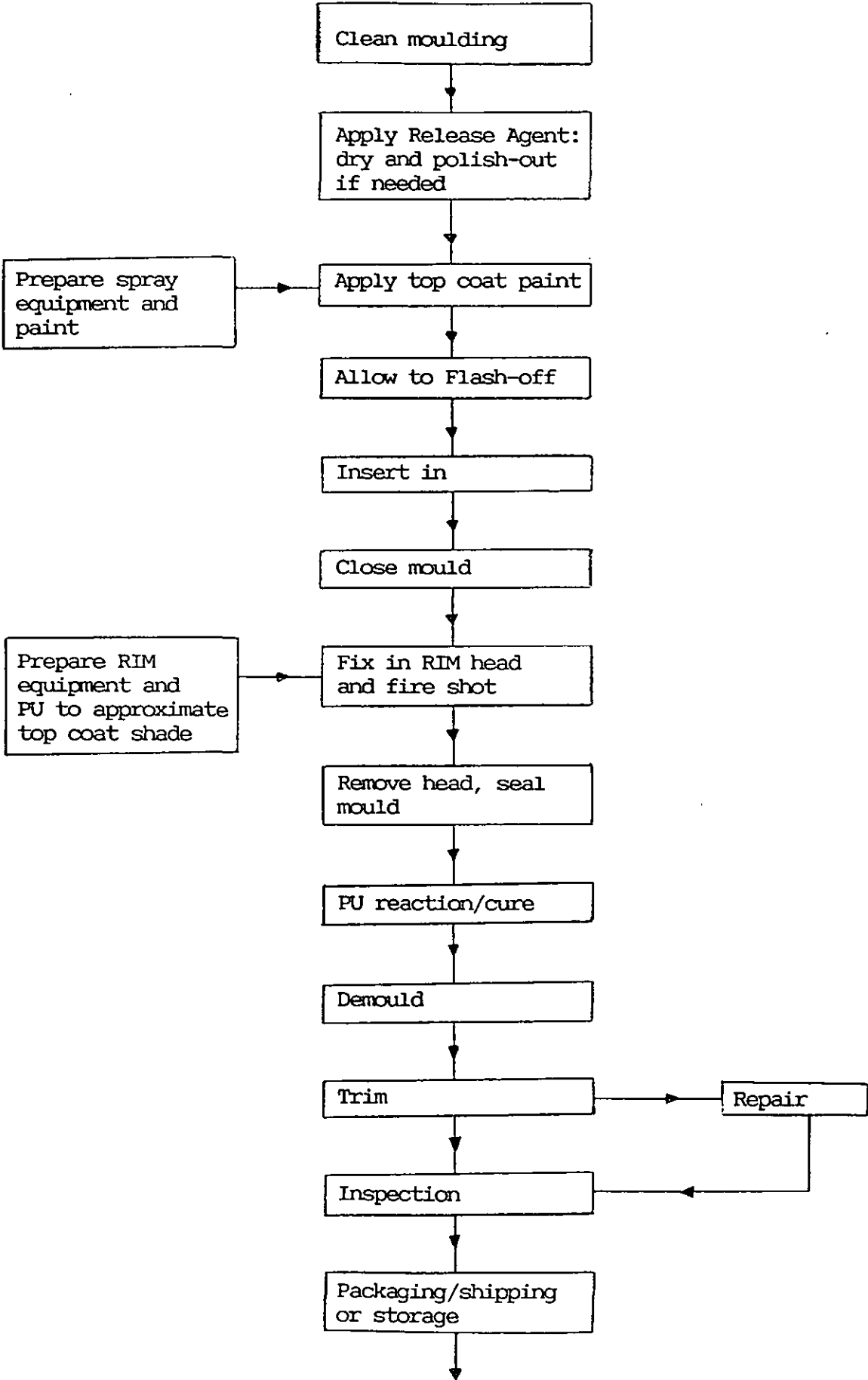
In experiments in the late 1960s [9] by companies including Shell Chemicals, rigid skinned PU foam shells were made by slush-moulding a pigmented liquid PU system onto the inner surface of the mould and then PU foam ingredients were poured in the mould. This was an early basis for IMC in PUs. IMC was specifically developed in Europe and the USA in the mid 1970s for self-skinned foamed PU mouldings and sheet moulding compounds [105]. It was further developed in the late 1970s by the cooperation between moulders, paint companies and the PU foam suppliers into viable commercial process for many aspects of PU industry [9]. Many of the IMC principles can be seen in the gel coating of glass reinforced plastic structures, based on unsaturated polyester resin or epoxides.

The production flow diagram for IMC shown in Table 3.4 is different to that of PMC. During the ICM process, a wet surface coating is applied to the mould internal surface (as substrate) as a step of the moulding cycle, with some increase to the cycle time, but with considerable reductions in the other steps associated with PMC. Therefore in IMC, the action of the paint and the polymer substrate are in reverse order, with the former becoming a thin substrate onto which a thick coating is applied.

#### A. Coating process for IMC

The release agent is usually applied to the mould at the start of each moulding cycle, allowing easy removal of the finished article without affecting the paint's finish. As soon as the release agent has flashed off, the paint can be applied by normal spraying techniques. The quality of the mould is extremely important for IMC, since the coated side will become the visible surface of the finished product. The

TABLE 3.4: Flow Diagram for In-Mould Surface Coating Process [9]



moulds for IMC must have good heating and cooling control. The greatest delay to the moulding cycle, relates to the rate of solvent evaporation from the wet paint film. Fast drying solvents such as MEK are normally used. With the heated moulds, chlorinated hydrocarbons are employed which may give rise to health and safety risks and require good extraction facilities. Modern mini-spray booths and flash off stations, given their extraction systems, once built in the carousel or conveyor lines, would eliminate the problem of having a separate painting area.

In IMC, solvent entrapment should be avoided, since a wet paint may cause the paint film blister on the mould release and it may also affect the foam's skin thickness. Air circulation and mould temperature will aid the evaporation of the solvents. Once the solvents have flashed off, the PU foam ingredients are poured in and the mould is closed or in the case of RIM, the mould closed and the mix-head located and a shot fired. Some manufacturers claim that the surface coating on the mould's surface facilitates flow of the PU foam ingredients and reduce the risk of air trapping and blistering.

The PU coatings for IMC, supplied either as one or two pack systems can be pigmented, tinted or clear. Clear coatings are not very common as it is difficult for the operator to see whether the mould is completely covered [40]. Also, matting or texturing agents are not used since the coating should take the surface characteristics of the mould. Surface effects such as matting are usually achieved by sand blasting the mould surface, or by using additives in the release agent. The paint application is normally in the form of top coating, omitting the primer or undercoat processing. Hence very thin films may be produced in one coat, making IMC very viable for special cases such

as UV resistance coatings for interior and exterior applications where coating thicknesses of about 5 and 15 microns respectively are sufficient to give the desired property [9].

IMC is made easier, while less film thickness is required where the substrate is approximately the same colour as the paint or moulds have simple shapes. Also minor painting defects will be subsequently buried into the substrate.

#### B. Final stages of IMC

Following demould, process operations must be limited to deflashing and inspection, to keep costs down. In many cases the only trim needed involves the cutting of a thin flexible film at the flash line without cutting into and exposing the substrate. To avoid the need to do any post moulding repairs, the mould wear must be kept to a minimum e.g. by using replaceable mould liners.

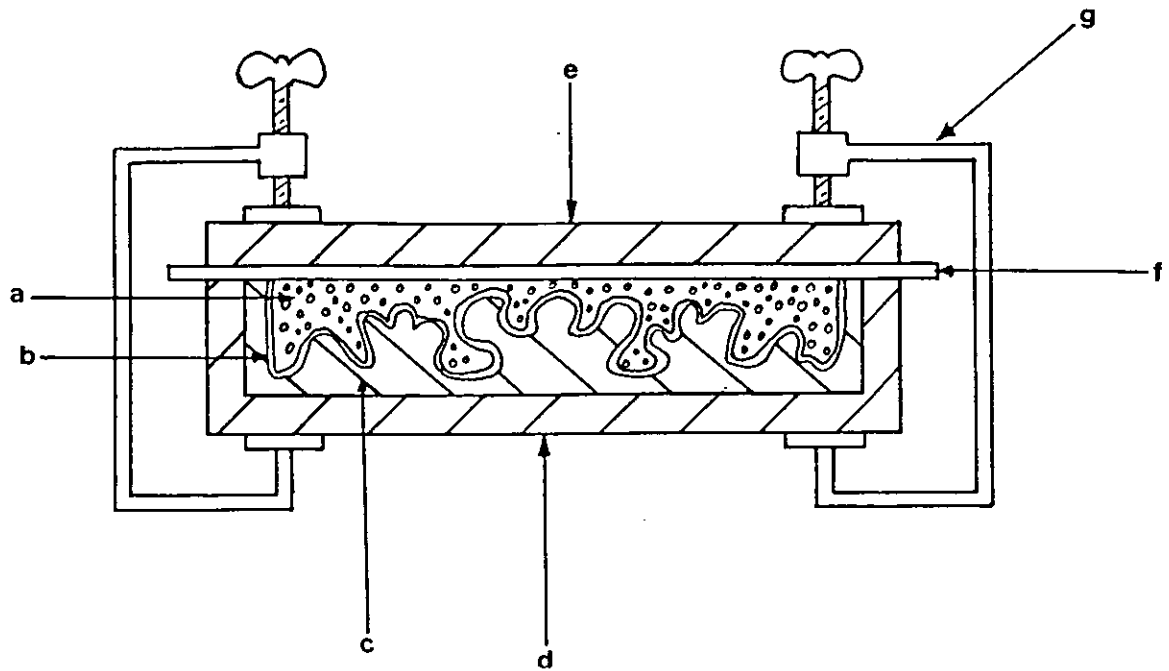
##### 3.4.2.1 Barrier release coats (BRC)

BRC is a specific example of IMC, having combined properties of a release agent and a primer, giving excellent adhesion to any coating applied subsequently [9].

It is normal to use flexible moulds (e.g. based on silicone or PU elastomers) supported by a rigid frame box, usually made of epoxide in a wooden or steel frame (Figure 3.2).

PU ingredients poured into the mould are allowed to foam and cure, then the silicone liner is peeled away, cleaned and reused. Table 3.5 shows the flow diagram for BRC.

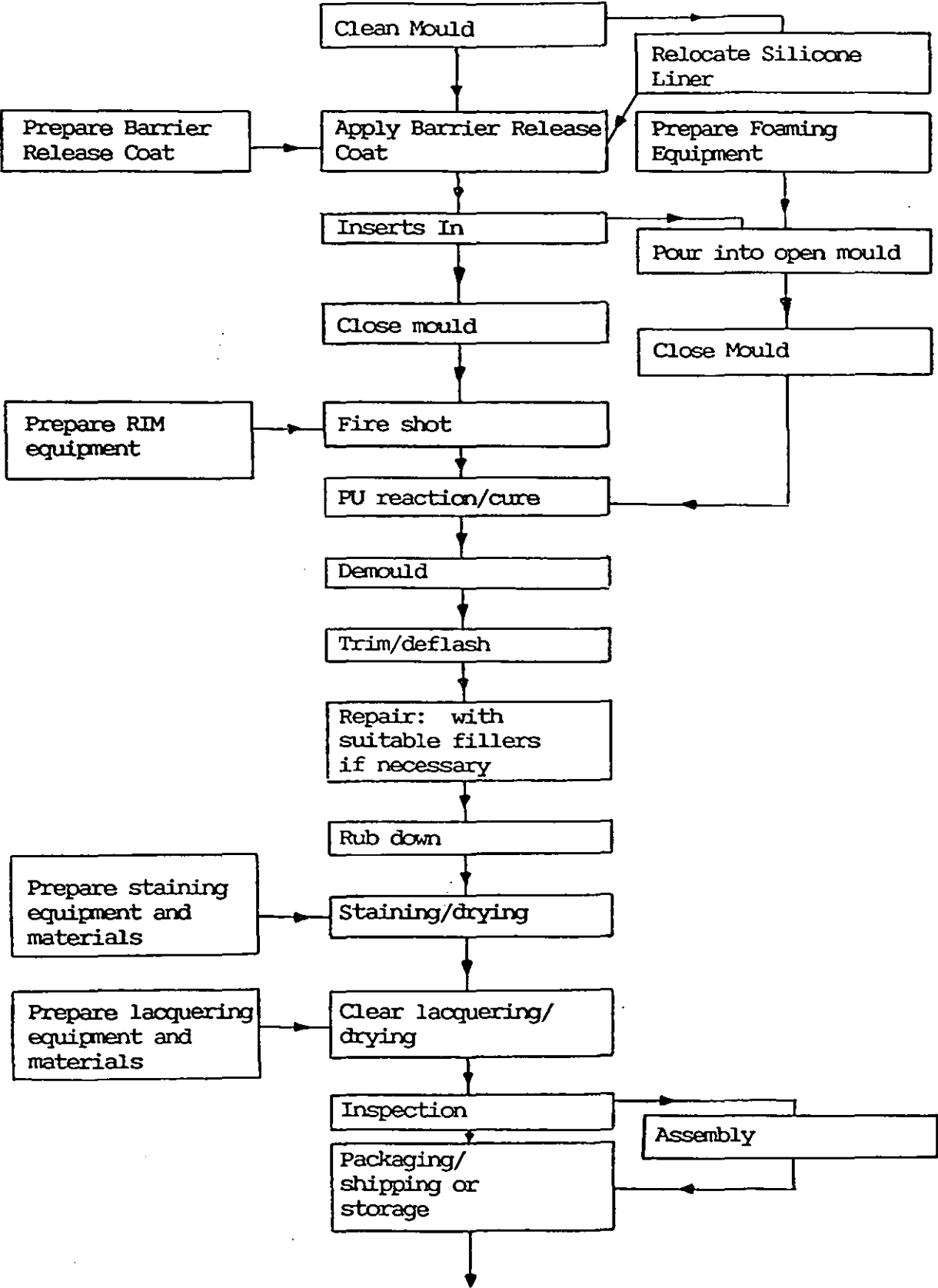
FIGURE 3.2: Cross-Section of a Silicone Mould During the PU Curing Stage [9]



Key:

- a) Decorative PU foam moulding, showing 3-dimensional relief
- b) Barrier release coating
- c) Silicone elastomer mould liner
- d) Epoxide supporting base mould
- e) Epoxide mould lid
- f) Paper backing card, acting as a release medium from the lid and as a permanently attached backing for the moulding
- g) G-cramp

TABLE 3.5: Flow Diagram for In-Mould Barrier Release Surface Coating Process [9]



BRC applied to silicone moulds, in part increases the working life of the mould by acting as a barrier against amine attack, and also by improving the skinning of the mould, reduces some of the post moulding operations. The barrier release systems are mainly used for rigid PU foam formulations, resulting in decorative simulated wood or stone mouldings.

### **3.4.3 General Properties of IMC and PMC**

The advantages and disadvantages of IMC and PMC for PU systems [9,69,93] are illustrated in Table 3.6.

## **3.5 ALTERNATIVES TO SURFACE COATING**

Application of a surface coating to any moulding increases its cost. For plastics moulding, additional raw materials, production time (in preparation, surface pretreatment, priming, top coat, painting, drying and inspection), shopfloor utilisation, skilled labour requirement (or robots), and health and safety installations increase the manufacturing cost of the product [93]. These are the main arguments against coating plastics. Therefore the alternatives to PU surface coating used commercially must initially appear attractive, and essentially improve the PUs resistance to UV and oxygen (see 3.2.1.1). Where limited exposure to UV is expected, a mixture of antioxidants and UV stabilisers can be used. The majority of PU products are based on MDI (although it only has a slight edge over TDI for flexible foam). MDI is pale yellow to brown in colour, which is passed onto the PU, so a moulder often has little choice but to accept a limited range of darker colours and less often subtle light pastel shades.

	Advantages	Disadvantages
IMC	Lower capital investment when a mini spray booth is incorporated into the moulding carousel	Mould design limited to simple less projection shapes
	Saving in paint usage and achieving a satisfactory coverage specially with similar colours in coating and substrate	Possible reduction in the evaporation rate, due to heavy vapours of some solvents
	Very low finished component rejects i.e. about 1% compared with about 8-10% for PMC [12]	Extra stage in moulding cycle
	Saving time and energy in applying and curing many PU coating systems with the aid of heat from tooling and the exothermic reaction	Repairing and touching up of defects more difficult than in PMC
	Almost perfect reproduction in the mould's surface	
PMC	Excellent adhesion between coating and substrate in most cases	
	Good mechanical and chemical properties in most cases	Good adhesion between coating and substrate requires extensive preliminary preparation of the substrate
	Good reproduction with complex mould designs	More time, labour and energy required due to many operations involved
		A separate painting area needed

TABLE 3.6: In-Mould and Post-Mould Coating of PU Materials



Strongly coloured pigments which are UV stable will give some success in masking the discolouration resulting from subsequent degradation. Carbon black at 5 to 10% loading is an effective UV stabiliser while masking flow and striation markings, but the colour choice is limited [9].

Anti-degradants, which are solids, may be used as much as 10 to 20% by weight of polyol [9], but lead to difficulties of dispersion in the polyol, and some detrimental effects on processing and mechanical properties of the finished product i.e. acting as particulate fillers.

## CHAPTER 4

### ADHESION AND INTERFACIAL BONDING

#### 4.1 ADHESION: INTRODUCTION

There is no single definition for "adhesion" which is completely satisfactory or universally accepted [106]. In part, this is due to any satisfactory definition having to account for both the thermodynamic and the mechanical aspects of adhesion along with phenomena which inhibit it. According to ASTM (D907-70), adhesion is "the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking forces or both" [107]. At the simplest level, adhesion is the act of joining together of two similar or dissimilar materials and then remaining together by forces acting across their common boundary (interface).

The properties of any substance depends on the structure, shape, and size of its constituent molecules and on the nature and magnitude of the forces between them [108]. The molecules in the surface region of a material are subjected to attractive forces from those in the interior, resulting in a net attraction into the bulk phase, in direction normal to the surface (Figure 4.1). The intermolecular forces exerted to the two potential adhering systems must be close enough for various interactions to take place. In practice this means that the surfaces must be within a few atom spacings of each other (i.e.  $< 10\text{\AA}$ ) [109].

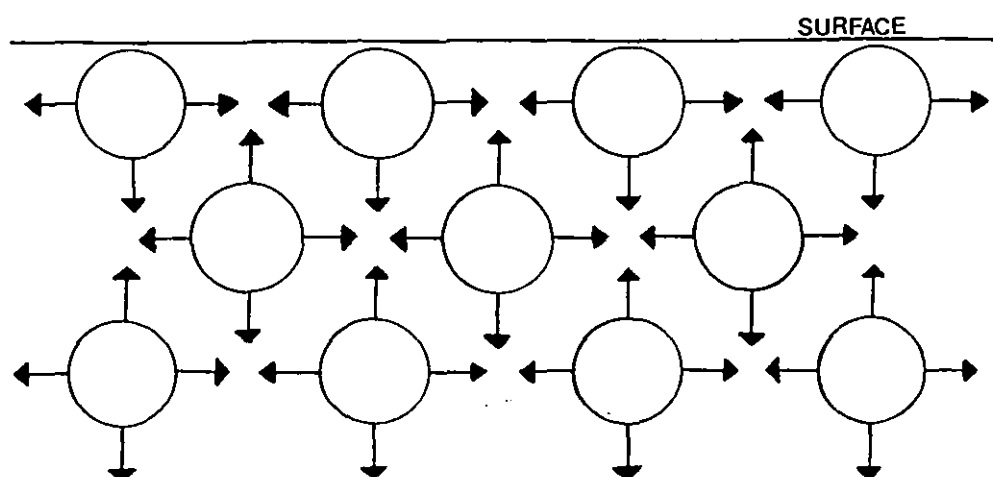


FIGURE 4.1: Molecular Attraction

The subject of adhesion has become increasingly important as a result of the improved understanding in areas such as structural bonding, surface coatings and lubrication, which in turn relate to many aspects of the coatings industry [104,110-113]. To date, there is greater understanding of the action of adhesives than of surface coatings, although it may be expected that they have many properties in common.

#### 4.2 THEORIES OF ADHESION

Several theories have attempted to explain the mechanisms of adhesion, wetting and interfacial bonding [114-119]. These theories need to be modified to be able to explain the complex interactions between often a reacting liquid resin in a surface coating and a solid polymeric substrate. The five main mechanisms of adhesion that have been proposed are:

- a) Adsorptive effects;
- b) Electrical double layer theory;
- c) Weak Boundary Layer (WBL) effects;
- d) Mechanical interlocking and related surface topography theories;
- e) Diffusion theory.

Allen [120] has explained the adhesion phenomenon by combination of all the theories of adhesion proposed:

$$\tau = \alpha\tau_m + \beta\tau_A + \gamma\tau_D + \delta\tau_E + \dots + \omega\tau_\infty$$

where  $\tau_m$ ,  $\tau_A$ ,  $\tau_D$  and  $\tau_E$  are mechanical, adsorption, diffusion and electrostatic components of adhesion respectively, and  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are respective mixing components. If one of the components does not exist (or its value is relatively very small), the corresponding value of the constant would become zero.

It is argued that one or more of these effects may be in existence in different examples of adhesion bonding, but none of the theories is able to explain all types found in practice.

#### 4.2.1 Adsorptive Effect

According to this theory, adhesion is dependent on molecular forces acting across the interface to hold the surfaces together. In a composite the interfacial effects can be explained in terms of the forces acting between the molecules comprising the bodies [121].

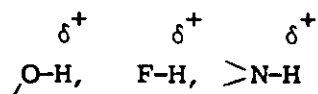
This theory has been discussed in depth by Kemball [122], Huntsberger [123], Staverman [124] and Wake [125]. Normally when two surfaces come together, consisting of neutral molecules (i.e. where no potential for chemical reaction exists), the forces of attraction and repulsion developed will relate to the atomic structure of their surface molecules. More specifically, Keesom [126] and Debye [127] respectively showed that dipole-dipole and dipole-induced dipole interactions (by orientation and induction), play an important role. London [128] discovered that dispersive forces (dispersion) will

promote the interaction between two molecules lacking any dipoles. These three physical phenomena are known as the Van der Waals forces of molecular interaction and are present in all molecules and contribute approximately 80% of the total cohesion forces of organic compounds [129].

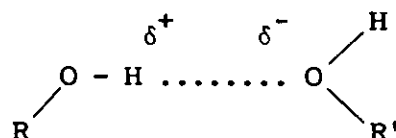
Bancroft [130] and De Bruyne [131] suggested that adhesion is due to Van der Waals interaction between surface molecules and adhesive and substrate (or adherend). These forces being adequate to ensure a strong bond. McLaren et al [132-134] developed the theory and suggested that the formation of adhesive bond can be divided into two stages. The first adhesion stage comprises the migration of large polymer molecules from solution, or melt, to the surface of adherend as a result of micro-Brownian motion. As a consequence polar groups (including hydrogen bonding groups) of macromolecules of the adhesive approach the similar groups in the substrate. Through pressure and a decrease in viscosity, due to a high temperature or solvent action, the active groups may approach the surface very closely, even if no solvent is used. The second stage of adhesion consists of the adsorption process. The Van der Waals forces act only at short range and in order to establish strong interfacial attraction, surfaces must be brought almost within molecular width (i.e.  $< 10 \text{ \AA}$ ) of each other. McLaren [132] has shown the adhesion as a surface effect, resulting in adsorption of certain segments of the adhesive molecule onto the surface of the substrate. The relative polar nature of the surface is seen to be important.

One other major interaction has been recognised, that of molecular interaction, for which an electrostatic attraction occurs between polar molecules. Hydrogen bonding is its usual form, where the

hydrogen atom on a molecule has a partial positive charge associated with some acidic character, e.g.



As the pendant hydrogen atom of a molecule approaches an electron rich atom of a neighbouring molecule, often associated with a basic character, a weak bond results, e.g. oxygen in water or alcohol, or nitrogen in amines, urethanes, or ureas.



The hydrogen bond length is about  $2.7 \text{ \AA}$ , too long to be a true stable covalent bond, but with a bond strength greater than that associated with Van der Waals forces [135]. Fowkes [136,137] and Drago et al [78,138] have suggested hydrogen bonding is highly specific and a type of Lewis acid-base interaction. Risberg [88] has argued that the adhesion between the paint and the substrate depends on an electromagnetic interaction between polar groups in the molecules in the two materials.

Chemisorption, in which the adsorbed molecules are held to the surface by covalent, ionic or metallic bonding will occur under certain circumstances. The interaction with the surface is much more specific resulting in a better interfacial bond strength which is most resistant to adhesive failure and attack by solvents or surfactants. It has also been shown that covalent bond formation is associated with

adsorptive bonding at the interface [139-141]. Wake [142] has argued that although there are good grounds for believing that covalent bonds form across interfaces contributing to adhesion, Van der Waals forces of interaction in general and the London dispersion forces in particular are also very important in explaining the adhesion phenomena. Salomon [143] has also discussed the low probability of chemical bonds at interfaces. Matting and Ulmer [144] have refuted the existence of any chemical interaction between adhesives and metallic substrates.

A comparison of bond strengths for adsorptive and chemisorptive systems is given in Table 4.1.

TABLE 4.1: Bond Energies for Adsorption and Chemisorption Systems [145]

Bond Energy (KJ.mol <sup>-1</sup> )	
Primary Bonds (Chemisorptive):	
Ionic	600 to 1100
Covalent	50 to 700
Metallic	110 to 350
Secondary Bonds (Adsorptive):	
Hydrogen bonding with fluorine	Up to 40
Hydrogen bonding without fluorine	10 to 25
Dipole-dipole	1.5 to 20
Dipole-induced-dipole	0.5 to 2.0
Dispersion forces	0.01 to 40

The terms primary and secondary in Table 4.1 are in a sense a measure of the relative strength of the bonds. Owens et al [146] have argued that in theory the attraction due to secondary forces and hydrogen

bonding is in itself sufficient to produce adhesive joints between polymers of strength equal to that of the polymers themselves without the need for chemical bonds. The potential energy curves for different types of intermolecular forces are shown in Figure 4.2.

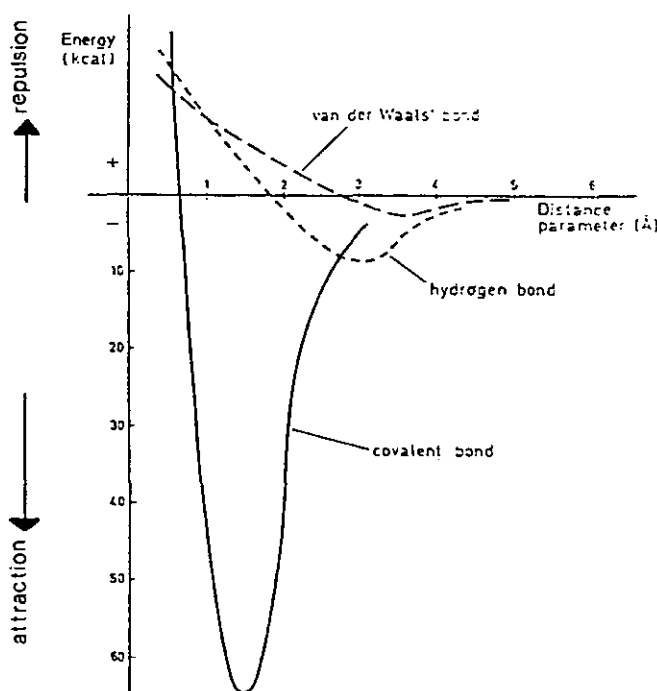


FIGURE 4.2: Potential Energy Curves of Various Bonding Forces [147]

Although the adsorption theory of adhesion is well documented, it has been found to have the following shortcomings:

- a) Derjaguin and Krotova [148] showed that the peeling work of the adhesive film can reach values as high as  $10$  to  $10^3$  Nm, but the work required to overcome molecular forces does not exceed  $10^{-1}$  to  $10$  Nm. In other words, the real work of adhesion is several magnitudes higher than that expected from molecular forces.



- b) Voyutskii and Vakula [149] demonstrated that generally too high a polarity of the polymer tends to decrease adhesion to very polar adherend. This finding contradicts the adsorption theory because if adhesion was determined only by adsorption, it would increase in this case. MacLaren [132] has disagreed with this generalisation and argued that in some cases where moderate contents of polar groups such as chlorine, carboxyl, carbonyl, and hydroxyl are added to the polymer it may improve the adhesion to a polar adherend.
- c) Adsorption theory cannot account for the high adhesion that may be found between non-polar polymers. For example non-polar polymers such as natural rubber and polyisobutylene show good adhesion to a number of adherends [149].

#### 4.2.2 Electrical Double Layer (EDL) Theory

This theory was suggested by Derjaguin et al [150,151], who stated that at any boundary an electrical double layer is produced and the consequent coulombic attraction might account for adhesion and resistance to separation. In fact, the EDL theory was suggested by Derjaguin and Krotova [148] in order to explain the situations mentioned earlier (see 2.2.1) that adsorption theory could not clarify. Their explanation was based on observations made while peeling an adhesive film from a substrate. They concluded that [129]:

1. work of adhesion was much higher than could be expected from molecular forces;
2. work of adhesion was dependent on the rate of separation of the adhesive film;

3. it was difficult to explain the adhesion between the non-polar high polymers based on adhesion theory;
4. bond rupture can lead to electrification of the ruptured surfaces and sometimes such electrostatic build up can be discharged during separation.

Voyutskii [152], Schonhorn [153] and Huntsberger [123] have criticised the EDL theory for its inconsistency in many systems. Voyutskii has questioned this theory with respect to the adhesion of rubbery polymers to one another. He has argued that if contact potentials gave rise to double layers of the strengths required to explain adhesion then why were dissimilar polymers less adherent than similar polymers? It has also been shown that the contribution from electrostatic forces is significantly lower than that from Van der Waals interactions [154].

Roberts [155] has concluded that maximum contribution to the thermodynamic work of adhesion for a natural rubber/glass interface is about  $10^{-5} \text{ mNm}^{-1}$ , which is negligible compared to the contribution from Van der Waals forces of about  $60 \text{ mNm}^{-1}$ . Weaver [156,157] has employed a 'scratch test' to investigate the adhesion of various metallic films on a range of polymeric substrates. Previous work on metallic coatings on glass had suggested that increase in scratch resistance upon ageing metal/glass interfaces were due to increased oxidation of the metal surface with time leading to stronger interfacial bonding, possibly due to an oxide bond between the metal and glass with an oxygen atom acting as a bridge [158]. To eliminate this possible oxide bond, Weaver included gold in his list for the metal/polymer interfaces and reported that upon ageing various metal/polymer interfaces large

increases in the scratch resistance were found for copper, silver or gold coatings and smaller increase for aluminium. Due to these and other experiments Weaver concluded that the Fermi level (i.e. where Fermi level is defined as the average energy for the valence electrons in orbit around a nucleus) in the polymer was initially above that in the metal and thus the charge transfer producing adhesion might be due to possible hole injection, i.e. electron transfer from polymer to metal.

Wake [125] has indicated that the nature of the charge-carrying bodies in polymers is not well established, it is known that additives and impurities may drastically affect their ability to form electrical double layers. Thus he suggested that data from radiation polymerised material made from a highly purified monomer would be more valid.

Voyutskii et al [149] suggested that the electric theory of the polymer to polymer adhesion is only applicable in cases when polymers are incompatible or insoluble in each other. Where both polymers are compatible it would be necessary to distinguish between two cases: adhesion of non-polar and that of polar polymers. When a bond forms between non-polar polymers, the electrical mechanism is not acceptable since such polymers could not be electron donors. It was argued that adhesion in this case is caused by the interlacing of the surface macromolecules due to their mutual diffusion. As a result of bonds formed between polar polymers the double electric layers can arise. However if the polymer molecules are capable of intense thermal motion then the joining of both layers will also occur as a result of diffusion (see 4.2.4).

Fowkes [159] has suggested a different approach to the EDL theory of adhesion based on donor/acceptor relationships existing at the interface but not within the bulk of either material separately. He has realised that acid-based interactions are not the only ones occurring at an interface and they add to the existing Van der Waals forces of dispersion. Gent and Schultz [160] have followed their experiments on this basis and reported that the forces attributed to EDL effects has magnitude similar to that of the dispersion forces.

Despite a number of criticisms, the electrical double layer theory can be demonstrated for freshly cleaved surfaces of mica (which are very flat), being brought back together, and also in explaining colloidal systems.

#### 4.2.3 Mechanical Interlocking and Related Surface Topography Theories

The mechanical theory proposes that mechanical keying, or interlocking, of the adhesive into the irregularities of the substrate surface is the major source of intrinsic adhesion [161]. McBain and Hopkins [162] examined this theory, distinguishing between true adhesion and mere interlocking.

As early as 1949, Borroff and Wake [163] demonstrated the importance of mechanical adhesion by embedding textile fibre ends in the rubber. With sufficiently long fibres, provided there is specific adhesion (even quite small) acting over the area of fibre, the total shearing force would exceed the tensile (breaking) strength of the fibre. The intrinsic adhesion between fibre and rubber arises from primary or secondary forces, either chemical or Van der Waals bonds, but is only of indirect importance since it will simply determine the length of fibre which is needed to be embedded before the interfacial shear strength exceeds the tensile strength of the fibre. If the fibre ends are removed by employing a fabric woven from continuous filament yarn

then this mechanical interlocking mechanism can no longer operate. Hence, some pretreatments on continuous fibres is necessary in order to increase the contribution from primary and secondary interfacial forces to the intrinsic adhesion [161].

Metal plating of polymers where a chemical pretreatment of the polymeric substrate is employed prior to plating is another example, where mechanical interlocking may contribute significantly to the intrinsic adhesion. Examples are bonding between metal and polypropylene [164,165] and in metal plated ABS [166,167].

By increasing the roughness of a surface, the real surface area increases and the topography of the surface is changed [93,119,129]. While this is usually beneficial for adhesives, it has mixed results for solvent based coatings. As a result more work has to be done in delamination to overcome the friction developed in the combined surfaces and interlocking at the interface. The latter is related to the cohesive strengths of the coating and substrate material. If there is not intimate contact between the coating and the substrate, increasing the roughness can lead to decreased adhesion by producing uncoated areas or voids or vacancies in the coating (Figure 4.3).

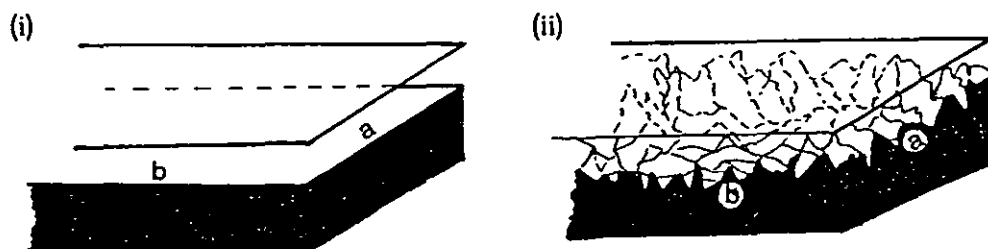


FIGURE 4.3: The Effect of Surface Roughness:

- i) perfect surface: area of contact =  $ab$  if completely wetted out;
- ii) roughened surface: area of contact  $\gg ab$  if completely wetted out.

Some work has been carried out by Packham et al [168,169] to show the importance of substrate surface topography. Their findings on the adhesion of polyethylene to metallic substrates clearly demonstrated that high peel strengths were obtained when a very rough, fibrous type, oxide surface was formed on the substrate. The argument of roughness increase of the substrate surface resulting in a better joint strength has been shown by Jennings [170], Bascom et al [171] and Mulville and Vaishnov [172]. Kinloch [173] has argued that this joint strength enhancement need not necessarily arise either from a mechanical interlocking mechanism or from an increase in surface area for bonding or from improved kinetics of wetting. As Kinloch has stated the measured adhesive joint strength almost always reflects the value of two parameters: (a) the intrinsic adhesion, and (b) the energy dissipated viscoelastically and plastically in the highly strained volume around the tip of the propagating crack and in the bulk of the joint. Several authors [174,175] have suggested that the importance of high surface irregularity is to increase the latter parameter.

As indicated earlier, many investigations have shown better adhesion to smoother surfaces. Taylor [176] applied tensile tests of polyethylene on nine different metals with various types of surface finish. The adhesion measured was inversely proportional to roughness. As discussed earlier (see 4.2.1), Risberg [88] has strongly argued that the adhesion of a paint to plastic substrate depends mainly on pure chemical connections such as intermolecular interaction between polar groups in the paint and in the substrate and not on solvent attack on the substrate or surface roughness with one exception, the thermosetting materials where release agents are being used. He believes only in cases such as polyurethane moulding where

polypropylene waxes are often used as release agents, a change in solvent blend may affect the adhesion.

It is argued that the proposed chemical connections may occur as e.g. covalent bonding in some in-mould coated PU/PU systems (see Chapters 1 and 5).

Wake [177] has followed the theories suggested by Andrews and Kinloch [178] and Gent and Schultz [179], and argued that for the maximum joint strengths both mechanical and chemical properties of the substrate are important. Therefore, the effects of mechanical interlocking and surface free components could be multiplied to give a result for the measured joint strength:

$$\text{Joint strength} = \text{constant} \times \left( \begin{smallmatrix} \text{mechanical} \\ \text{component} \end{smallmatrix} \right) \times \left( \begin{smallmatrix} \text{surface free} \\ \text{components} \end{smallmatrix} \right)$$

This equation shows that the substrate must possess, simultaneously, the topography and surface chemistry necessary to produce the highest extent of mechanical interlocking and surface free contributions.

The viscosity has a direct effect on surface coating ability to flow over and into the substrate surface. The surface coating droplet size varies in different viscosities which has to be considered for various applications. The viscosity and the rate of solvent evaporation should be controlled in such a way that the initial low viscosity would allow an effective paintability and wettability in a short space of time followed by the rapid loss of solvents by evaporation resulting in a rise in viscosity and a rapid change from wet to dry state. This would stop any undesirable surface effects being produced.

Abrasive treatment of PU substrates and to a limited extent vapour or solvent wash degreasing in preparation for primer painting will increase the real area of the surface while removing some release agent, if present. However cutting into the cellular structure of a self-skinned foam will only prove attractive if high thicknesses of coating are applied subsequently. Surface coatings having low solids content will wet and cover surface imperfections initially, but due to solvent loss mainly from the wet film thickness, the resulting dry film will reproduce those imperfections (Figure 4.4). Air entrapment and reluctance of a higher viscosity coating to flow into smaller surface imperfections will reduce the total area of contact and therefore affect the adhesive strength of the bond.

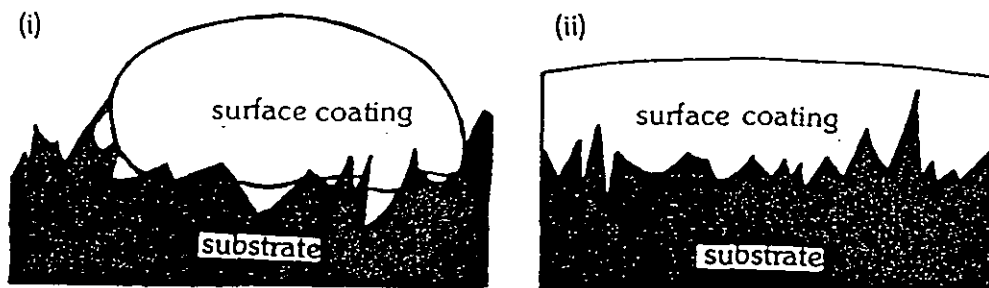


FIGURE 4.4: Surface Coating of a Substrate:

- i) poorly wetted substrate and/or high-viscosity coating: low area of interfacial contact,
- ii) completely wetted substrate, low-viscosity coating: extensive interfacial contact.

#### 4.2.4 Diffusion Theory

This theory was originally advanced by Russian scientists [152,180,181]. It assumes that if molecules on the two surfaces are in a fluid and mobile state, diffusive bonding will take place.



However, the diffusion theory is related to some earlier work [182] which showed that the interdiffusion of high polymers across an interface is possible if the polymers are at temperatures above their glass transition temperatures ( $T_g$ ). This was suggested on the basis of self-tack of rubbers and the term autohesion. Voyutskii et al [149,152] argued that for many cases adhesion between polymers, as well as their autohesion, could be reduced to the diffusion of chain-like molecules and as a result leads to the formation of a strong bond between adhesive and adherend. Therefore it requires that the macromolecules or chain segments of the polymers (i.e. coating and substrate) possess sufficient mobility and are mutually soluble, that is that they possess similar values of the solubility parameter. The solubility parameter,  $\delta$ , may be defined by [173]

$$\delta = \left( \frac{\Delta H_v - RT}{V} \right)^{1/2}$$

where  $\Delta H_v$  is the molar heat of vaporisation,  $R$  is the gas constant,  $T$  is the temperature (K) and  $V$  is the molar volume. Hence, a fundamental feature of the theoretical treatment of diffusion is that thermodynamic compatibility must exist between the materials. With autohesion there is no problem but the theory could not automatically be applied to the adhesion of two polymers for which solubility parameters are different. Radiometric studies [183] have shown the presence of macromolecule diffusion in compatible polymers. Mutual solubility of the components is important for their adhesion [184] and in the first approximation is determined by the polarity of the polymers; it is also in good agreement with the known empirical de Bruyne's rule, according to which adhesion is strong only when both polymers are either polar or non-polar and is made more difficult in the case of polar plus non-polar polymers.

The essential peculiarity of the diffusion theory, in which it differs from the other theories of adhesion, lies in the fact that it involves the most characteristic properties of polymeric substances, i.e. their chain-like structure, the flexibility of their molecules, and the ability of the latter for micro-Brownian motion. Voyutskii [152], on the basis of his experimental observations proposed that bond strength will increase with:

- a) process conditions: long contact time, high temperature, high pressure. The latter two will relate to the viscosities of the mating surface and, therefore an optimum shear rate must be considered (see 4.4).
- b) molecular structure considerations: low molecular weight species, high chain flexibility, absence of bulky side groups and no or low orders of crosslinking.

Thus, according to this theory, there exists no clear cut boundary at the interface due to the diffusion but there exists instead a transition layer. This suggests that adhesion is a three-dimensional volume process rather than a two-dimensional surface process. Vasenin [185,186] has approached this theory in a more fundamental and theoretical manner and with regard to the autohesion of polyisobutylene, derived an equation relating contact time and molecular characteristics of the polymer chain to measured joint strengths (Figure 4.5).

Some results [187] using techniques of optical microscopy, including luminescence analysis in UV light, has indicated that in compatible, non-polar polymers the zone of interfacial boundary dissolution due to

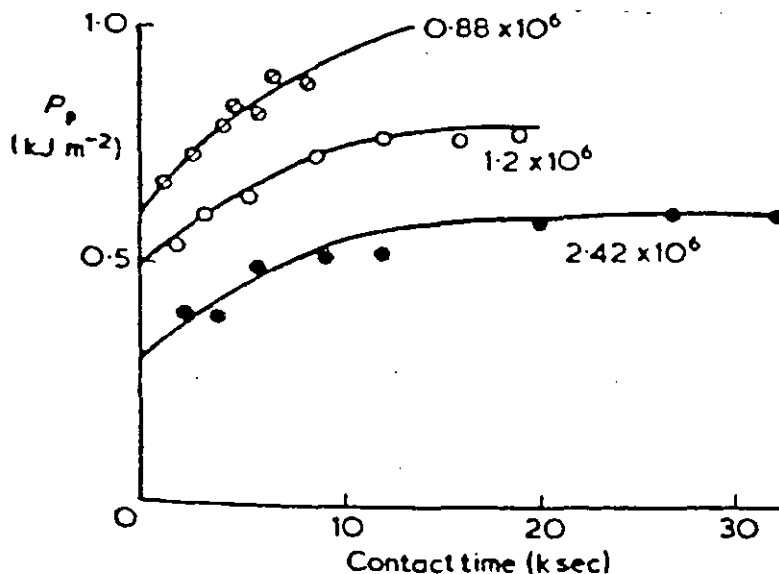


FIGURE 4.5: Relation Between Measured Peeling Energy,  $P_p$ , and Contact Time for the Autohesion of Polyisobutylenes of Various Molecular Weights  
(After refs 185 and 186)

diffusion may be about ten microns deep. The autohesion of elastomers and the solvent welding of compatible, amorphous plastics, having mutual solubility and sufficient mobility of the macromolecules is based on the interdiffusion of polymer chains across the interface. Nevertheless, if the solubility parameters of the two materials are not similar, or if one polymer is crosslinked, is crystalline or is below its glass transition temperature, then interdiffusion is an unlikely mechanism.

Diffusion processes have an important significance in the formation of adhesion joints of polymers with metals. It has been established [188] that as a result of the interaction of polyolefins with metal surfaces, fatty acid salts are formed which then diffuse into the bulk polymer. Many authors [189,190] have observed the appearance of metal-containing compounds in the bulk polymer.

Kamenskii et al [191] have followed the same trend as Voyutskii [152] and stated that in many cases the bonding of polymers, impregnation of fibrous materials with polymer dispersions and deposition of coatings, amount to reciprocal (mutual) diffusion. Krotova et al [192] studied the mutual diffusion under a microscope on sections of two-layer films produced from the test polymers. The boundary between polymers using different UV luminescence was also studied by microscopy. It was found that the interface is always broadened on the contact of two non-polar polymers of approximately the same structure. From this the authors concluded that the adhesive bond establishment in this case must be due to mutual diffusion. Heat treatment of the double films caused a sudden increase in the blurring of the surface. Systems with components differing considerably in chemical structure gave a narrow blurring zone. Later, in conclusion of their work they stated that the boundary blurring was not due to the diffusion of macromolecules or their segments, but to the transfer of whole structural complexes from one phase to the other.

Kamenskii et al [191] have seen the limitations on microscopy analysis using visible or UV radiation for studying the diffusion interpenetration and have adopted the use of electron microscopy. They chose two sets of pairs of polymers: polymethylmethacrylate (PMMA)/polyvinylchloride (PVC) and polybutylmethacrylate (PBMA)/PVC. The polymers were then welded into pairs, i.e. they were kept in contact for a certain time at a temperature sufficient for vigorous thermal movement of the molecular chains or their segments. Their conclusion has revealed that the PMMA/PVC and PBMA/PVC show mutual diffusion at 160-220°C and the mutual penetration becomes easier as the temperature rises. Mutual penetration was found to be less in the case of PBMA/PVC. On one hand, this may be due to poor compatibility of PVC

and PBMA due to the low polarity of the latter, on the other hand it may be due to the large side branches (butyl groups) in the PBMA molecules. By using electron microscopy, Kamenskii et al showed that the mutual penetration of micromolecules to depths from tens up to thousands of angstrom is possible. Since mutual penetration of polymer molecules even to 20 to 30 Å, may increase the adhesive strength several times, their findings have again confirmed the importance of diffusion effects in the formation of adhesive joints between polymers. In a later study the same authors [193] showed that with compatible polymers the diffusion continues until the components have completely dissolved, whereas with incompatible polymers diffusion proceeds only up to a certain point changing the interfacial boundary between the polymers into transitional layers. The equilibrium thickness of this layer depends on the nature of the polymers in question.

The diffusion theory is relevant to several aspects of PU coating and adhesion. For solvent based coatings, having spread and wetted an area of substrate, there may be conditions in which the residual solvent may have time to solvate a surface layer of the PU substrate. This means there is some diffusion and swelling in the polymer matrix, which may allow molecules of the resin binder to also diffuse into the substrate. With eventual evaporative loss of the solvent, resin molecules will remain. It may be suggested that this effect should be enhanced with two-pack surface coatings, consisting of low molecule weight oligomeric materials.

#### 4.2.5 Weak Boundary Layer (WBL) Effects

A boundary layer may exist on the surface of a substrate [194,195]. The layer may be made up of mobile species migrating from the body of

the substrate, or from environmental contamination before coating (dust, oil, moisture, oxygen), or even mobile, low molecular weight, surface active species present in the surface coating which are attracted preferentially to the substrate, or release agents. If the boundary layer has poor adhesion to the substrate or coating, and/or has poor mechanical properties, the interface is stressed showing an apparent adhesion failure at the substrate coating interface: this is known as weak boundary layer. It may be argued that adhesives, coating and other polymeric materials acting as matrices for composite may provide WBL material.

The WBL is present normally as adsorbed and chemisorbed species on the substrate's surface and usually reduces the potential for wetting and spreading of a liquid and hence good interfacial bonding. If bonding should occur, a boundary layer of low cohesive strength will be the site of failure under load. Interference of the interactions between substrate-coating can be due to a single molecule thickness of adsorbed species, e.g. silicone oil based release agents.

According to WBL theory, first advanced in 1947 [196], the failure between the main mated surfaces is always cohesive rather than adhesive in nature. This theory further suggests that no correlation between adhesion and surface properties could be expected. There are studies and data [197,198] to demonstrate the presence of WBLs. Other studies [199,200] have however, shown a correlation between adhesive strength and surface chemical properties of the joint constituents.

Bikerman [197,201] has suggested a number of conditions which would lead to a WBL. He has also initiated a debate to explain why joints never fail interfacially. Bikerman argued [197,202] that the strength

of an adhesive bonding is not determined by the molecular attraction between the adherend and the adhesive but by the mechanical properties of the two phases or in some cases the properties of a weak boundary layer formed between the phases. By considering a two-dimensional structure, Bikerman [203] argued that a crack situated at the interface must propagate either between two molecules of the adhesive or between two molecules of the substrate, or between a molecule of each. If these three conditions are equally probable then the probability of the crack propagating along the interface between  $(n+1)$  pairs of dissimilar molecules is  $(1/3)^n$ , and this probability of course decreases even further if a three-dimensional structure is considered. Bikerman concluded that in such cases the fracture can never occur only along the adhesive/substrate interface for purely statistical reasons.

Later, Bikerman considered the forces of attraction between two dissimilar molecules such as gases and showed that the attraction between two dissimilar molecules is smaller than between two identical strong molecules, but greater than between two weak molecules and hence concluded that molecules favour rupture in cohesion in the weaker phase. He also indicated that rupture rarely proceeds exactly between the adhesive and adherend, that the "failure in adhesion" need not be treated in any theory of adhesive joints [204].

Bikerman's ideas have been critically examined by many scientists [125,205-207]. Huntsberger [205] and Voyutskii [152] have shown that these simplified assumptions are not valid in most practical systems and argued that a shortcoming of WBL theory is where the structure of polymeric adhesives are not taken into account. They pointed out that structural features such as chain entanglements, crystallinity, and

orientation of chains and crosslinks will result in the cohesive fracture stress often being much greater than that required for interfacial failure where often only secondary intermolecular forces are involved. Further, even if the locus of joint failure is cohesive in the adhesive or substrate, close to the interface, this does not necessarily imply the presence of a weak boundary layer.

Good [206] amongst many others have suggested that the stress distribution in the joint and around the tip of a crack propagating close to the interface causes mechanical focusing of the failure path close to the interface. Good [207] argues that despite some practical usefulness of the WBL theory, the experimental proof has never been shown for the universality of the theory. Good and others [205,206,208-210] have shown experimentally that the interfacial failure can occur and does so fairly frequently due to WBL.

By applying Auger electron spectroscopy and X-ray photoelectron spectroscopy more cases of interfacial failure have been confirmed [211-213]. For example, Gettings et al [212] applied (AES) and (XPS) to show the locus of failure on epoxy resin/metal joints. For dry joints the fracture is near but not exactly at the interface whereas after exposing the joints to water, the fracture occurs interfacially between the adhesive and metal oxide interface. Briggs [211] by examining the fractured joint of polyethylene/epoxide adhesive by XPS could show that there was no evidence of the transfer of polyethylene to the epoxide.

Schönhorn et al [153,194,195,214] adopted the WBL theory to investigate the gas plasma treatment and other methods on improving the adhesive bonding of many polymeric substrates. Crane and



Hammermesh [215] showed that the adhesion of thin plasma polymer films to a number of plastics substrates is a function of the chemical nature of the substrate and not that of the film, also the bond between film and substrate is probably chemical in nature.

The character and cause of boundary layers are well defined for polyolefins [145]. Bikerman [216] rejected a long established idea that the poor adhesion of commercial polyethylene was due to its non-polar nature. This polymer contains impurities such as monomers, oligomers, and surface active additives (e.g. blowing agents, lubricants, and antioxidants) which may reach to the surface of the polymer causing a weak boundary layer. Bikerman showed that purified polyethylene, which is less polar than commercial grades, formed proper joints in all tests. Therefore he emphasised that the poor adhesion could not be due to the non-polarity of the surface but mainly the result of impurities which spread between coating and the substrate.

#### 4.3 INTERFACIAL BONDING

##### 4.3.1 The Interface: Observations

It is important to recognise that the interface is a region of finite thickness, wherein the segments of macromolecules may interpenetrate. Its mechanical strength will very much depend on its structure. Interfacial region or interphase possesses a certain thickness and its mechanical properties are different from those of the contiguous phases [217,218]. A practical definition of "good adhesion" is that the interfacial region (or nearby material) does not fail under service conditions nor at unacceptably low stress levels under test conditions [219]. If the interface is stronger than either of the two

adherends, failure occurs within the weaker adherend; this is termed cohesive failure. If failure occurs at the original interface this is termed adhesive or interfacial failure.

Mattox [219] has argued that adhesion or adhesive strength being a macroscopic property depends on the chemical and mechanical bonding across the interfacial region, the intrinsic stress and other gradients and the adhesive failure mode. The failure mode depends on the interfacial structure and the stress to which the interface is subjected. Hence the good adhesion is promoted by: strong bonding across the interfacial region, low stress levels, absence of easy deformation or fracture modes and no long-term degradation modes. Different types of interfacial region have been classified [219,221]:

a) Mechanical interface:

This type of interface is formed by mechanical interlocking of the coating material with a rough porous substrate. The adhesion depends on the mechanical properties of the combination of materials;

b) Monolayer on monolayer interface:

This interface is characterised by an abrupt change from the coating to the substrate in a thickness of the order of the separation between atoms (2 to 5 Å). Interfaces of this type may be formed when there is no diffusion and little or no chemical reaction between the coating atoms and the dense and smooth substrate surface. This lack of interaction may be due to the lack of solubility between materials, little reaction energy available, or the presence of contaminant layers. In this type of interface, defects and stresses will be combined to a narrow region;

c) Chemical bonding interface:

The chemical or compound interface is characterised by a constant chemical composition across several lattices. The formation of the interface layer results from the chemical reactions of coating and substrate atoms which may also be influenced by the residual gas. The compound formed may be either an intermetallic compound or alloy or a chemical compound such as an oxide or a nitride etc. They are usually brittle materials showing some porosity in the interfacial region;

d) Diffusion interface:

In this type of interface there is a gradual change in the lattice and the composition in the coating/substrate transition region. Some partial solubility is required for diffusion between the coating and substrate to take place. Different rates of diffusion of the coating and substrate atoms may result in Kirkendall porosity in the interfacial area. For thin films Kirkendall porosity may not develop because of rapid surface diffusion. This type of interface has advantageous characteristics of forming transitional layers between very different materials, e.g. for reducing mechanical stresses resulting from thermal expansion;

e) Pseudo-diffusion interface:

This type of interface can be formed under more energetic situations such as ion bombardment, ion implantation or melting/quenching. Pseudo-diffusion interfaces have the same advantageous characteristics as diffusion interfaces, but in contrast with the latter they can be formed from materials that do not mutually diffuse i.e. which are normally insoluble. Ion bombardment before coating can increase the interfacial solubility which in effect will increase the diffusion by creating high concentrations of point defects and stress gradients.

Pulker et al [221] have argued that one type of interface seldom occurs alone and in normal practice, combinations of the various types of interface layers often occur simultaneously.

In another method of classification [218] the interfaces are divided into two main types: sharp and diffuse, and three types of adhesive behaviour may be observed:

1. sharp interface with weak molecular force;
2. sharp interface with strong molecular force;
3. diffuse interface with any molecular force.

#### 4.3.2 Interfacial Properties

Although attempts to form chemical bonds between adherends are commonly made, the real nature of the interface and the extent of chemical coupling achieved are generally rather uncertain [219,221]. In chemical bonding the interaction is due to the transfer or sharing of electrons. In true chemical bonding such as covalent and ionic bonding as well as in metal bonding the bonding forces are very strong, depending on the degree of electron transfer. A high degree of electron transfer will result in compounds or ionic solids which are normally strong but brittle, whereas electron sharing will produce alloys or metallic type materials which are more ductile.

It has been argued [222] that a strong joint would be developed from Van der Waals forces alone and that strong (chemical) bonding at the interface is not really necessary. It has even been questioned whether interfacial chemical bonds are formed at all. It has been suggested [223] that in some cases, as little as  $10^{-3}$  to  $10^{-2}$  mole fraction of appropriate reactive functional groups, when incorporated into

polymers, can greatly increase the adhesive bond strength. At such low amounts, polymer bulk properties and wettability are practically unchanged. Furthermore, the effectiveness of functional groups in adhesion promotion is quite specific with respect to surface chemical composition. These findings suggest that the improved adhesion results from interfacial chemical bonding. Wake [223] has concluded that an excess amount of functional groups should be avoided as they may degrade the bulk properties and thus adversely affect the joint strength.

Some authors [218] have emphasised the importance of the intimate molecular contact at the interface for achieving a strong adhesive bond. They have argued that because Van der Waals attraction between two planar macroscopic bodies diminishes rapidly with distance by  $z^{-3}$  (where  $z$  is the distance of separation) and that the equilibrium interfacial separation is typically 2 to 5 Å, then an intimate molecular contact at the interface is necessary to obtain strong interfacial attraction. Without intimate molecular contact, interfacial attraction will be very weak, and the applied stress that can be transmitted from one phase to the other through the interface will accordingly be very low. They have concluded however, that in many cases an intimate molecular contact alone is not sufficient to give a strong adhesive bond.

Voyutskii [224] has argued that the first step in the formation of an adhesive bond is the establishment of interfacial molecular contact by wetting. The molecules will then undergo motions towards preferred configurations to achieve the adsorptive equilibrium, diffuse across the interface to form diffuse interfacial zones, and/or react chemically to form primary chemical bonds across the interface.

#### 4.4 INTERFACIAL AND ADHESION PROPERTIES OF POLYMERIC SYSTEMS

Most research has been reported on the adhesion of metal-polymer joints [119,125,167,225] and the real interest in polymer-polymer systems has only started in the last decade and is proving to be more complex. Polymer surfaces and interfaces are mobile and will rearrange or reorient at the interfaces to minimise the interfacial free energy with the surrounding zone [226]. This is contradictory to the classical surface chemistry which assumed that solid surfaces were rigid and immobile. Although some motions and relaxations may be expected from polymer molecules in the near surface or interface region, they are not identical to the motions observed in the bulk due to the different interfacial environment. Some studies on the structure and dynamics and mobility of polymer surfaces and interfaces have been reported [227,228].

Andrews and Kinloch [222,229] studied the adhesion of a styrene-butadiene copolymer (SBR) crosslinked in situ on various substrates, including poly(tetrafluoroethylene-co-hexafluoropropylene) after various surface treatments, and a number of other plastic materials: poly(chlorotrifluoroethylene), polyamides and poly(ethylene terephthalate). The work of detachment was measured over a range of rate of separation and of temperature. Under given conditions, the work of detachment was found to be greater for chemically treated than for untreated or plasma treated surfaces. It was suggested that chemical treatments create surface unsaturation which can form primary chemical bonds with SBR layers during the crosslinking reaction.

It has also been noted [221] that in many cases the coating/substrate system is not totally stable once the coating process has ended, and

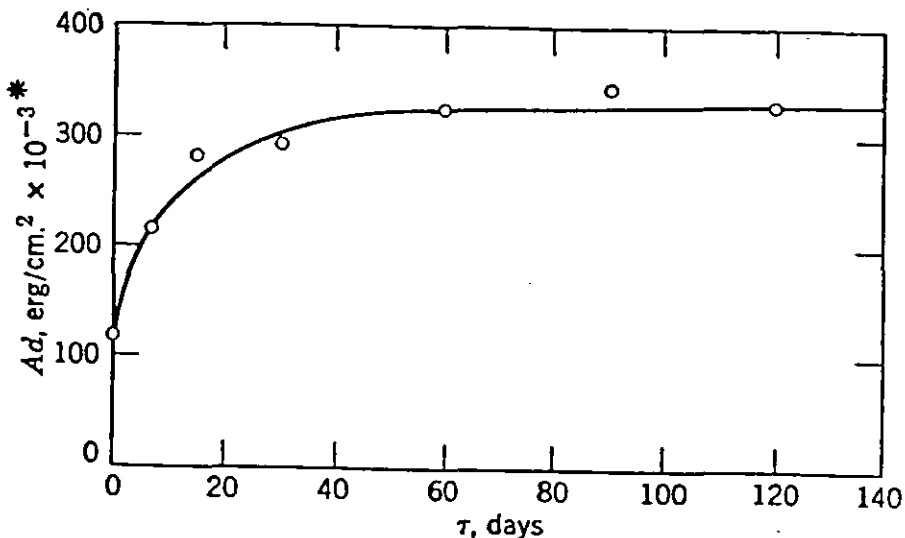
it continues to change physically and chemically until it reaches a stable condition. The adhesion of the coating to its substrate often undergoes marked changes during this time. Three processes, which generally progress slowly, have been recognised responsible for this ageing: chemical reactions in the interface layer area, solid body diffusion across the interface layer, and changes in the crystal structure (recrystallisation through self-diffusion). These processes are strongly dependent on temperature. Their speed usually increases with increasing temperature.

#### 4.5 FACTORS AFFECTING THE ADHESION

Adhesion of a coating to a substrate is a complex property which depends on a large number of factors. Some of these are based on the chemical and mechanical properties of the two components. The others are influenced by the preparation of the substrate, the coating process and the environmental properties after the coating process is completed. Some of the more important of these parameters are reviewed here.

##### 4.5.1 The Effect of Contact Time on Adhesion

The influence of contact time between coating and substrate provides one of the most essential proofs of the diffusion theory of adhesion [149,152]. Figure 4.6 shows a typical curve, obtained by Voyutskii et al [149] characterising the variation in adhesion of butadiene-acrylonitrile copolymer to "cellophane" as a function of time from the moment of preparing the bonded sample to the moment of its peeling.



\*  $1\text{J} = 10^7 \text{ ergs}$

FIGURE 4.6: Dependence of Adhesion,  $Ad$ , of Copolymer SKN-40 to Cellophane on Time,  $T$ , Elapsed from the Moment of Preparing the Bonded Specimen to the Moment of Testing [230]

As shown in the above figure, the adhesion of a high molecular adhesion to a polymeric substrate increases rapidly with contact time at first and then more slowly approaching a definite limiting value. Similar results have been observed by Forbes and MacLeod [231] who investigated the adhesion of different elastomers pressed together (autohesion) under low pressure at varying times. This finding ignores the possibility of explaining the increase in adhesion as a result of evaporation of remaining solvent in a coating. By applying these and other analogous results, Voyutskii et al have concluded that when the system consists of two elastomers the limiting adhesive strength is established more rapidly than when one of the high molecular components of the sample is in a glassy state and its molecules or their segments are incapable of thermal motion.



#### 4.5.2 The Effect of Pressure on Adhesion

Some studies on the adhesive films, coated on the substrate surface from a solution have shown that an increase in pressure has no effect on the adhesion strength. At the same time the positive effect of pressure on adhesion has been demonstrated when a solid adhesive is brought into contact with the substrate [232]. This dependence is explained by the fact that, other conditions being equal, an increase in pressure ensures more complete contact between the two phases owing to elastic or plastic deformations of the irregularities of the surface. The adhesion of polymers to metals having a rough surface has been studied by Packham [233]. Considering the effect of various idealised surface features Packham has stated the following equation:

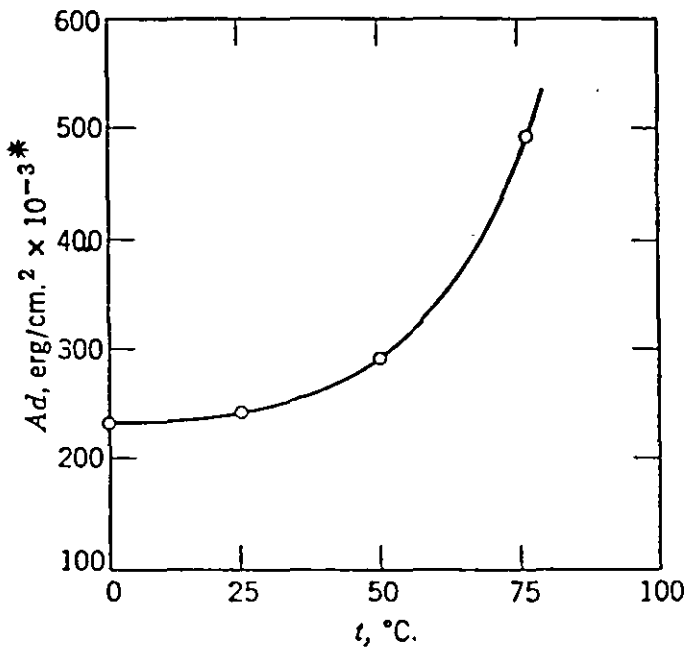
$$\chi = \ell \left( 1 - \frac{P_a r}{\gamma_{LV} \cos \theta + P_a r} \right)$$

$\ell$  is the length of a cylindrical shaped roughness with a radius of  $r$ .  $\gamma_{LV}$  and  $\theta$  respectively are the surface energy and contact angle (see Chapter 5) of the adhesive (coating).  $\chi$  is the distance of penetration and  $P_a$  is the atmospheric pressure. More detailed studies on this and corresponding relationships are reviewed in Chapter 5.

#### 4.5.3 The Effect of Temperature on Adhesion

According to the diffusion theory [149,152], the adhesion and autohesion mechanism, do not differ in principle. Therefore it can be assumed that the action of temperature in bonding high polymers of different kinds will be the same as that in bonding high polymers of the same kind. The dependence of adhesion on the bonding temperature has been shown by Voyutskii et al [232] for bonded samples of cellophane and butadiene-acrylonitrile copolymer. The bonded samples

were heated at different temperatures for 40 minutes before peeling. The adhesion strength increased without tending to a definite limit (Figure 4.7).



\* 1J = 10<sup>7</sup> ergs

FIGURE 4.7: Dependence of Adhesion, Ad, of Copolymer SKN-40 to Cellophane on the Temperature, t, of Heating the Bonded Specimen [234]

Some other experiments [234] using high polar butadiene-acrylonitrile copolymers and various elastomers showed that the contact temperature is only effective with polar elastomers. Hence they concluded that the incompatibility of polymers owing to their major polarity differences would result in no or poor adhesion.

CHAPTER 5  
THERMODYNAMICS OF ADHESION

5.1 AN INTRODUCTION TO WETTING AND ADHESION

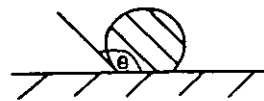
Wetting is usually referred to as the interfacial interaction and the extent of spreading of a liquid over a solid surface; it is expressed quantitatively in terms of "work of adhesion" (see Section 5.2).

The possible actions of a drop of liquid (i.e. point) contacting an ideal flat solid surface are shown in Figure 5.1. The balance of surface tensions (energies) between a liquid resting on a solid, and the related magnitude of the angle of contact,  $\theta$ , will influence and direct the wetting conditions. The surface energy of liquids are easier to measure than those of the solids, and are well documented for various liquids (see Section 5.5 and Appendix 1).

FIGURE 5.1: Possible Actions of a Droplet of Liquid Contacting a Solid Surface

- a) It will remain as a drop

$$\theta > 0^\circ$$



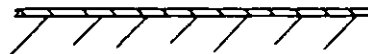
- b) It will spread to form a thin film and remain in place without any real change

$$\theta = 0^\circ$$



- c) It will spread out initially (i), then retract to form droplets having modified the surface (ii)

(i)



(ii)



e.g. due to liquid dissolving material foam substrate which affects surface tension or liquid losing volatiles and changing surface tension.

The ability of solids to be wetted out and have a uniform film of liquid across their surfaces can be better understood from determining their respective surface tension,  $\gamma_S$ , and critical surface tension,  $\gamma_C$ , values.

The methods of measurement of surface tension of solids, and the mathematical relationships existing between  $\gamma_S$  and the other wetting parameters are reviewed here.

## 5.2 WORK OF ADHESION AND COHESION

The reversible work of adhesion, ( $W_A$ ), required to separate the interface between two systems, was first put forward by Dupré in 1869, almost 60 years after the Young's equation was proposed [104,114,121, 125,235,236] (see Section 5.7.1.1)

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (\text{Young's equation}) \quad (1)$$

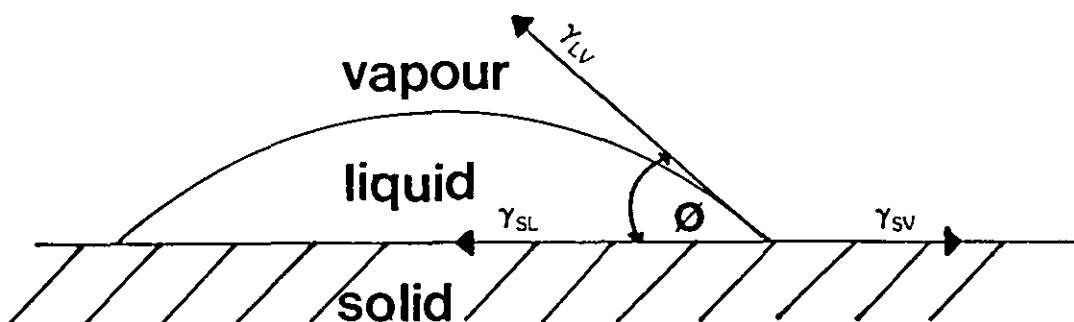


FIGURE 5.2: The Mechanical Equilibrium of a Drop Resting on a Plane Solid Surface Under the Action of Three Surface Tensions

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (\text{Dupré equation}) \quad (2)$$

(see Figure 5.3)

Combining equations (1) and (2) will give:

$$W_A = \gamma_{LV} (1 + \cos\theta) \quad (\text{Young-Dupré equation}) \quad (3)$$

where  $\gamma_{LV}$  = the surface energy of the liquid in contact with its vapour.

$\gamma_{SV}$  = the surface energy of the solid in contact with the liquid's vapour.

$\gamma_{SL}$  = the surface or interfacial energy between the solid and the liquid.

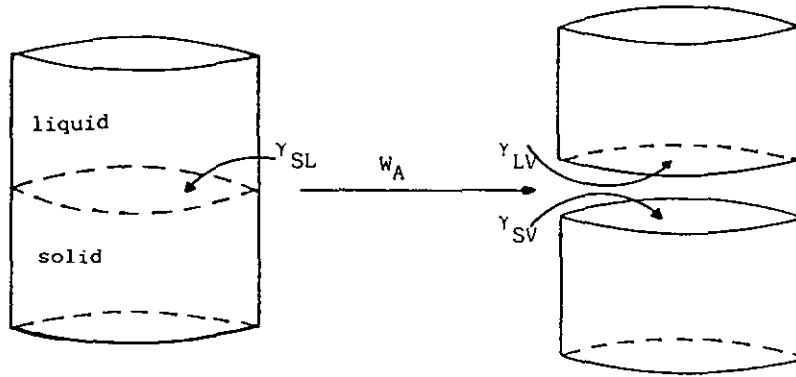


FIGURE 5.3: Schematic Illustrating the Work of Adhesion in Separating a Liquid from a Solid's Surface

Therefore the two quantities necessary to calculate the work of adhesion are the surface tension of liquid and the equilibrium contact angle.

In a similar approach, taking a homogeneous system and producing separation to two fresh surfaces, the reversible work is the work of cohesion ( $W_C$ ) (see Figure 5.4):

$$W_C = 2 \gamma_{SV}$$

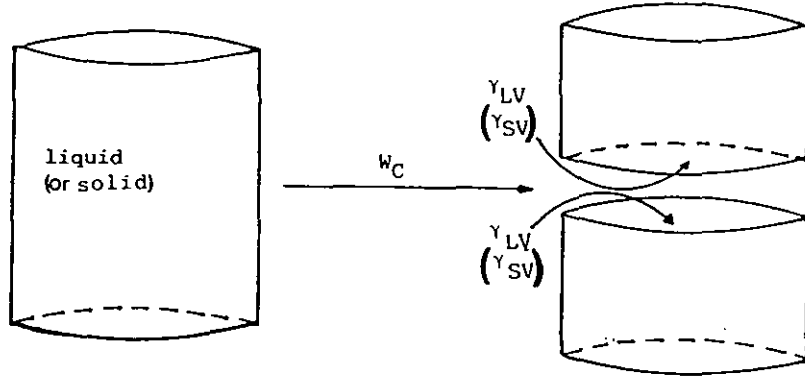


FIGURE 5.4: Schematic Illustrating the Work of Cohesion in Separating a Liquid or Solid into Two Parts

### 5.3 THE EQUILIBRIUM SPREADING PRESSURE, $\Pi_e$

Adsorption of liquid vapour on a solid substrate tends to lower the surface tension of the solid and increase the contact angle. The amount of decrease in surface tension is defined as the equilibrium spreading pressure of the vapour on the substrate,  $\Pi_e$  [104,121, 125,233]:

$$\Pi_e = \gamma_S - \gamma_{SV}$$

where  $\gamma_S$  = the surface tension of the substrate (solid or liquid) in vacuum (or in equilibrium with its own vapour) and

$\gamma_{SV}$  = the surface tension of the substrate in equilibrium with the saturated vapour of the wetting liquid.

Bangham and Razouk [237], and Boyd and Livingston [238] showed that when studying the work of adhesion of a liquid to a solid (see Section 3.2) the vapour adsorption on the surface must be taken into account

$$W_A = \gamma_{LV} (1 + \cos\theta) + \Pi_e$$

The  $\Pi_e$  is usually assumed to be negligible when  $\theta > 10^\circ$ , but more significant when  $\theta < 10^\circ$  [239].

Some typical results for organic vapours on metals and metal oxides are shown in Table 5.1.

TABLE 5.1: Equilibrium Spreading Pressure Obtained by Vapour Adsorption Measurement at 25°C (After Ref 240)

Solids	Liquids	Contact Angle $\theta$ , degree	$\Pi_e$ (mN.m <sup>-1</sup> )
Copper	n-Heptane	0	29
Silver	n-Heptane	0	37
Lead	n-Heptane	0	49
Iron	n-Heptane	0	53
Tin	n-Heptane	0	50
	Water	-	168
	1-propanol	0	83
Fe <sub>2</sub> O <sub>3</sub>	n-Heptane	0	54
SnO <sub>2</sub>	n-Heptane	0	54
SiO <sub>2</sub>	Water	0	316
TiO <sub>2</sub>	Benzene	0	85

On low energy solids such as polymers,  $\Pi_e$  is usually very small or zero [241]. On the other hand, there is some evidence, where high values of  $\Pi_e$  with large contact angles was found [242] (Table 5.2). It may be proposed that normal RIM mould pressures (i.e. between 1 to 3 bars) [244] will aid contact between PU coating and substrate

materials, i.e. influence the spreading pressure,  $\Pi_e$ . This so called "mechanically imposed wetting" is also utilised in many printing processes involving viscose inks, including screening, litho, gravure, etc. Here the sharpness of the printed image is dependent on the surface energetics of ink and substrate, and the shear rates employed [245].

TABLE 5.2: Equilibrium Spreading Pressure Calculated from the Contact Angle at 20°C (After Ref 243)

Solid	Liquid	$\gamma_{LV}$ (mN.m <sup>-1</sup> )	Contact Angle, $\theta$ , degree	$\Pi_e$ (mN.m <sup>-1</sup> )
Polyethylene	Water	72.8	94	0
	Methylene iodide	50.8	52	0
	Hexadecane	27.6	0	7.6
	Hexane	18.4	0	14.5
Poly(methyl methacrylate)	Water	72.8	76	9.2
	Methylene iodide	50.8	41	0
	Hexane	18.4	0	10.0

#### 5.4 THE SPREADING COEFFICIENT, $S_C$

The spreading coefficient of a liquid on surface,  $S_C$ , has been defined by Harkins [246] as the energy released per unit area when the liquid with a free surface spreads over the surface. The liquid spreads such that for each unit area of solid/vapour interface which disappears, equivalent areas of solid/liquid and liquid/vapour interfaces are formed. In other words, the spreading coefficient is the difference in energy equivalent to  $\gamma_{SV} - (\gamma_{LV} + \gamma_{SL})$  [247,248]



$$S_C = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) \quad (1)$$

For spontaneous spreading of a liquid on a solid, i.e. zero contact angle

$$S_C \geq 0$$

therefore  $\gamma_{SV} \geq \gamma_{LV} + \gamma_{SL}$

It has been assumed [248] that since  $\gamma_{SL}$  is often negligibly small, then

$$S_C = \gamma_{SV} - \gamma_{LV}$$

and therefore a useful approximation,  $\gamma_{SV} > \gamma_{LV}$ , for spreading. Considering the Young's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (2)$$

and combining equations (1) and (2)

$$S_C = \gamma_{LV} (\cos \theta - 1) \quad (3)$$

A useful relationship established between work of adhesion,  $W_A$ , work of cohesion  $W_C$ , and the spreading coefficient is given as [248,249]:

$$S_C = W_A - W_C \quad (4)$$

where  $W_A = \gamma_{LV} (1 + \cos \theta)$

$$W_C = 2 \gamma_{LV}$$

Therefore for spontaneous spreading,  $W_A \geq W_C$ . It has been emphasised that the relationship (4) is only an indication for initial spreading coefficient and a final coefficient exists under the condition that once spreading has occurred that liquid can remain spread.

Fox and Zisman [250] studied the surface energy relations of various liquids on some fluorinated polymers, as shown in Figure 5.5. It was concluded that, as the liquid surface tension decreases, the contact angle on a given surface decreases, and the spreading coefficient increases [252].

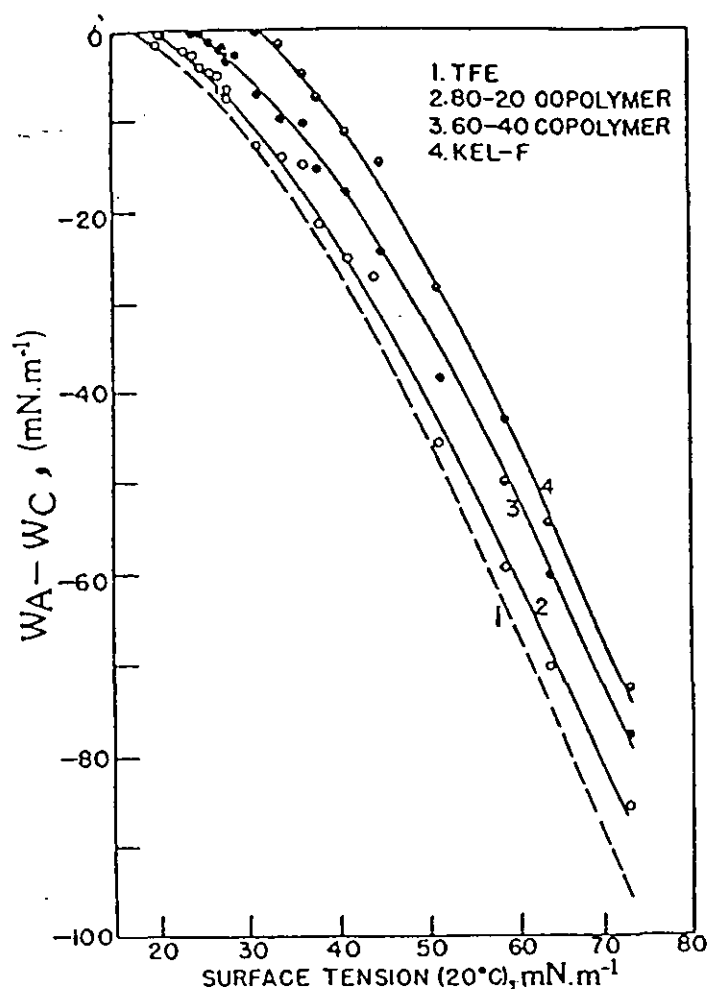


FIGURE 5.5: Surface Tension vs Spreading Coefficient of Some Liquids on Fluorinated Polymers (after Ref 251)

A method for measuring the spreading coefficient,  $S_C$ , depending on the sessile drop height,  $h$ , resting on a smooth, solid, flat surface, where no edge effects occur, was introduced by Padday [253] (Figure 5.6).

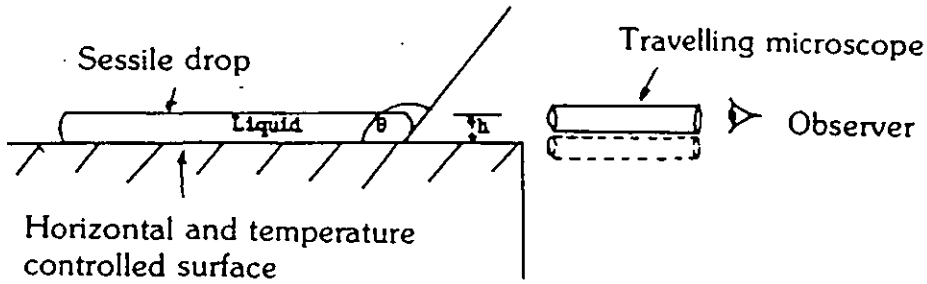


FIGURE 5.6: Schematic Diagram Illustrating Test Method Used to Measure Spreading Coefficient of a Liquid on a Solid (After Ref 104)

The spreading coefficient for a liquid on a solid is given by:

$$S_C = - \frac{1}{2} \rho g h^2 \quad (5)$$

The relationship (5) was found on the basis that after a sessile drop is formed, then further adding of the liquid will only increase the drop diameter but not its height above the solid surface. It was concluded that the validity of this relationship was only accepted when:

- a) the edge effects can be neglected and the sessile drop treated as a cylinder
- b) that the solid surface is uniformly smooth
- c) an equilibrium is reached in the system.

5.5 THE SURFACE ENERGY (TENSION) OF LIQUIDS AND SOLIDS

The surface energy of a liquid or solid is the amount of energy required to form a unit area of new surface. The surface molecules are in constant inward attraction from the bulk material. This attraction tends to reduce the number of molecules in the surface layer region, resulting in an increase in intermolecular distance. Hence, the surface layers have a higher energy level than the bulk and the excess is the surface energy,  $\gamma$  [119,254].

Since energy is required to produce new surfaces, the surface has properties equivalent to it being in tension, hence the term often used "surface tension". For pure liquids, the free surface energy is equal to the surface tension. The surface free energy of various liquids is shown in Table 5.3. It is worth mentioning that surface energy units can be presented both in  $\text{mN.m}^{-1}$  and  $\text{mJ.m}^{-2}$  units (i.e. since energy (J) = force (N) x distance (m)). It should be noted that mixed systems such as liquid surface coatings, will have a value of surface free energy dependent on the type and proportion of additives present [93]: solvents, wetting agents, spreading agents and pigments will have a marked effect on the value of the resin binder.

TABLE 5.3: Surface Free Energy Components of Various Liquids  $\text{mN.m}^{-1}$  [255]

Liquid	$\gamma_{LV}$	$\gamma_{LV}^d$	$\gamma_{LV}^p$
Water	72.8	21.8	51.0
Glycerol	63.4	37.0	26.4
Formamide	58.2	39.5	18.7
Methylene iodide	50.8	49.5	1.3
Ethan 1,2 diol.	48.3	29.3	19.0
Dimethyl sulphoxide	43.54	34.86	8.68
Tri-cresyl phosphate	40.70	36.24	4.46
Pyridine	38.00	37.16	0.84
Dimethyl formamide	37.30	32.42	4.88
2-ethoxyethanol	28.6	23.6	5.0
n-hexadecane	27.6	27.6	-

Brewis [256] has stated that the surface energies of an adhesive and an adherend are two of many factors which can affect the resultant breaking stress of an adhesive joint.

## 5.6 SURFACE TENSION OF LOW AND HIGH ENERGY SOLID SURFACES, $\gamma_s$

The surface tension or surface energy is a useful parameter in determining many surface characteristics of solids, i.e. polymers. Solid organic polymers and substances such as waxes are classed as low surface energy solids [257,258] with  $\gamma_s$  usually less than  $100 \text{ mN.m}^{-1}$  (Table 5.4). In contrast, metals and metal oxides belong to high energy solid surfaces [262] normally having  $\gamma_s$  greater than  $500 \text{ mN.m}^{-1}$  (Table 5.5).

TABLE 5.4: Surface Tension of Some Low Energy Solid Surfaces (After Refs 259,260)

Material	$\gamma_s$ at $20^\circ\text{C}$ ( $\text{mN.m}^{-1}$ )
<u>Polymers</u>	
Poly(tetrafluoroethylene)	19.1
Polypropylene	30.2
Polyethylene	35.7
Polystyrene	42.0
Poly(ethylene terephthalate)	47.3
Poly(vinyl chloride)	41.5
Poly(vinylidene chloride)	45.0
<u>Organic solids and pigments</u>	
Paraffin wax	32.0
Chlorinated copper phthalocyanine (green)	42.0
Copper phthalocyanine	46.9
Metal-free phthalocyanine	52.8
Toluidine red	53.0

TABLE 5.5: Surface Tension of Some Metals and Metal Oxides [261]

Material	Temperature °C	Surface Tension, $\gamma_S$ , (mN.m <sup>-1</sup> )
<u>Metals</u>		
Lead (MP 327.5°C)	327.5	470
Aluminium (MP 660°C)	660	873
Gold (MP 1064°C)	1064	1130
Copper (MP 1083°C)	1083	1300
Iron (MP 1535°C)	1535	1760
<u>Metal Oxides</u>		
PbO	900	79
FeO	1420	585
Al <sub>2</sub> O <sub>3</sub>	2080	700

The relationships between surface energies and wetting equilibria have been reviewed by many authors [14,114,116,119,247]. Fowkes, [263] considering the intermolecular forces existing in a system, proposed that the total free energy at a surface is the sum of dispersion and hydrogen bonding force components (Table 5.6).

$$\gamma = \gamma^d + \gamma^h$$

Following this suggestion, Owens and Wendt [146] considered a theoretical expression for the interfacial free energy between two substances (see Section 5.7.1.5)

TABLE 5.6: Surface Tension Components for Low and High Energy Solid Surfaces [260]

Material	$\gamma_S$ (mN.m <sup>-1</sup> )	$\gamma_S^d$ (mN.m <sup>-1</sup> )	$\gamma_S^p$ (mN.m <sup>-1</sup> )
<u>Low energy surfaces</u>			
Polytetrafluoroethylene	19.1	18.6	0.5
Polytrifluoroethylene	23.9	19.9	4.0
Poly(vinylidene fluoride)	30.3	23.2	7.1
Poly(vinyl fluoride)	36.7	31.3	5.4
Low density polyethylene	33.2	33.2	-
Polypropylene	30.2	30.2	-
Poly(methyl methacrylate)	40.2	35.9	4.3
Poly(vinyl chloride)	41.5	40.4	1.5
Poly(vinylidene chloride)	45.0	42.0	3.0
Polystyrene	42.0	41.4	0.6
Poly(ethylene terephthalate)	47.3	43.2	4.1
Poly(hexamethylene-adipamide)	40.2	35.9	4.3
<u>High energy surfaces</u>			
Al <sub>2</sub> O <sub>3</sub>	638	100	538
Fe <sub>2</sub> O <sub>3</sub>	1357	107	1250
SiO <sub>2</sub>	287	78	209

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2 (\gamma_1^d \gamma_2^d)^{1/2} - 2 (\gamma_1^h \gamma_2^h)^{1/2}$$

or

$$\gamma_{12} = [(\gamma_1^d)^{1/2} - (\gamma_2^d)^{1/2}]^2 + [(\gamma_1^h)^{1/2} - (\gamma_2^h)^{1/2}]^2$$

Substances 1 and 2 may either be liquids, or solids, or they may be a combination of a solid and a liquid.

It has been argued [264] that the polymer surfaces with a higher surface free energy ( $> 35 \text{ mN.m}^{-1}$ ) are better substrates for painting than those with lower free energies. Garrett [265] has shown that liquids having surface free energies in the order of about  $37 \text{ mN.m}^{-1}$  or less rest on all solids with some work of adhesion, whereas surfaces having free energies greater than  $37 \text{ mN.m}^{-1}$  exhibit higher work of adhesion on strongly polar solids than on non-polar solids.

Gray [266] based on Dupre's equation suggested that higher values of work of adhesion,  $W_A$ , can be achieved by lowering the surface energy between solid and liquid,  $\gamma_{SL}$  (see Section 5.2)

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (\text{Dupre's equation})$$

This means that the adhesive (coating) should show chemical affinity or interaction with the adherent (substrate). He suggested that similarities in properties like molecular size, shape, cohesive energy density and ability to swell or diffuse into one another lead to low  $\gamma_{SL}$ .

The concept of low surface free energy inhibiting adhesion of paint films has been challenged by Sharpe and Schonhorn [267,268]. Their criterion essentially proposes that a mobile liquid with small or zero contact angle, which will spread readily, flow into crevices and achieve true contact with little opportunity for the voids which may act as stress concentrators, is of prime importance. Furthermore, it has been suggested that an additional requirement is that the interfacial free energy,  $\gamma_{SL}$  should be as low as possible.



## 5.7 SURFACE TENSION OF SOLIDS: METHODS OF MEASUREMENT

Compared to the liquid surfaces, solid surfaces are in many ways more difficult to treat from a theoretical point of view and also more difficult to quantify in certain important respects. One of the major problems in describing the solid state is that the surface tension of the solid is not susceptible to direct measurement. For a liquid, the newly formed surface rapidly takes upon equilibrium conformation, whereas the same is not true of a solid surface. The latter is likely to have a considerable range of values of surface free energy, varying from region to region on the surface, and also at any one point, unlike the surface of a liquid, the surface tension need not be the same in all directions.

The usual techniques of measurement of surface tension of solids can be divided into: direct and indirect methods [269-271]. The direct methods, reviewed in the relevant literature [272], have little importance as they are often very complicated and rarely give reliable or repeatable results. The indirect methods are more common and are reviewed here.

### 5.7.1 Indirect Methods of Measurement for $\gamma_s$

Indirect methods are those in which the surface tension is deduced from the measurement of one of its effects on the equilibrium properties of a solid. It is worth mentioning that some of these so called methods are basically treatments of results from a single method (i.e. contact angle). Some of the more important indirect methods/treatments are as follows [273,274]:

1. contact angle
2. critical surface tension
3. application of acid/base theory
4. the harmonic mean method.
5. the geometric mean method.
6. the equation of state method.

The liquid homology (molecular weight dependence) method, and polymer melt (temperature dependence) method have also been proposed and reviewed in the related literature [274,275].

#### 5.7.1.1 Contact angle

The idea of contact angle and how a drop of liquid, resting on a flat solid surface could come to equilibrium under the action of forces shown in Figure 5.2, was initially put forward by Thomas Young over 180 years ago [235,263].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (\text{Young's equation})$$

Later, it was Bangham and Razouk [237] who expressed the surface tension of liquids and solids by considering the adsorption of liquid vapour on the solids and taking the saturated vapour into account (see Section 5.3).

Zisman et al [14,250,252,277,278] were the first to study and develop an empirical relationship based on  $\cos \theta$ , and the surface tension of the wetting liquids, on low energy polymeric surfaces. They stated that for a sufficiently smooth and homogeneous solid surface, the tendency of a given mass of liquid to spread will increase as the contact angle,  $\theta$ , decreases. Hence, the contact angle is a valid

inverse measure of wettability, whereas,  $\cos \theta$ , is a useful direct measure. It has been shown that in general  $\theta$  decreases as  $\gamma_{LV}$  decreases, for a given variety of liquids on a given surface (Table 5.7). The exception to this generalisation may occur if the  $\gamma_{SL}$  of the liquid giving the lower angle is much smaller than that of the liquid giving the higher angle. The relationship between  $\cos \theta$  and  $\gamma_{LV}$  for the four series of liquids on polytetrafluoroethylene, given in Table 5.7, are shown in Figure 5.7.

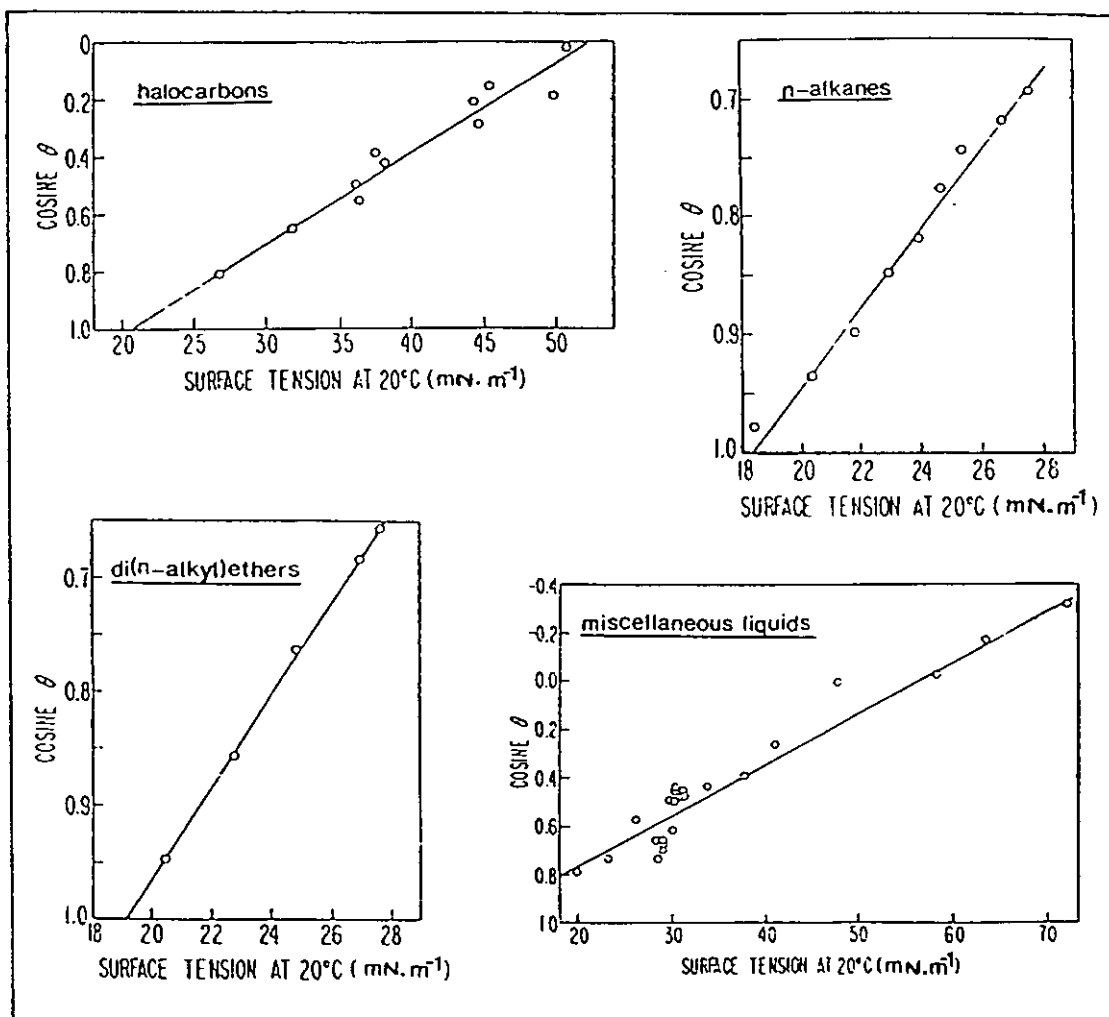


FIGURE 5.7: Liquid Surface Tension vs Cosine  $\theta$  for Four Series of Liquids on PTFE at 20°C (After Ref 252)

TABLE 5.7: Surface Energy and Contact Angle of Four Series of Liquids on Polytetrafluoroethylene at 20°C [278]

Liquid	$\gamma_{LV}$ (mN.m <sup>-1</sup> )	$\theta$ (degree)
<u>n-Alkanes</u>		
Hexadecane	27.6	46
Tetradecane	26.7	44
Dodecane	25.4	42
Undecane	24.7	39
Decane	23.9	35
Nonane	22.9	32
Octane	21.8	26
Heptane	20.3	21
Hexane	18.4	12
Pentane	16.0	Spreads
<u>Di(n-alkyl) ethers</u>		
Octyl	27.7	49
Heptyl	27.0	47
Amyl	24.9	40
Butyl	22.8	31
Propyl	20.5	19
Isopropyl	17.8	Spreads
<u>Halogenated Compounds</u>		
Methyl iodide	50.8	88
-Bromonaphthalene	44.6	73
Sym-tetrachloroethane	36.3	56
Hexachlorobutadiene	36.0	60
Tetrachloroethylene	31.7	49
Carbon tetrachloride	26.8	36
Perfluorotributylamine	16.2	Spreads
<u>Miscellaneous Liquids</u>		
Water	72.8	108
Glycerol	63.4	100
Formamide	58.2	92
Ethylene glycol	47.7	90
tert-Butyl naphthalene	33.7	65
Polyethyl siloxane	23.3	43
Triptane	18.9	<5

It was also argued by Zisman [280] that for a good adhesion between an adhesive and a substrate, the contact angle of adhesive must be zero. This will result in an increased area of mutual contact between the surfaces and minimum stress concentrations. This in turn leads to a better interfacial contact and leads to maximising molecular attraction across the interface.

It is apparent that solid surfaces are not always homogeneous and/or planar. The contact angle,  $\theta_A$ , observed when a liquid wets and advances initially over a dry solid surface and  $\theta_R$ , observed on a receding liquid from a previously wetted surface have been investigated by many authors [14,121,226,227,280]. Zisman [14] has stated that by careful preparation and handling of smooth surfaces, no significant differences are found between the slowly advancing and the receding contact angles of pure liquids. Ellison and Zisman [277] reported that with many liquids having  $\theta < 50^\circ$ , adding more liquids to the drop would not increase the contact angle. In many instances where the surface has been solvated or otherwise chemically attacked by the liquid, only the initial contact angle has been reported.

Bikerman [216] has pointed out that only the liquids which form very small contact angles are capable of wetting a solid surface and if the value of  $\theta$  is large no satisfactory contact between the coating (liquid) and substrate is achieved. He has emphasised the importance of reporting all the facts and observations for each pair of wetting liquid and substrates and hence avoiding generalised statements such as: the wetting liquid is no good because of its poor adhesion!

Rance [247] showed that by measuring the dimensions of a drop of liquid being small enough ( $V < 10^{-10} \text{ m}^3$ ), so that gravitational

distortion will be negligible then the contact angle can be measured from the height,  $h$ , and base diameter,  $d$ , by:  $\tan\theta/2 = 2h/d$ . This method can be applied to all drops considered to be a segment of a sphere where  $d < 0.5 \text{ mm}$  and  $\theta < 90^\circ$  [281,282].

Ellison and Zisman [276,277] studied the wettability of a number of polymer surfaces with different end-groups, using hydrogen-bonding and halogenated liquids (Figure 5.8). They showed that the wettability by polar hydrogen-bonding liquids is increased by the presence of both the amide and the ester group in the solid surfaces but to a much greater extent by the amide group. The wettability by organic halogenated liquids is less affected by the amide or ester groups as might be expected from the inability of these liquids to form hydrogen bonds.

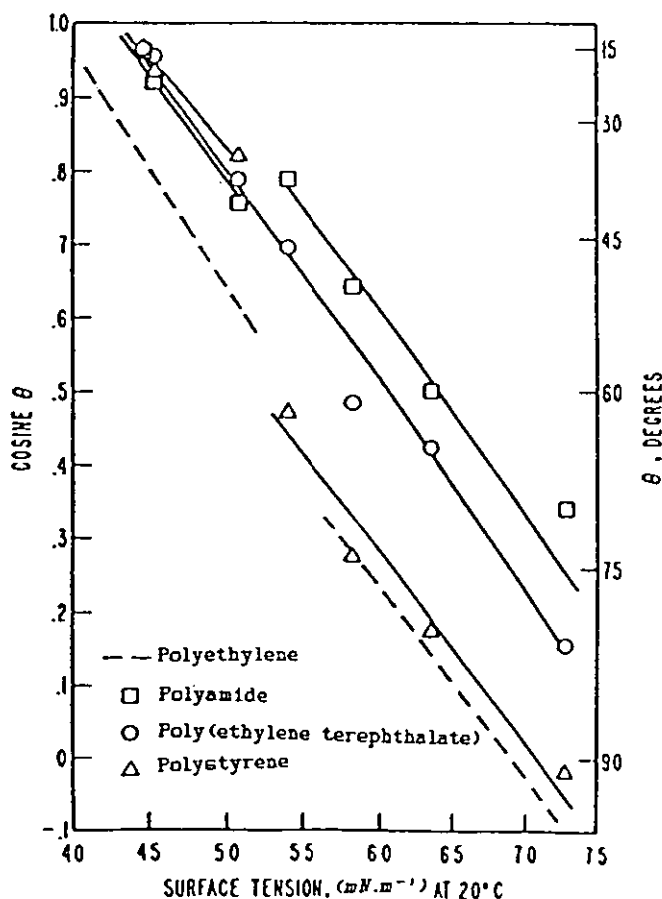


FIGURE 5.8: Liquid Surface Tension vs Cosine of the Contact Angle for Several Liquids on Surfaces of High Polymers Studied (After Ref 277)

### 5.7.1.2 Critical surface tension, $\gamma_C$

Zisman et al [14,250,252,276,277,279] measured the contact angles formed by many homologous series of liquids on a number of low energy solid surfaces. As a result, a linear relationship between the cosine of the contact angle ( $\cos \theta$ ) and the surface tension of the liquid ( $\gamma_{LV}$ ) was observed. At the intercept of the line  $\cos \theta = 1$  (i.e.  $\theta = 0^\circ$ ) with the extrapolated straight line, a new parameter,  $\gamma_C$ , critical surface tension, was defined [93,104,119,121,256] (Figure 5.9).

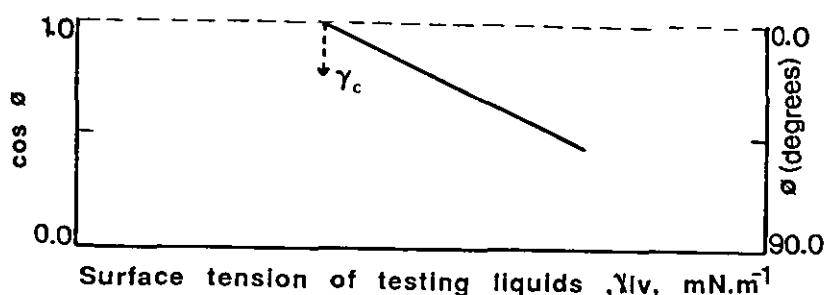


FIGURE 5.9: Critical Surface Tension,  $\gamma_C$

Critical surface tension,  $\gamma_C$ , is used as a measure of the wettability of a solid surface, dependent on the type of liquids used, and is expressed in units of  $\text{mN.m}^{-1}$  with the testing temperature being specified, consequently all liquids for which  $\gamma_{LV} < \gamma_C$  should spread on that solid surface.

When a series of homologous pure liquids are used, a straight line or a narrow band is often obtained [14] (Figure 5.10), whereas with non-

homologous liquids, the data is often scattered within a rectilinear band or a straight line with upward curvature for hydrogen bonding liquids (Figures 5.11 and 5.12).

Zisman [14] has stated that with rectilinear bands,  $\gamma_C$  is chosen as the intercept of the lower limb of the band at  $\cos\theta = 1$ . The critical surface tension values for a number of solid surfaces are shown in Table 5.8.

TABLE 5.8: Critical Surface Tension of Wetting of Some Solid Surfaces (After Refs 259,260)

Material	$\gamma_C$ at 20°C (mN.m <sup>-1</sup> )
<u>Polymers</u>	
Poly(tetrafluoroethylene)	18.5
Low density polyethylene	31.0
Polypropylene	31.0
Poly(vinyl chloride)	39.0
Polystyrene	43.0
Poly(ethylene terephthalate)	43.0
Polyamide 6.6	46.0
<u>Organic solids and pigments</u>	
Paraffin wax	23.0
Chlorinated copper phthalocyanine (green)	27.5
Toluidine red	27.5
Copper phthalocyanine	31.3
Metal-free phthalocyanine	35.6



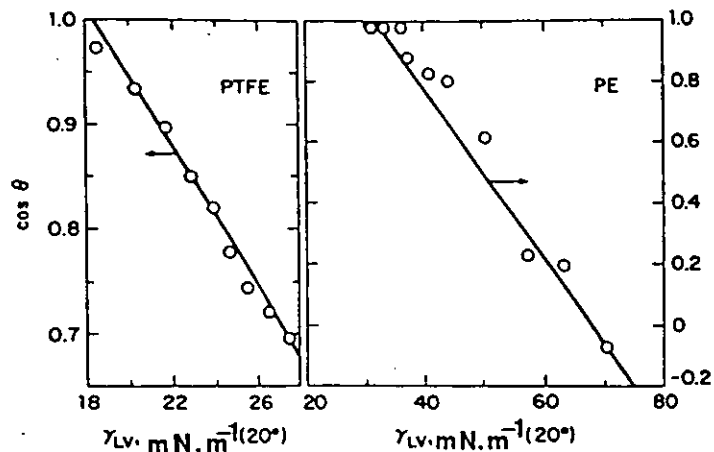


FIGURE 5.10: Zisman plots for polytetrafluorethylene (PTFE) using *n*-alkanes as the testing liquids, and for polyethylene (PE) using various testing liquids (After ref 283)

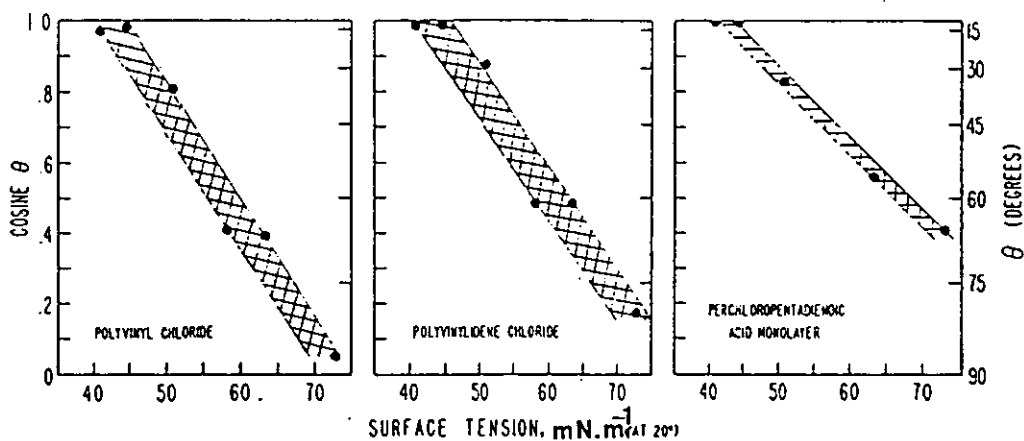


FIGURE 5.11: Wettability of polyvinyl chloride, polyvinylidene chloride, and a close-packed monolayer of perchloropentadienonic acid on platinum, by various liquids (After ref 284)

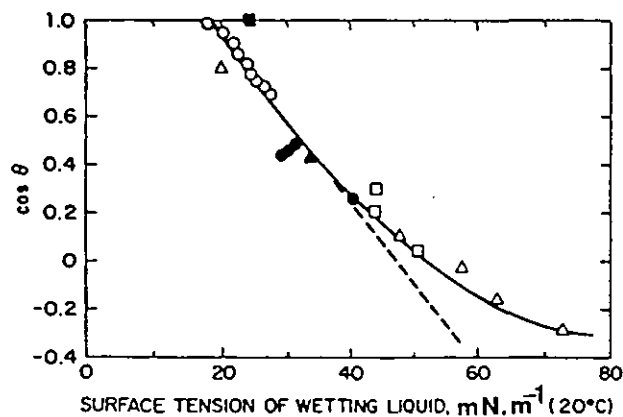


FIGURE 5.12: Zisman plot for polytetrafluorethylene using various testing liquids:  $\circ$ , *n*-alkanes;  $\blacktriangle$ , miscellaneous hydrocarbons; esters;  $\square$ , nonfluoro halocarbons;  $\blacksquare$ , fluorocarbons;  $\Delta$ , miscellaneous liquids (After ref 283)

Different values of  $\gamma_C$  may be obtained using polar, non-polar, or hydrogen bonding liquids [250,279,280]. It has been argued by Hata et al [285] that the highest value of  $\gamma_C$  should be taken into account because under these conditions,  $\gamma_{SL}$  will be minimum [235], i.e.

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \quad (\text{Young's equation})$$

For wetting:

$$\gamma_{LV} = \gamma_C \text{ and } \cos\theta = 1$$

Therefore: 
$$\gamma_C = \gamma_{SV} - \gamma_{SL}$$

It has been shown [247] that by the replacement of protons in the molecular structure of many monomers by more polar atoms or groups or the insertion of polar molecules along the main chain results in an increase in  $\gamma_C$  of the polymer. This increase in  $\gamma_C$  has been observed by Zisman [14] in the case of replacement of fluorine by hydrogen atoms on the surface of bulk polymers. Table 5.9 shows the  $\gamma_C$  of a number of polymers, where chemical structure of monomers is compared with ethylene and arranged in an increasing order relating to the relative increase in the polarity of the compounds.

#### 5.7.1.3 Applications of acid-base theory

A useful approach in understanding the wetting phenomena is based on Lewis' acid-base theory [273,286,287]. An acid is considered electrophilic, thus being an electron acceptor (proton donor), and a base, nucleophilic, and thus an electron donor (proton acceptor). Many authors [288-290] have shown the possibility of explaining the adhesion properties of a system by using the acid-base interactions expressed through electron donor/acceptor properties.

TABLE 5.9: Critical Surface Tension of Wetting of Some Polymers [260]

	Chemical Structure of monomer compared with ethylene	$\gamma_c$ at 20°C (mN.m <sup>-1</sup> )
Polytetrafluorethylene	4H replaced by F	18.5
Polytrifluorethylene	3H replaced by F	22
Poly(vinylidene fluoride)	2H replaced by F	25
Poly(vinyl fluoride)	1H replaced by F	28
Low density polyethylene	-	31
Polypropylene	1H replaced by CH <sub>3</sub>	31
Poly(methyl methacrylate)	1H replaced by ester	39
Poly(vinyl chloride)	1H replaced by Cl	39
Poly(vinylidene chloride)	2H replaced by Cl	40
Polystyrene	1H replaced by benzene ring	43
Poly(ethylene terephthalate)	Polar monomers inserted	43
Poly(hexamethylene adipamide)	(ester, amide) in hydrocarbon chain	46

Pimentel and McClellan [291] have classified the solvents according to acid-base theory (Table 5.10):

TABLE 5.10: Solvents Classification According to Acid-Base Theory (After Ref 286)

Proton donors (electron accep- tor or acidic)	Proton acceptor (electron donor or basic)	Proton donor or proton acceptor	Not-forming hydrogen bonding
Chloroform	ketones ethers esters aromatic hydro- carbons	water alcohols carboxyl acids primary and secondary amines	Aliphatic hydrocarbons

Small [292] pointed out that polymers can also be characterised as proton donors and proton acceptors. Table 5.11 shows the types of hydrogen bonding capability for a number of polymers.

TABLE 5.11: Polymer Classification According to Acid-Base Theory (After Ref 247)

Proton donor (electron acceptor or acidic)	Proton acceptor (electron donor or basic)	Proton Acceptor and Proton donor
PVC Chlorinated polyethy- lenes or polypropy- lenes Poly(vinylidene) fluoride Ethylene-acrylic acid copolymers	Polymethylmethacrylate Polystyrene  Ethylene vinylacetate copolymers Polycarbonate	Polyamides Polyimides  Poly(vinyl alco- hol)

Fowkes and Maruchi [136,293] studied the wettability of a number of acidic and basic polymers by applying a range of acidic and basic liquids. Their studies were based on earlier work by Drago et al [78,138] who regarded hydrogen bonding as a sub-set of Lewis acid-base interactions. Fowkes concluded that liquids and solids which may be polar but have the same electron accepting (or donating) capability interact by dispersion forces alone. For a basic surface, only acidic liquids were found to produce a positive contribution to  $w_A^{ab}$ , where ab refers to acid-base attractions. Hence it was argued that the contribution to interfacial interactions by purely dipolar forces,  $w_A^D$ , is very small and may be neglected.

$$w_A = w_A^d + w_A^{ab}$$

and

$$\gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^{ab}$$

#### 5.7.1.4 The harmonic mean method

This method has been advocated for obtaining surface tension,  $\gamma_S$ , of low-energy solids, i.e. polymers [273,294,295]. It is based on the assumption that surface tension is the sum of dispersive and polar components; and that harmonic mean relations exist:

$$\gamma_S = \gamma^d + \gamma^p$$

$$W_A = 4 \left[ \frac{\gamma_{SV}^d \gamma_{LV}^d}{\gamma_{SV}^d + \gamma_{LV}^d} + \frac{\gamma_{SV}^p \gamma_{LV}^p}{\gamma_{SV}^p + \gamma_{LV}^p} \right]$$

(harmonic mean equation)

Using the harmonic mean in the Young's equation gives

$$(1 + \cos \theta) \gamma_{LV} = 4 \left[ \frac{\gamma_{SV}^d \gamma_{LV}^d}{\gamma_{SV}^d + \gamma_{LV}^d} + \frac{\gamma_{SV}^p \gamma_{LV}^p}{\gamma_{SV}^p + \gamma_{LV}^p} \right]$$

By applying the contact angles of two testing liquids

$$\text{For liquid 1: } (1 + \cos \theta_1) \gamma_1 = 4 \left[ \frac{\gamma_1^d \gamma_S^d}{\gamma_1^d + \gamma_S^d} + \frac{\gamma_1^p \gamma_S^p}{\gamma_1^p + \gamma_S^p} \right]$$

$$\text{For liquid 2: } (1 + \cos \theta_2) \gamma_2 = 4 \left[ \frac{\gamma_2^d \gamma_S^d}{\gamma_2^d + \gamma_S^d} + \frac{\gamma_2^p \gamma_S^p}{\gamma_2^p + \gamma_S^p} \right]$$

If the intermolecular attractions of the testing liquids are known, the dispersion and polar components of solid surface tension can be obtained by solving the two simultaneous equations.

#### 5.7.1.5 The geometric mean method

The idea of critical surface tension introduced by Zisman [14,279] was developed by Girafalco and Good [296], and Fowkes [121,297] who emphasised on bringing all forces acting across an interface and shaping it in the form of a geometric mean relationship. Fowkes suggested that with non-polar liquids in contact with another material, the mutual interaction is due to the dispersion interactions of the two materials only.

$$\gamma_{AB} = \gamma_A + \gamma_B - 2 (\gamma_A^d \gamma_B^d)^{1/2}$$

It has been shown [273] that the dispersive component of a liquid (i.e. liquid 1) could be calculated from its interfacial tension with a saturated hydrocarbon (i.e. liquid 2) for which the polar component of the surface tension is zero, i.e.

$$\gamma_2 = \gamma_2^d$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2}$$

The surface free energy components of various liquids are given in Table 5.3 (see Section 5.5). Although Fowkes had only applied this method to liquids, later others adopted this approach and combined it with Young's equation to measure the dispersive and polar components of solid surface free energies [298,299]:

$$(1 + \cos\theta) \gamma_{LV} = 2 [(\gamma_S^d \gamma_{LV}^d)^{1/2} + (\gamma_S^p \gamma_{LV}^p)^{1/2}]$$

(or  $W_A$ )

Using two testing liquids of known surface tension, respective contact angles are measured and solving the two simultaneous equations will give  $\gamma_S^d$  and  $\gamma_S^p$  of the solid

For liquid 1:  $(1 + \cos \theta_1) \gamma_1 = 2 [(\gamma_1^d \gamma_s^d)^{1/2} + (\gamma_1^p \gamma_s^p)^{1/2}]$

For liquid 2:  $(1 + \cos \theta_2) \gamma_2 = 2 [(\gamma_2^d \gamma_s^d)^{1/2} + (\gamma_2^p \gamma_s^p)^{1/2}]$

It has been argued [299] that this method is inadequate for low energy surfaces i.e. polymers, but preferred for high-energy surfaces, i.e. metals.

#### 5.7.1.6 The equation of state method

This method for finding the surface tension of a solid, uses the critical surface tension,  $\gamma_C$ , of a surface obtained from the contact angle measurements of a series of testing liquids. The  $\gamma_C$  plotted against  $\gamma_{LV}$  will result in a curve known as the equation of state plot, in which the maximum critical surface tension value will be equal to the surface tension of the solid:

$$\gamma_C = \lim_{\theta \rightarrow 0} \gamma_{LV}$$

$$\cos \theta = 2 \left( \frac{\gamma_C}{\gamma_{LV}} \right)^{1/2} - 1$$

or it can be arranged to:

$$\gamma_C = \frac{1}{4} (1 + \cos \theta)^2 \gamma_{LV} \quad (\text{equation of state})$$

The equation of state plots for a number of polymers are shown in Figure 5.13. The Zisman's critical surface tensions designated as  $\gamma_{C,z}$  are shown in these figures.

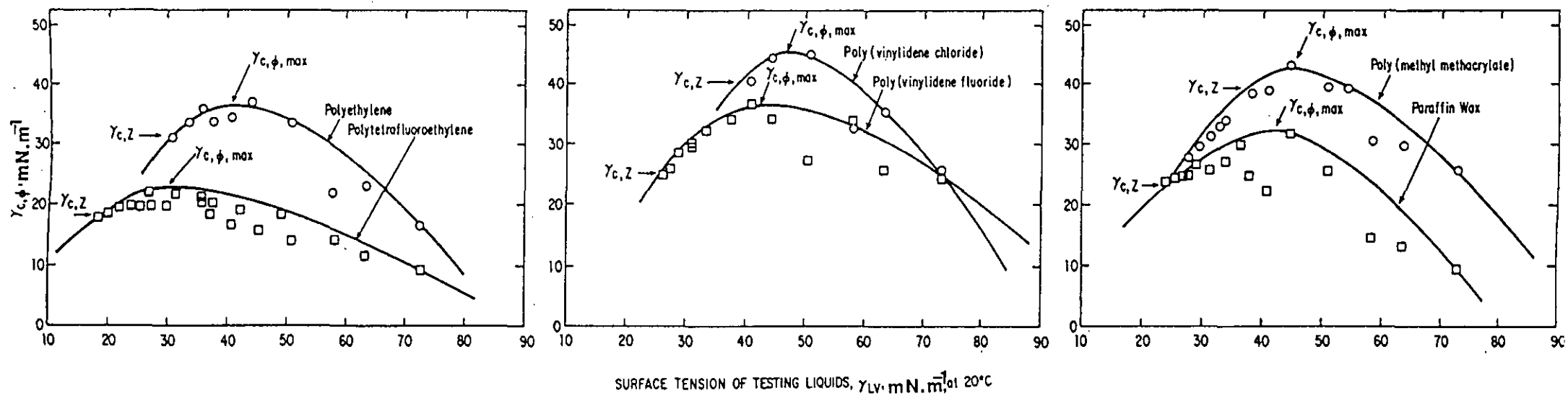


FIGURE 5.13: Equation of state plots for some polymers at 20°C (After ref 300)



## CHAPTER 6

### RESEARCH PROJECT: AIMS AND OBJECTIVES

#### 6.1 PROJECT AIMS AND OBJECTIVES

The main objective of this research project is to investigate the adhesion phenomena occurring between a number of polyurethane substrates and various one- and two-pack PU surface coatings.

The literature review presented in the preceding Chapters 1 to 5 has demonstrated a number of relevant conclusions:

1. PU mouldings surface coated by the IMC technique impart many advantages both in process cost saving and in the improvement of the finished properties.
2. Several theories have been put forward to explain the mechanisms of adhesion, wetting and interfacial bonding. However most of these theories have been reported on the adhesion of metal-polymer joints and the real interest in polymer-polymer systems has only started in the last decade and proves to be more complex.
3. Many factors may contribute to the adhesion between two polymeric surfaces such as substrate and coating in which one material is initially in a mobile, fluid state and solidifies in the processing stage for the establishment of the bond. The ultimate adhesion properties will not only depend on the actual strength of the individual bonds, but also on the wetting and

thermodynamic properties, the surface effects (e.g. WBLs) and environmental factors. The resultant microscopic air bubbles in the interfacial region giving rise to stress concentrators, differences in pressure, temperature and other external factors may also affect the adhesion properties of these systems.

4. A number of discussions with relevant polymer moulding and paint manufacturers have shown that although several of these companies cautiously welcomed the concept of IMC and its extension to a wide range of polymer substrates, this idea has not been fully accepted by many others. It seems reasonable to assume that this lack of interest reflects the conservatism in both the polymer and paint industries.

During the preliminary stage of this research it was recognised that introducing polyester substrates (as additional polymeric materials) could be beneficial in order to provide a more complete understanding of interfaces produced.

The primary aims of this research are:

1. To provide a detailed study of adhesion/bonding in PU and polyester IMC and PMC systems using established and modified/devised test techniques.
2. To gain a fuller understanding of the mechanisms of interfacial formation between PU substrates and PU based coating materials under different processing and environmental conditions.

3. To study the influence of different factors such as the effect of coating, substrate, coating process and others on the adhesion properties of coated systems. The parameters giving optimum properties and also those factors giving rise to defects will be identified.

It is hoped that this project might help to fill the gap in this particular area of research.

A number of experimental programmes were selected and the corresponding testing techniques were carried out. Several of these tests did not give satisfactory results with coated samples in this research. This was partly due to the near chemical composition of the substrate and coating materials. For example, the analysis of urethane/urethane systems with X-ray photospectrometry (XPS) and secondary ion mass spectrometry (SIMS) techniques proved problematic and did not work for our purpose (see Chapter 8).

Other techniques such as X-ray diffraction, infra-red spectroscopy, acoustic scanning microscopy (ASM), thermogravimetric analysis (TGA) and dielectric thermal analysis (DETA) provided some information about the single polymer (i.e. substrate or coating) but their application for coated systems where the interfacial region was of major interest could not give useful/meaningful results.

Given the above aims, the structure of the thesis continues as follows. Chapter 7 describes the materials, equipment and techniques used for the preparation of the IMC and PMC mouldings. Chapters 8 to 11 discuss the measurements and present the results and discussion of surface analysis, mechanical, thermal and microscopy techniques.

Chapter 12 will try to draw together various results, and develop an overall thesis of the adhesion phenomena related to PU surface coating on PU substrate. The final chapter brings together a number of points which emerge from the preceding chapters and gives some suggestions for further work.

CHAPTER 7  
MATERIALS, EQUIPMENT AND SAMPLE PREPARATION

7.1 INTRODUCTION

This chapter is divided into two parts. The first part will review the materials and equipment used in this research. The second part will describe the preparation of various IMC and PMC polyurethane and polyester samples.

TABLE 7.1: Coating Materials

Type and Specification	
MRC (120N)*	One-pack air drying PU paint 2 to 3 mins drying time at 20°C Flash point: below 32°C low flash Thinners: FB/2/141* Cleaners: Acetone, MEK or standard cellulose thinners
MRC (200)*	Two-pack PU paint Viscosity: 22 to 38 secs (Ford B4 St at 20°C) Ratio of Components: 9 vols. Component A (i.e. polyol mixture) 1 vol. Reactor (i.e. isocyanate mixture) Drying time: Approximately 5 mins at 20°C Thinners/Cleaner: 8/333* Flash point: Below 22°C Pot life: 3 working hours

Table 7.1 (continued)

Type and Specification	
MRC (600 S/R)*	<p>One-pack self-releasing PU barrier coating</p> <p>Supply: 2 volumes MRC (600) type lacquer 1 volume MRC (600) thinner</p> <p>Viscosity: (Before thinning) 30/32 secs (Ford B4 St at 20°C) (After thinning) 22/24 secs (Ford B4 St at 20°C)</p> <p>Drying time: Approximately 20/30 secs at mould temperature of 40°C</p> <p>Cleaner: 4031-025*</p> <p>Flash point: -2°C</p>
X-225/C2885+	<p>This is an 8% solids solution of a vinyl chloride, vinyl acetate, vinyl alcohol terpolymer in methyl isobutyl ketone and 1,1,1-trichloroethane.</p>
X-220/C2075/C770+	<p>X-220 is a hydroxy terminated acrylic system containing a di-functional polyester. The solids are 10% in xylene, methyl isobutyl ketone and 1,1,1-trichloroethane.</p> <p>The above system is reacted with C770, an isocyanate terminated prepolymer. The ratio is 100:7.</p>
X-226/C2885+	<p>This is a fully reacted aliphatic isocyanate based polyurethane polymer in xylene, methyl isobutyl ketone, 1,1,1-trichloroethane and isopropanol. The solid is 4%.</p>

\* Manufactured by MacPherson Coatings Limited, London

+ Manufactured by Compounding Ingredients Limited, Blackburn

## 7.2 MATERIALS AND EQUIPMENT

### 7.2.1 Coating Materials

A number of one and two pack PU based coatings manufactured and supplied by MacPherson Coatings Limited (Barking), and Compounding Ingredients Limited (Blackburn) were used throughout this work. These are conventional commercial systems. These coating types and specifications are shown in Table 7.1.

### 7.2.2 Materials and Formulations for PU-RIM Moulding

The specification and processing data for the isocyanate and polyol components supplied by Baxenden Chemical Company (Accrington), and used for polyurethane RIM production in this research are shown in Table 7.2.

TABLE 7.2: PU-RIM Material and Processing Data<sup>/</sup>

---

<u>Specification</u>	
Hydroxyl number:	448 )
Water content (%):	0.65 ) Polyol component
Viscosity at 25°C (mPas):	4500 )
Processing formulation:	Polyol: (HE-DO-60-004)* 100 pbw
	Blowing agent: TCFM 6 to 10 pbw
	Isocyanate: Polymeric MDI
	(Desmodur 44V10B)* 129 pbw
<u>Processing Data</u>	
Cream time (sec):	16
Gel time (sec):	32
Temperature of the raw materials (°C)	20 to 25
Mould temperature (°C):	45 to 75
Density, free rise with 10 pbw TCFM blowing agent (kg/m <sup>3</sup> ):	65
Density of self-skinned foam (kg/m <sup>3</sup> ):	300 to 700
Demould time for 10 mm wall thickness (min):	4 to 6

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<sup>/</sup> Data from the manufacturer

\* Manufacturer's designated reference.

### 7.2.3 Materials for PU Foams Processing

The properties and processing data for materials supplied by MacPherson Polymers Ltd (Stockport), and used in the production of self-skinning, semi-flexible and rigid polyurethane mouldings in this research are shown in Table 7.3.

TABLE 7.3: PU Foam Materials and Specifications<sup>/</sup>

	Semi-flexible Polyurethane	Rigid Polyure- thane
<u>Isocyanate system</u>		
Product type and reference:	Polymeric MDI (2875/003)	Polymeric MDI (2875/000)
-NCO value (%):	27.5 to 29.5	29.0 to 30.5
Appearance:	Clear dark brown liquid	Clear amber liquid
Specific gravity at 25°C:	1.22	1.20
Viscosity at 25°C (mPas):	170 to 230	200 to 250
Recommended storage temperature (°C):	5 to 25	5 to 25
<u>Polyol System</u>		
Product type and reference:	Polyether polyol (SR711 pigmented)	Polyether polyol (pigmented)
Appearance:	Brown liquid	Black liquid
Functionality/equivalent weight:	3+/1500 to 2000	4+/1000 to 1500
<u>Blowing Agent</u>		
	TCFM	TCFM
Typical mixing ratios, Polyol/blowing agent/ isocyanate (g):	104/15/41	68/12/76
Mould temperature (°C):	45 to 60	40 to 60

<sup>/</sup> Data from the manufacturer



#### 7.2.4 Polyester Materials

##### a) Polyester Liquid Resins

Three chemically different polyester resins, supplied by Scott Bader Company Limited (Wellingborough), were used as the basis materials for formulation and processing applications in this research. The resins properties are listed in Table 7.4.

TABLE 7.4: Typical Properties of Liquid Crystic Polyester Resins<sup>/</sup>

	Crystic 196*	Crystic 198*	Crystic 199*
Chemical type	Orthophthalic	Orthophthalic	Isophthalic
Appearance	Light straw	Light straw	Straw
Viscosity at 25°C (Poise)	9	5.5	6
Specific gravity at 25°C	1.12	1.11	1.10
Acid value (mg KOH/g)	21	24	26
Volatile content (%)	33	36	38
Stability in the dark at 20°C (months)	6	6	12
Gel time at 25°C (mins) using: Crystic polyester 100 pbw Catalyst Paste H 4 pbw Accelerator E 4 Pbw	8	12	16

Test methods as in BS 2782: 1976

<sup>/</sup> Data from the manufacturer

\* Curing agent was presumed to be styrene (at normal stoichiometric amounts)

##### b) Catalysts

Catalysts for use with polyester resins are usually organic peroxides. Since pure catalysts can be unstable, they are supplied as a paste or liquid dispersion in a plasticiser, or as a powder in an inert filler. A 50% solution of medium reactivity methyl ethyl ketone peroxide for cold curing formulations, manufactured and supplied by Scott Bader Ltd under the name catalyst M was used in this work.

### c) Accelerators

Many chemical compounds will act as accelerators for polyester resins, but those most commonly used are based on cobalt soaps or tertiary amines.

A solution of cobalt soap (0.4% cobalt) with the storage life approximately six months in the dark at 20°C and supplied by Scott Bader Ltd designated as accelerator E was used in this work.

### 7.2.5 Materials for Coated PU Spray Foam Production

The substrate material used was "ISOFOAM SS-0658", a two component polyurethane foam system designed for spray applications, supplied by IPI, USA. The polymeric isocyanate component, "SS-0658A", contained reactive isocyanate groups. The polyol component "SS-0658B", was a combination of polyols, catalysts and TCFM. A more reactive version of polyol systems was "SS-0658EM". The raw materials specification and typical physical properties of ISOFOAM systems are shown in Table 7.5.

TABLE 7.5: Typical Properties of ISOFOAM Substrate Materials<sup>†</sup>

<u>Specification</u>	SS-0658A	SS-0658B
Viscosity at 20°C (Poise):	3	6.5
Specific gravity at 20°C:	1.23	1.13
Mixing ratio (Pbv):	100	100
Spray reactivity, tack free (secs):		
SS-0858B		7
SS-0858EM		4
<u>Physical Properties</u>	ISOFOAM SS-0658	
Density, core (kg/m <sup>3</sup> ):	40	
Closed cell content (%):	>90	
Humid ageing at 70°C, 100% RH,		
Volume change (%):		
1 day	+4	
7 days	+7	
14 days	+10	
28 days	+12	

Test methods as in ASTM: D-16, D-21, D-28

<sup>†</sup> Data from the manufacturer

The coating material was "FUTURA-THANE 5000", a 100% solids, two component, fast curing urethane based elastomer manufactured by Futura Coatings Inc (New Jersey), USA. The physical and performance properties of Futura coating used in this research are shown in Table 7.6.

TABLE 7.6: Typical Properties of FUTURA-THANE 5000 Coating<sup>†</sup>

<u>Specification</u>	Component A	Component B
Mixing ratio (Pbv)	1	1
Solids (mixed) (%):		
by weight		100%
by volume		100%
Storage stability (months):	6	8
<u>Performance Properties</u>	FUTURA-THANE 5000	
Hardness (Shore A):		80 $\pm$ 5
Water absorption, 3 days at 25°C (%):		<1.5

Test methods as in ASTM: D-1475, D-1353

<sup>†</sup> Data from the manufacturer.

#### 7.2.6 Mould Release Agent

The mould release agents MACWAX (RL47) and MACSIL (RL110) manufactured and supplied by MacPherson Coatings Limited were used in this research. MACWAX is a high-boiling hydrocarbon wax in aerosol form especially formulated for use at moderate temperatures in areas where a silicone release agent is not desired. MACWAX is particularly effective for the release of microcellular and integral-skin foams.

MACSIL is a silicone aerosol release agent. It has a special formulation enabling it to form a more even coating on the mould surface than other silicone compounds, resulting in the use of less

materials to achieve satisfactory release. The specifications of both types are shown in Table 7.7.

TABLE 7.7: Mould Release Agents Specifications<sup>/</sup>

	MACWAX (RL47)	MACSIL (RL110)
Type:	Wax blend	Silicone blend
Solids (%):	2.4	3
Specific gravity:	0.937	0.990
Solvent:	TCFM/aliphatics	
Drying time at 15°C (sec)	50	50
Mould types:	All types of mould surfaces	
Flammability (°C):	>32	>32
Health and safety (TLV):	1000 ppm for TCFM 400 ppm for aliphatics	

<sup>/</sup> Data from the manufacturer.

### 7.2.7 Spraying Equipment

Two types of spray guns suitable for the type and dimensions of mouldings studied in this research were used. An "Aerograph Sprite Airbrush" manufactured by the Devilbiss Company Limited (Bournemouth) was used for smaller mouldings. The Sprite is based on the design of Aerograph "Super 63" and is a gravity feed airbrush incorporating a 5 ml capacity cup and requires 0.2 cfm of compressed air at 30 psi. At a later stage of this research, a Sprite Major Airbrush, having a higher capacity, double-action suction feed, model was also used. Similar to the Sprite model, this version also operated from an air compressor or propellant canister, requiring 0.29 cfm of air at 30 psi.

The principal design features of the Sprite airbrush shown in Figure 7.1 include:

1. twin-action trigger for retractable needle and air valve control and also precision manufactured air cap and nozzle assembly gives infinitely variable spray pattern and eliminates paint spatter;
2. adjustable tubular cam ensures positive needle control and pre-set pattern width;
3. plastic paint bowl and glass container are used for quick paint change and ease of cleaning.

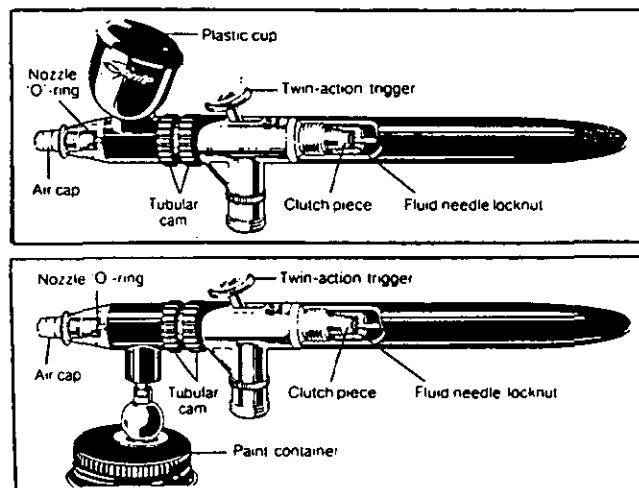


FIGURE 7.1: The Sprite Airbrush

The spray guns used for coating the larger mouldings (especially PU-RIM mouldings) were of the types "MGL" and "Hobbit", both manufactured by the Devilbiss Company. For proper painting applications, the gun was held perpendicular to the spray surface at all times. It was shown in practice that arcing the gun during spraying resulted in an uneven coat of paint (Figure 7.2).

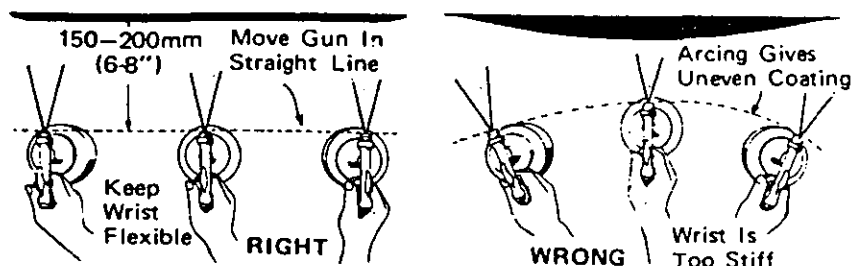


FIGURE 7.2: Spraying Action

The manufacturer's recommended spraying distance between 150 to 200 mm was practised throughout the spraying.

#### 7.2.8 Health and Safety Considerations

Isocyanates, like many other reactive chemicals, can be hazardous if handled incorrectly. However, in recent years, due to their increased use in various industries producing PU products, more vigilant health and safety precautions, control limits and threshold limit values (TLV) have been recommended. These precautions are shown in Appendix 2.

### 7.3 SAMPLE PREPARATION

#### 7.3.1 PU-RIM Processing and Sample Preparation

The processing was carried out using a high pressure RIM machine: Battenfeld SH-40-40, supplied and demonstrated by the Baxenden Chemical Company, Accrington, UK. A schematic diagram of the RIM machine used is shown in Figure 7.3.

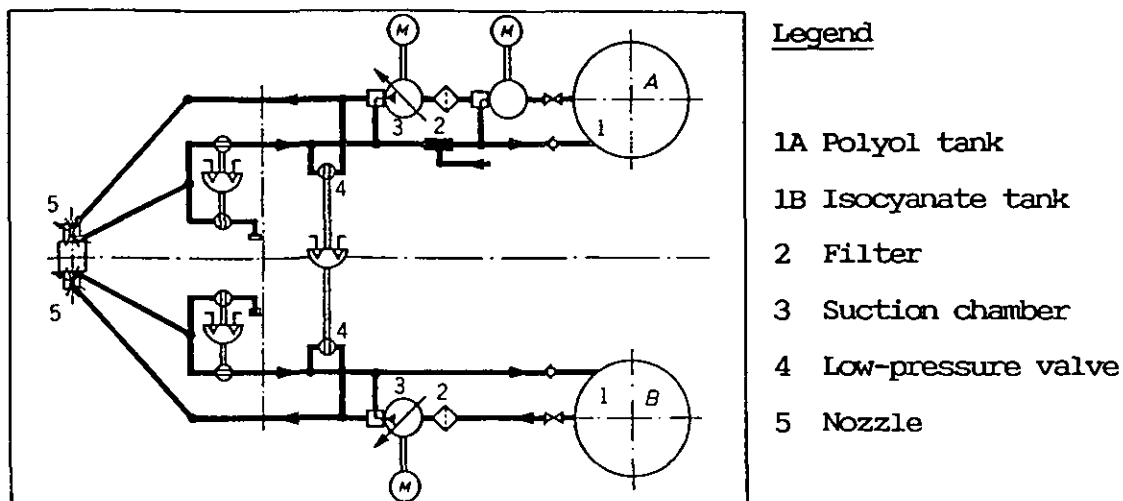


FIGURE 7.3: Schematic Diagram of RIM Machine

The isocyanate and polyol components were forced out of the pressurised tanks through filters into the suction chambers of the pumps. From these chambers, the material was conveyed by the infinitely adjustable high-pressure pumps within the machine into a low pressure circulation. After a foaming programme had been initiated, the high-pressure circulation was started by closing the low pressure valves. The components then circulated via an adjustable nozzle through the mixing head and back into the tanks. This circulation ensured exact temperature control in the material. While the high-pressure circulation was proceeding, the reaction injection process was initiated by a change-over in the mixing head. At the end of the set foaming time, the system was changed back to high-pressure circulation. The metering units were then switched off. The reactants were allowed to form a partially cured, solid PU after which it was demoulded. A number of PU mouldings for PMC application were made. All samples were allowed a minimum of 7 days to reach a state of full cure.

For IMC PU mouldings, the mould was cleaned and release agent MACWAX was thoroughly applied to inner surfaces. The paint system was then applied to the warmed interior surfaces of the mould and allowed to dry. RIM inserts were incorporated, the mould then closed and liquid reactants were injected in the same manner as described above. A minimum of eight IMC mouldings for each type of paint were produced.

### 7.3.2 PU Foams Sample Preparation

For both semi-flexible and rigid processes, the isocyanate and polyol systems were obtained as ready formulated raw materials (i.e. catalysts, foam stabilisers, pigments, and other additives, had already been introduced). The moulding preparation was carried out by a hand-casting technique.

The cleaned and solvent wiped (i.e. trichloroethylene treated) open mould of dimensions 162 x 118 x 14 mm was left in the oven at 80°C for about 10 min. Once the mould was removed from the oven, the release agent was then applied evenly and sufficiently to the warmed mould interior and left to dry. Meanwhile, the polyol and blowing agent were mixed and stirred using paddle type stirrer for about 30 sec at 1500 rpm. The isocyanate part was then added to this mixture and stirred for another 10 sec at 1500 rpm. This mixture was quickly poured into an already prepared mould which was closed rapidly and clamped under pressure. The clamped mould was transferred to an oven at a pre-set constant average temperature and kept throughout the time necessary for the component to cure. Once the moulding was removed from the mould, the mould was cleaned and the above procedure was repeated.



For PMC application, the mouldings were carefully solvent wiped and inspected (see Section 3.4.1). They were then dried for about 10 min in the oven at 60°C. The mouldings were transferred to the spray booth where a number of coated mouldings using one- and two-pack PU coatings (see Section 7.2.1) were produced.

For IMC application, as soon as the release agent was flashed-off, the paint system was applied to the inner mould using a spray gun (40 to 60 psi) under the spray booth. Release agent application was not necessary with the self-releasing barrier coats (e.g. MRC (600 SR)). However, in order to avoid any possibility of sticking, an occasional coating of release agent acted as a safety barrier. Once the thinners in the paint had flashed-off, the polyol/isocyanate mixture was added and the same procedure outlined above for uncoated mouldings was repeated.

### **7.3.3 Polyesters Formulations and Sample Preparation**

Crystic polyesters are normally used in both hot and cold curing formulations. Crystic 196 is suitable for cold curing only. Therefore the cold curing route was chosen for all three polyester resins in order to have a uniform system throughout the moulding process.

The formulation used for all Crystic resins was based on 100 pbw polyester resin, 2 pbw catalyst M and 1 to 4 pbw accelerator E. Polyester resins were initially allowed to attain room temperature before being formulated for use. The catalyst was then thoroughly dispersed in the resin. The catalysed resin without accelerator remained usable at room temperature (i.e. about 20°C) for approximately 8 hours. Shortly before use the correct amount of accelerator E was added and stirred into the catalysed resin.

When accelerator E is added to resin which had been catalysed for several hours, the gel time would be shorter than that for freshly catalysed resin. It must be noted that catalyst and accelerator should not be mixed directly together since they can react with explosive violence.

The amount of accelerator E controls the gel time of the resin formulations. This can be approximately determined from Table 7.8.

TABLE 7.8: The Effect of Accelerator E on Gel Time of Resins<sup>/</sup>

	Crystic 196				Crystic 198				Crystic 199			
Parts of Accelerator E to 100 parts of catalysed polyester	1.0	2.0	3.0	4.0	1.0	2.0	3.0	4.0	1.0	2.0	3.0	4.0
Gel time at 15°C (mins)	25	14	11	10	51	32	24	19				
Gel time at 20°C (mins)	14	10	8	7	30	20	16	12	70	52	38	30
Gel time at 25°C (mins)	11	7	6	5	19	13	10	7				

<sup>/</sup> Data from the manufacturer.

Polyester resins formulated outlined above were then poured into open aluminium moulds (200 x 200 x 20 mm) already pretreated with release agent and kept at a temperature of 20° to 25°C. Satisfactory polyester mouldings for PMC applications could be made by curing at room temperature (20°C). However it was realised that for having optimum mechanical properties, the mouldings should be post-cured according to their requirements.

After release from the moulds, polyester C196 and C198 mouldings were allowed to mature for 24 hours at room temperature. They were then post-cured for a minimum of three hours at 80°C, although a longer period at a lower temperature gave almost the same result. It is worth noting that post-cure was most effective when it was carried out immediately after the 24 hour maturing period.

Following the manufacturer's recommendation, polyester C199 mouldings were cured at room temperature for several days, and then post-cured. The post-curing temperature was built up in increments of 20°C. A minimum of 4 hours post-curing time at each 20°C increase was carried out.

For IMC polyester mouldings, after the paint systems applied to released moulds were allowed to flash-off, the formulation and processing of resins were followed in the same manner as that for uncoated mouldings.

#### 7.3.4 Coated PU Spray Foam Preparation

The coated PU products especially prepared for this research were made using the substrate and coating materials (see Section 7.2.5) at Gusmer Corporation, New Jersey.

The application of coating to substrate was carried out at different times and under various environmental conditions (Table 7.9), so that the effect of these variables on adhesion properties of coated foams could be studied.

TABLE 7.9: Various Coated PU Spray Foam Combinations

Sample No	Time and condition after which coating was applied
1	+ 30 sec
2	+ 30 min
3	+ 45 min
4	+ 60 min
5	+ 24 hour (outdoor)
6	+ 48 hour (indoor)
7	+ 3 day (indoor) + 3 day (outdoor)
8	+ 20 day (indoor) + 3 day (outdoor)
Indoor: 18°C, 60% RH	
Outdoor: 27°C ± 5°C, 80 ± 10% RH*	

\* Typical New Jersey July conditions

## CHAPTER 8

### SURFACE ANALYSIS TECHNIQUES

#### 8.1 INTRODUCTION

Physical and chemical information (including thermodynamic, compositional, chemical state and molecular bonding) about the outermost atomic layers of solid surfaces provides some useful data enriching the understanding of a number of surface process phenomena such as adhesion, wetting and interfacial bonding.

The surface analytical techniques studied in this Chapter are broadly divided into two main groups: physical and chemical. First, the methods measuring the physical properties (i.e. thermodynamic, wettability and surface tension measurements) of surfaces are reviewed. This is followed by methods of measurement of contact angle, its experimental procedure and a report of its results and discussion. A new technique for measuring the thermodynamic parameters of polymeric surfaces is also presented. Second, some of the most important techniques, currently available, capable of determining chemical compositions of the surface layer are reported. Their application and limitations in the polymer field with their especial relevance to this research are reviewed. The results and discussion of chemical techniques are then reviewed.

#### 8.2 SURFACE ANALYSIS: PHYSICAL TECHNIQUES

Considerable effort has been devoted to developing surface analysis techniques to provide useful information on physical properties of surfaces.

Thermodynamic parameters of substrates and their application to the wettability and adhesion/interfacial bonding is of prime importance in this research (see Chapter 5).

The contact angle data may be used to quantify the wetting behaviour of each substrate in order to show its connection with the adhesion of different coatings to various substrates.

#### 8.2.1 Methods of Measurement of Contact Angle ( $\theta$ )

The direct and indirect methods for obtaining surface tension of solids have already been reviewed (see Section 5.7). The method of measuring contact angle  $\theta$  (i.e. an indirect method for obtaining  $\gamma_s$ ) is the most widely used technique and has been fully reviewed in many studies (see Section 5.7.1.1) [14,247,252,273,301].

The most common methods of measuring  $\theta$  for a drop of liquid resting on a flat surface of the solid substrate include projecting the drop profile on to a screen, photographing the drop profile, determining the angle at which light from a point source is reflected from the drop surface at the point of contact and the direct observation of the drop through a horizontal microscope fitted with a goniometer eyepiece. The latter method of direct "sessile drop" has been used in this research and will be reviewed here.

#### 8.2.2 Experimental Procedure

The contact angles of sessile drops resting on the flat solid substrates were measured directly with a goniometer eyepiece equipped with crosswires mounted on a horizontal microscope (see Section 5.4). For all substrate surfaces the following procedure was used: the specimen surface was allowed to equilibrate with the closed

surrounding in a controlled temperature ( $20 \pm 1^{\circ}\text{C}$ ) and relative humidity of  $50 \pm 5\%$  prior to any measurement. By doing so, unaccepted changes in the testing conditions were avoided and the possibility of any contamination was reduced.

Initially the eyepiece of the microscope was positioned in such a way that crosswires were in agreement with the goniometer. Prior to each test, the adjustable platform equipped with a spirit level was adjusted until the test surface was horizontal. A drop of liquid was then carefully dispensed by the needle from a syringe (i.e. capacity = 0.5 ml and graduated to  $10^{-2}$  ml) to the test surface. The syringe was fixed vertically on a stand and the needle tip remained in the drop during the measurements to avoid any vibration or distortion of the drop affecting the result. The needle tip was cut level so that the drop periphery could be advanced or receded at a constant rate, radially from the tip. The advancing contact angles were used in this research and were measured by increasing the volume of drop in small increments. The volume of drop was always maintained between 0.01 to 0.05 ml. No effect of drop volume on the contact angle was observed within these limits. The tube attached to the eyepiece was then rotated until the crosswires formed a tangent to the drop and hence allowed the contact angle to be measured from the position of the pointer. The surface tension of testing liquids used in this research have been reported in many articles [114,247,250,252]. The surface test fluids (inks) were manufactured by Sherman Treaters Ltd (UK) with a wide range of  $\gamma_{LV}$  values. However, the surface tension of all testing liquids used in this research were measured and rechecked using a ring balance tensiometer at different times during the experimental work.

Each reported  $\theta$  value is the average of a minimum of ten and a maximum of fifteen, separate measurements made on different places on a test solid specimen. The variation between contact angle measurements for a given system (i.e. a testing liquid on a substrate) was generally within  $\pm 1$  to  $\pm 2^\circ$ . Some difficulty, however, was encountered with PU foam substrates (especially with ISOFOAM-0658), mainly because of their surface character which resulted in the values of the contact angle being less than the advancing angle. To overcome this effect the sample was placed in the field of the goniometer as precisely as possible so that a minimum of manipulation was necessary to bring the liquid drop into position to read the angle. By doing so, a measurement could be taken within 6 seconds after the drop was placed and hence the adverse effect was minimised.

At a later stage of this research the contact angle measurements were carried out with an instrumented contact angle meter (Krüss G40) and its results showed close similarity with the results of a horizontal microscope.

### 8.2.3 Initial Investigation

Due to some comprehensive and collected information [14,114,250,252,276,280] on the wettability of polyethylene (PE) and polytetrafluoroethylene (PTFE) surfaces, the two polymers were chosen as initial substrates for contact angle measurements. Using these materials as references, the equipment and technique was developed. The contact angle results for PE and PTFE substrates are presented in Table 8.1 and Figure 8.1.

The relationship between  $\cos\theta$  and surface tension of testing liquids,  $\gamma_{LV}$ , showed a good agreement with some previously obtained data by



Testing Liquids	$\gamma_{LV}$ $\text{mN.m}^{-1}$	PE		PTFE	
		$\theta_{ave}$ (degree)	$\cos \theta$	$\theta_{ave}$ (degree)	$\cos \theta$
Water	72.8	96	-0.104	107	-0.29
Glycerol	63.4	79	0.19	99	-0.16
Formamide	58.2	76	0.24	92	-0.035
Methylene iodide	50.8	52	0.615	79	0.19
Surface )	50.0	49	0.656	80	0.17
test fluids )	47.0	43	0.73	76	0.24
(inks)	44.0	40	0.766	70	0.34
	41.0	37	0.798	65	0.42
	38.0	26	0.898	62	0.47
	35.0	15	0.965	53	0.6

TABLE 8.1: Contact Angle Measurements for PE and PTFE Substrates

Source of reference	Critical surface tension $\gamma_C, \text{mN.m}^{-1}$	Equation of the linear relationship between $\cos \theta \text{ v } \gamma_{LV}$	Correlation coefficient
<u>PE:</u>			
After Ref 302	37	$y = 2.26 - 3.36 e^{-2x}$	0.977
After Ref 303	34	$y = 1.94 - 2.76 e^{-2x}$	0.970
After Ref 304	31.5	$y = 1.84 - 2.71 e^{-2x}$	0.938
This research	35	$y = 2.02 - 2.90 e^{-2x}$	0.973
<u>PTFE:</u>			
After Ref 252	18	$y = 1.59 - 3.28 e^{-2x}$	0.989
After Ref 305	20	$y = 1.25 - 2.18 e^{-2x}$	0.970
This research	17	$y = 1.38 - 2.38 e^{-2x}$	0.986

TABLE 8.2: A Comparison of Various Contact Angle Results for PE and PTFE Surfaces

others [252,302-305] and shown in Figures 8.2 and 8.3. A comparison of these results is illustrated in Table 8.2 and Figure 8.4.

Critical surface tension,  $\gamma_C$ , values for PE and PTFE surfaces as obtained by the best fit linear relationship gives  $\gamma_C$  between 31.5 to 37 mN.m<sup>-1</sup> and 17 to 20 mN.m<sup>-1</sup> respectively. The range of  $\gamma_C$  values for PE is slightly larger than corresponding values reported by Zisman et al and others whereas for PTFE surfaces the  $\gamma_C$  values obtained are within the range of values reported by many authors [14,146,247,280].

It seems reasonable to assume that a rectilinear band engulfing all the contact angle results reported by various authors on the same substrate would give a better picture than a linear relationship for each case. In Figure 8.4 the rectilinear band produced for PE shows the region where  $\gamma_C$ , probably obtained at various conditions, is most likely to be found.

#### 8.2.4 Contact Angle and Wettability Results

The contact angle results for all the substrates are presented in Tables 8.3 and 8.4 and Figures 8.5 and 8.6.

By applying the contact angle results reported above in a number of surface properties relationships (see Chapter 5), some useful thermodynamic parameters could be calculated. The work of adhesion,  $W_A$ , and the spreading coefficient,  $S_C$ , are shown in Tables 8.3 and 8.4. The other parameters are discussed in the results and discussion sections to follow and further examined in Chapter 12 (see Section 12.2.2). The critical surface tension,  $\gamma_C$ , for all substrates can be found either from the corresponding graphs of  $\cos\theta$  against  $\gamma_{LV}$  (i.e. surface tension of the liquid at  $\cos\theta = 1$ ) or by using the linear

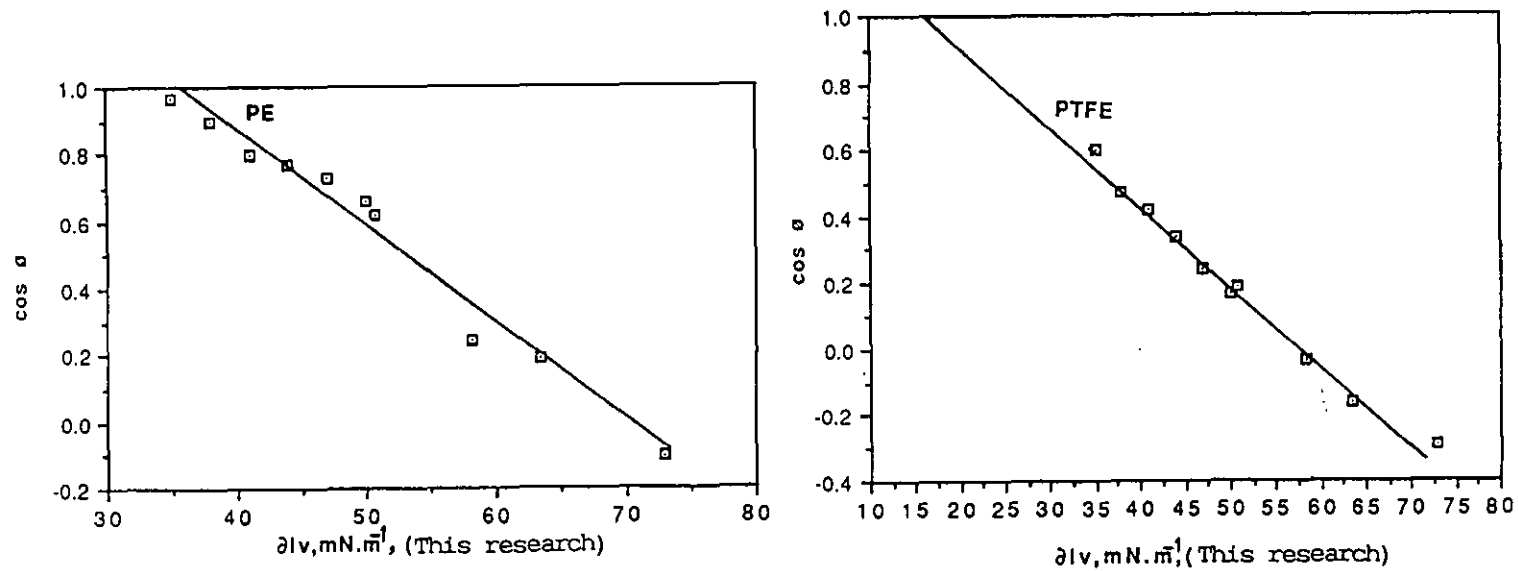


FIGURE 8.1:  $\cos \theta$  v  $\gamma_{LV}$  for PE and PTFE substrates (calibration)

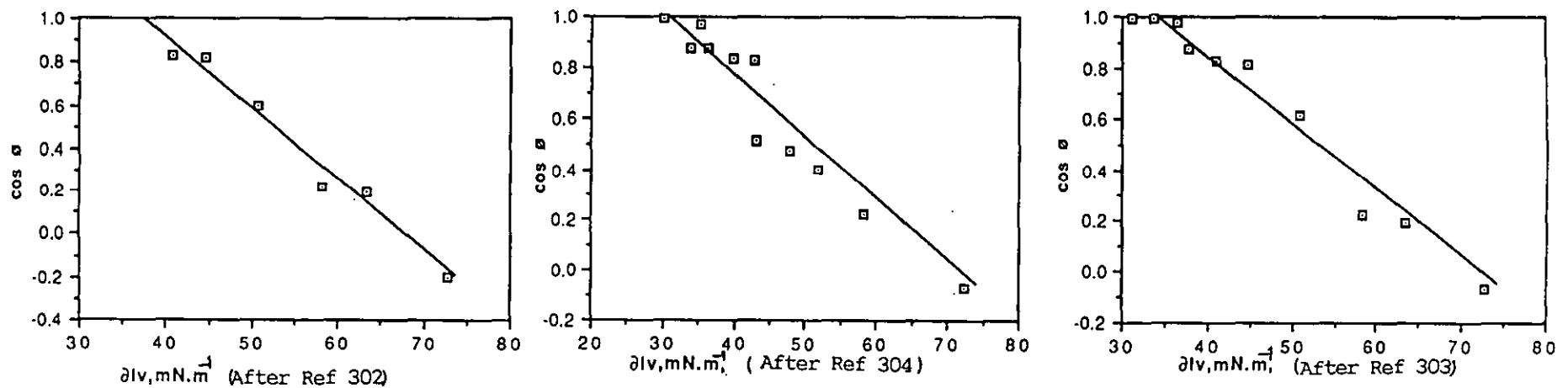


FIGURE 8.2:  $\cos \theta$  v  $\gamma_{LV}$  for PE substrates (data by others)

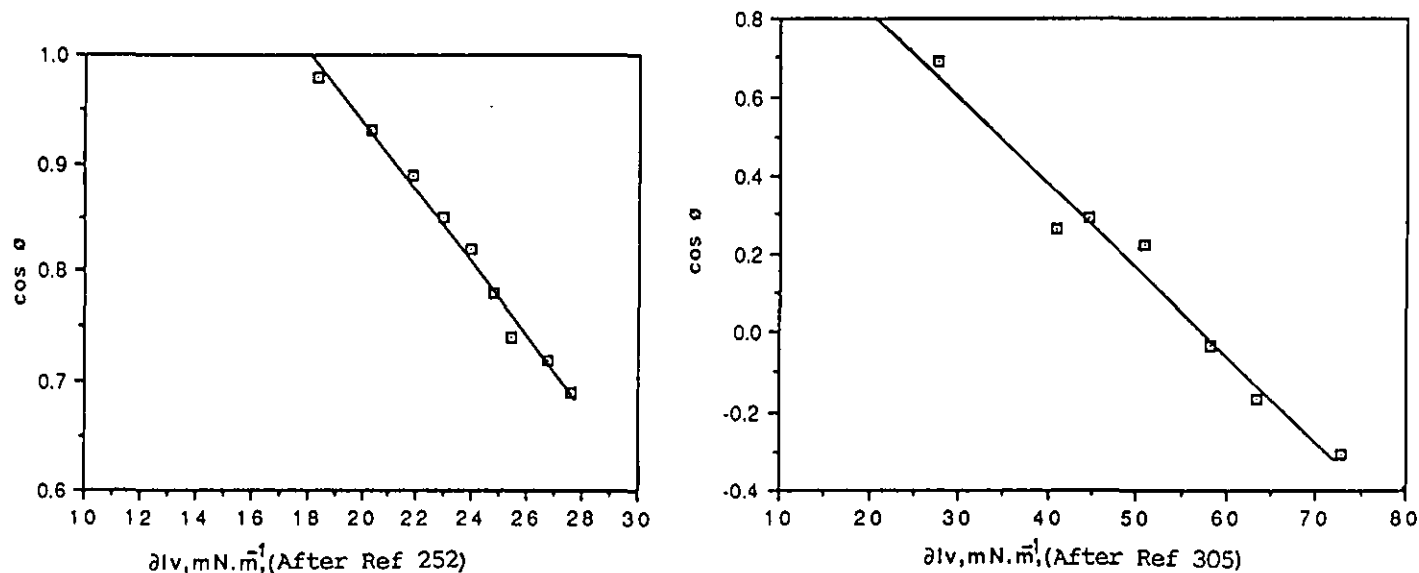


FIGURE 8.3:  $\cos \theta$  v  $\gamma_{LV}$  for PTFE substrates (data by others)

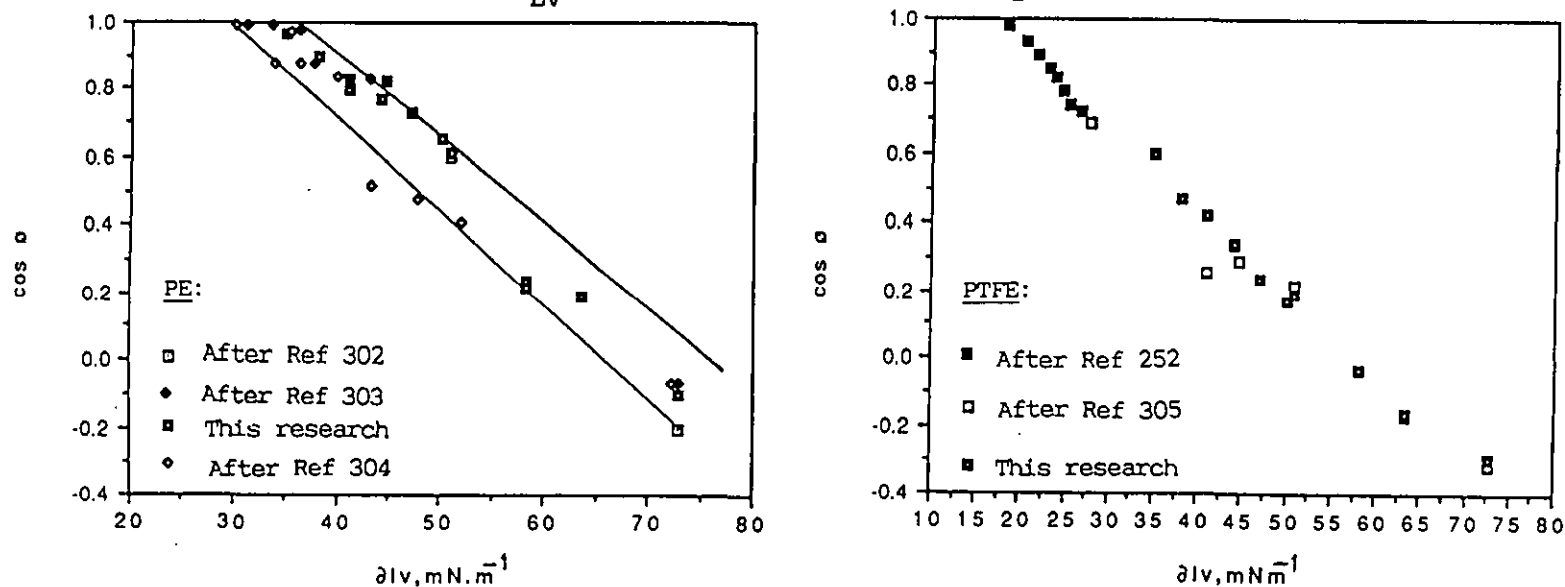


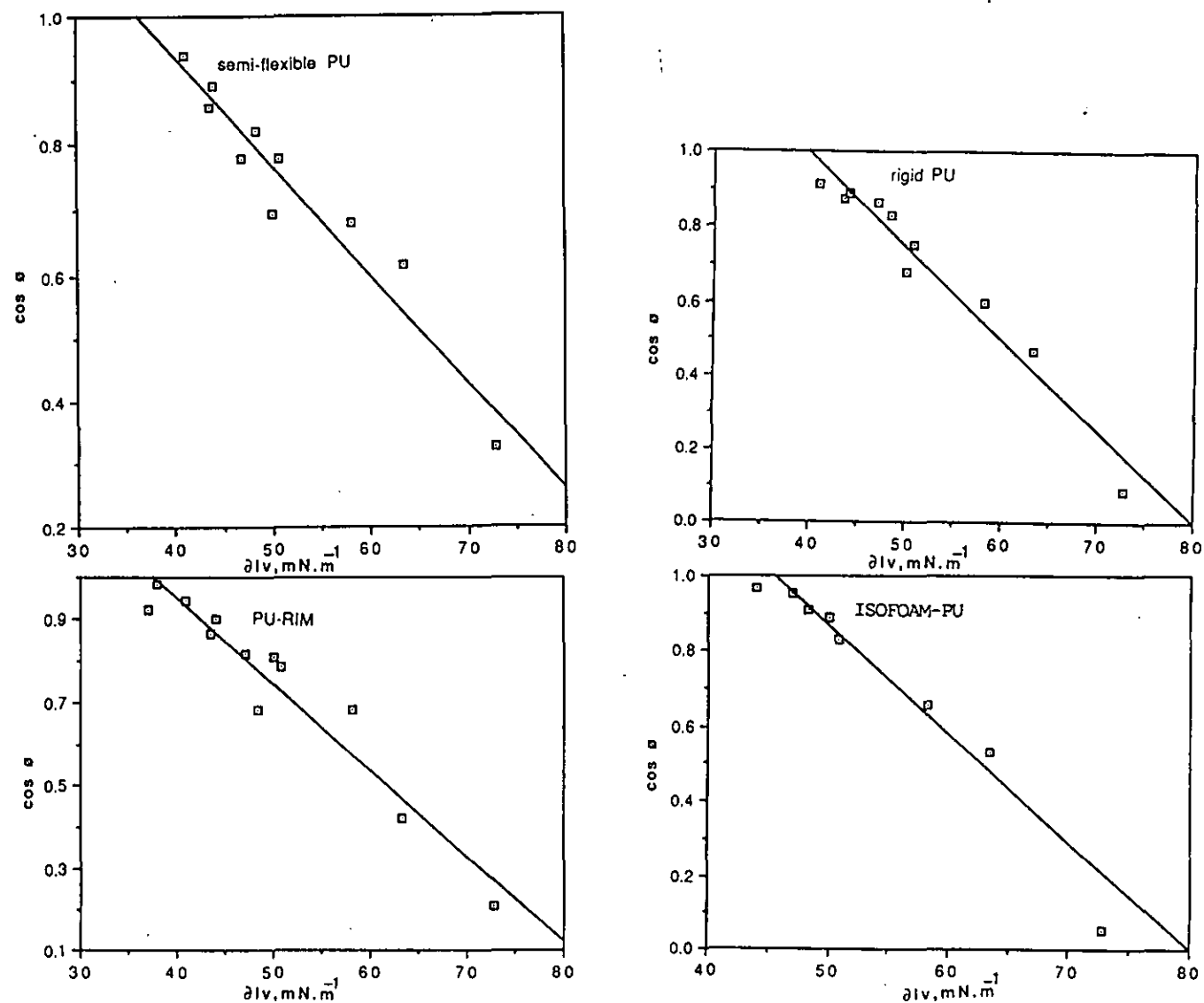
FIGURE 8.4: Comparison of wettability results for PE and PTFE substrates using various data

Wetting Liquids	$\gamma_{LV}$ $\text{mN}\cdot\text{m}^{-1}$	$\theta_{ave}$				$\cos\theta$				$W_A$ $\text{mN}\cdot\text{m}^{-1}$				$S_C$ $\text{mN}\cdot\text{m}^{-1}$			
		Semi- flexible	Rigid	RIM	ISOFOAM	Semi- flexible	Rigid	RIM	ISOFOAM	Semi- flexible	Rigid	RIM	ISOFOAM	Semi- flexible	Rigid	RIM	ISOFOAM
Water	72.8	71	85	78	87	0.325	0.087	0.207	0.052	96.5	79.1	87.9	76.6	-49.1	-66.5	-57.7	-69.0
Ethan-1,2-diol	48.3	35	34	47	25	0.819	0.829	0.681	0.906	87.8	88.3	81.2	92.0	-8.7	-8.2	-15.4	-4.5
DMSO	43.54	31	29	30	-	0.857	0.874	0.866	-	80.8	81.6	81.2	-	-6.2	-5.5	-5.8	-
DMF	37.10	-	-	23	-	-	-	0.920	-	-	-	71.2	-	-	-	-3.0	-
Surface test fluids (inks)	) 50	46	47	36	27	0.694	0.681	0.809	0.891	84.7	84.0	90.4	94.5	-15.3	-15.9	-9.5	-5.4
	) 47	39	30	35	18	0.777	0.866	0.819	0.951	83.5	87.7	85.5	91.7	-10.5	-6.3	-8.5	-2.3
	) 44	27	27	26	15	0.891	0.891	0.898	0.965	83.2	83.2	83.4	86.4	-4.8	-4.8	-4.5	-1.5
	) 41	20	24	19	-	0.939	0.913	0.945	-	79.5	78.4	79.7	-	-2.5	-3.6	-2.3	-
	) 38	-	-	10	-	-	-	0.984	-	-	-	75.4	-	-	-	-0.6	-
Glycerol	63.4	52	62	65	58	0.615	0.469	0.422	0.529	102.4	93.1	90.1	96.9	-24.4	-33.7	-36.6	-29.9
Formamide	58.2	47	53	47	49	0.681	0.601	0.681	0.656	97.8	93.2	97.8	96.4	-18.5	-23.2	-18.6	-20.0
Methylene iodide	50.8	39	41	38	34	0.777	0.754	0.788	0.829	90.3	89.1	90.8	92.9	-11.3	-12.5	-10.8	-8.7

TABLE 8.3: Contact angle measurements for polyurethane substrates

Wetting Liquids	$\gamma_{LV}$ $\text{mNm}^{-1}$	$\theta_{ave}$			$\cos \theta$			$W_A \text{ mNm}^{-1}$			$S_C \text{ mNm}^{-1}$		
		C196	C198	C199	C196	C198	C199	C196	C198	C199	C196	C198	C199
Water	72.8	65	85	93	0.423	0.087	-0.052	103.6	79.1	69.0	-42.0	-66.4	-76.6
Ethan-1,2-diol	48.3	38	51	55	0.788	0.629	0.573	86.4	78.7	76.0	-10.2	-17.9	-20.6
DMSO	43.54	23	38	46	0.920	0.788	0.694	83.6	77.8	73.8	-3.5	-9.2	-13.3
DMF	37.10	21	33	35	0.933	8.838	0.819	71.7	68.2	67.5	-2.5	-6.0	-6.7
Surface test fluids	) 50	33	52	57	0.838	0.615	0.544	91.9	80.8	77.2	-8.1	-19.2	-22.8
	) 47	27	45	52	0.891	0.707	0.615	88.9	80.2	75.9	-5.1	-13.8	-18.0
	) 44	25	40	50	0.906	0.766	0.642	83.9	77.7	72.3	-4.1	-10.3	-15.8
	) 41	22	37	43	0.927	0.798	0.731	79.0	73.7	71.0	-3.0	-8.3	-11.0
	) 38	20	36	41	0.939	0.809	0.754	73.7	68.7	66.7	-2.3	-7.2	-9.3
	) 35	14	32	36	0.970	0.848	0.809	68.9	64.7	63.3	-1.0	-5.3	-6.7

TABLE 8.4: Contact angle measurements for polyester substrates

FIGURE 8.5:  $\cos \theta$  v  $\gamma_{LV}$  for PU substrates

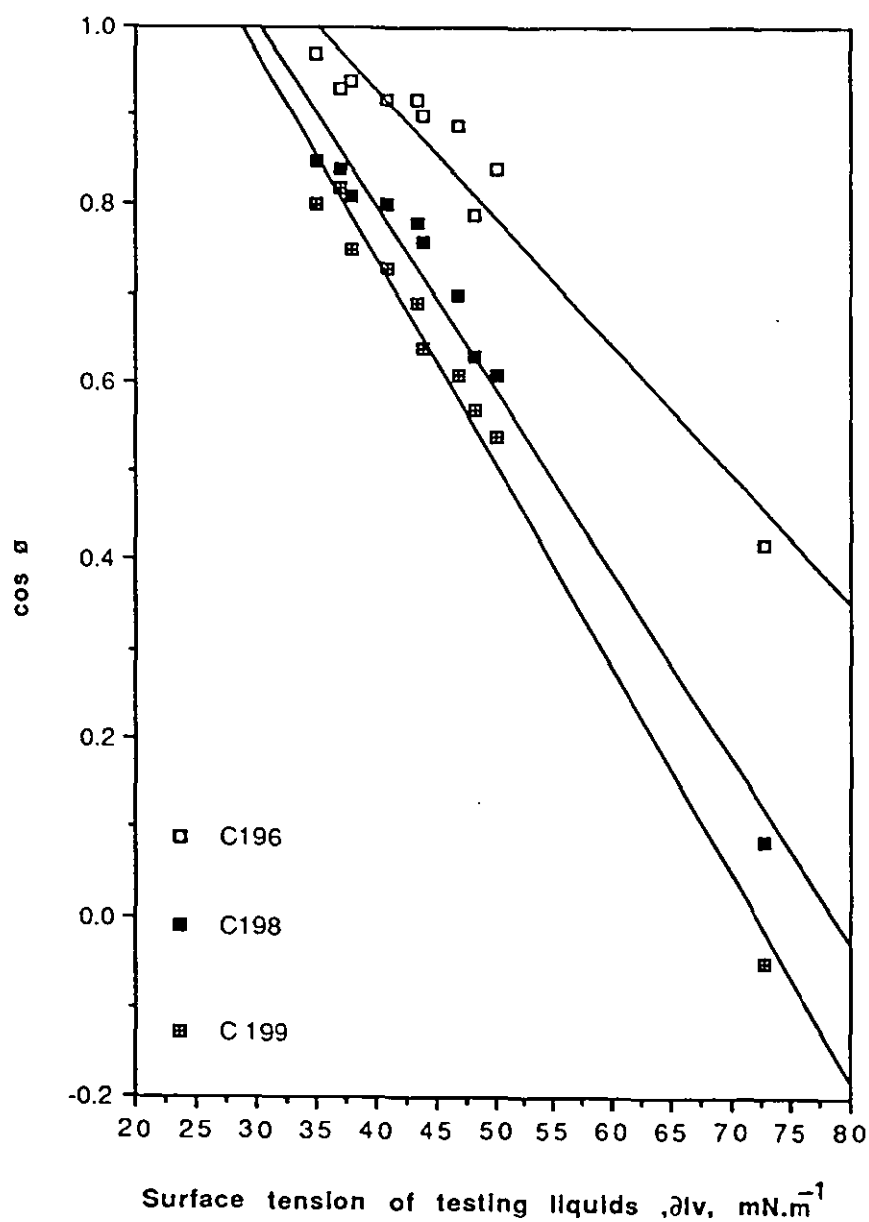


FIGURE 8.6:  $\cos \theta$  v  $\gamma_{LV}$  for polyester substrates



equation for each substrate. The general linear equation of  $y = ax + b$  where  $y$  and  $x$  represent  $\cos \theta$  and  $\gamma_{LV}$  respectively and  $\gamma_C$  for each substrate is shown in Table 8.5.

#### 8.2.5 The Relationship Between Work of Adhesion, $W_A$ , Spreading Coefficient, $S_C$ and the Surface Tension of Testing Liquids, $\gamma_{LV}$

Figures 8.7 and 8.8 show the relationships between  $W_A$ ,  $S_C$  and surface tension of testing liquids for all the substrates. Linear and polynomial (orders 2 to 6) relationships were tried and it was established that a polynomial relationship of order 2 (i.e. a quadratic equation) would hold true best for  $W_A$  and  $S_C$  plots against  $\gamma_{LV}$  for all substrates. The corresponding equations for PU and polyester surfaces are shown in Table 8.6. By comparing the equations for  $W_A$  and  $S_C$  for each substrate and considering the general quadratic equation of  $y = ax^2 + bx + c$ ,  $W_A$  and  $S_C$  can be expressed in the following forms:

$$y = -ax^2 + bx - c \quad (\text{for work of adhesion}) \quad (1)$$

$$y' = -a'x^2 + b'x - c' \quad (\text{for spreading coefficient}) \quad (2)$$

where  $y$  and  $y'$  represent the  $W_A$  and  $S_C$  respectively and  $x$  is  $\gamma_{LV}$  of wetting liquids. A further examination of all the reported equations (see Table 8.6) showed that the corresponding  $W_A$  and  $S_C$  equations for each substrate are identical and that:

$$a \cong a'$$

$$c \cong c'$$

$$b \cong b' + 2$$

As a result the equation for the spreading coefficient may be written as:

$$y' = -ax + (b-2)x - c \text{ (for spreading coefficient)} \quad (3)$$

In effect, the work of cohesion,  $W_C$ , which is the difference between  $W_A$  and  $S_C$  (see Chapter 5) would result from the subtraction of equation (1) from (2):

$$W_C = y' - y = 2x$$

The maximum work of adhesion,  $\text{Max } W_A$ , and the maximum spreading coefficient,  $\text{Max } S_C$ , for each surface can be found by using the corresponding graphs of  $W_A$  and  $S_C$  against  $\gamma_{LV}$ , or alternatively they can be calculated by differentiating the quadratic equations  $y$  or  $y'$  with respect to  $x$  (i.e. the maximum point occurs at  $dy/dx$  (or  $dy'/dx$ ) = 0)

From equation 1:

$$\frac{dy}{dx} = -2ax + b$$

for  $\text{Max } W_A$ :

$$\frac{dy}{dx} = 0$$

$$-2ax + b = 0 \quad x = \frac{b}{2a}$$

From equation (3):

$$\frac{dy'}{dx} = -2ax - b - 2$$

for  $\text{Max } S_C$ :

$$\frac{dy'}{dx} = 0$$

$$-2ax - b - 2 = 0 \quad x = \frac{b+2}{2a}$$

Table 8.7 shows the Max  $W_A$ , Max  $S_C$  and the corresponding  $\gamma_{LV}$  (i.e. at  $x = b/2a$  and  $x = b+2/2a$ ) for PU and polyester substrates.

#### 8.2.6 Surface Tension, $\gamma_S$ , of Polyurethane and Polyester Substrates

Tables 8.8 to 8.12 give the calculated values of  $\gamma_S^d$  and  $\gamma_S^p$ , dispersion and polar components of the surface tension, and also  $\gamma_S$  where  $\gamma_S = \gamma_S^d + \gamma_S^p$ , for polyurethane and polyester substrates according to Wu's harmonic mean method (see 5.7.1.4) and Fowkes-Young geometric mean method (see 5.7.1.5). The testing liquids of known dispersive and polar components used in these experiments are shown in Table 5.3. The contact angles,  $\theta$ , used in the calculations are the average of a minimum of ten readings. In most cases applying a pair of liquids in the harmonic or geometric equation would result in a specific  $\gamma_S$  value for that substrate. The surface tension values calculated for each substrate were then analysed and the unacceptable  $\gamma_S$  (i.e. exceptionally too high or too low) and no real  $\gamma_S$  values (i.e. a negative square root) were discarded. The average  $\gamma_S$  of the acceptable values for all the substrates is reported in Table 8.13.

The critical surface tension,  $\gamma_C$ , for polyurethane and polyester substrates calculated according to the equation of state method (see 5.7.1.6) are shown in Table 8.14. The equation of state plots for all substrates are illustrated in Figures 8.9 and 8.10. Contrary to the type of these plots reported in 5.7.1.6 to be of a curved shape, the results are so scattered that only a locus containing all the points may indicate an area where the maximum  $\gamma_C$  would give a close approximation of the surface tension,  $\gamma_S$ , of that substrate. The  $\gamma_S$  values calculated from these plots are reported in Table 8.13.

Substrate	Linear equation for $\cos \theta \quad v \quad \gamma_{LV}$	Correlation coefficient	$\gamma_C$ $\text{mN.m}^{-1}$
Semi-flexible PU	$y = 1.6149 - 1.6904e^{-2}x$	0.925	36.4
Rigid PU	$y = 2.002 - 2.5152e^{-2}x$	0.953	39.8
RIM-PU	$y = 1.7767 - 2.0703e^{-2}x$	0.923	37.5
ISOFOAM-PU	$y = 2.4167 - 3.1196e^{-2}x$	0.960	45.4
C196	$y = 1.5140 - 1.4462e^{-2}x$	0.940	35.5
C198	$y = 1.6351 - 2.0726e^{-2}x$	0.967	30.6
C199	$y = 1.6749 - 2.3252e^{-2}x$	0.984	29.0

TABLE 8.5: Wettability Equations and Critical Surface Tensions for Different Substrates

Substrate	Max $W_A$ $\text{mN.m}^{-1}$	$\gamma_{LV}$ for Max $W_A$ $\text{mN.m}^{-1}$	Max $S_C$ $\text{mN.m}^{-1}$	$\gamma_{LV}$ for Max $S_C$ $\text{mN.m}^{-1}$
Semi-flexible PU	99.1	67.9	-3.7	35.0
Rigid PU	92.2	57.7	-4.0	38.5
RIM-PU	93.2	60.8	-1.7	34.1
ISOFOAM-PU	97.7	56.5	-2.3	43.4
C196	103.6	72	-1.3	33
C198	84.6	59.6	-3.6	28.6
C199	78.2	56	-3.5	25.7

TABLE 8.7: Maximum Values of  $W_A$  and  $S_C$  for Different Substrates

Substrate	Quadratic Equation for $W_A \text{ v } \gamma_{LV}$	Correlation Coefficient	Quadratic Equation for $S_C \text{ v } \gamma_{LV}$	Correlation Coefficient
Semi-flexible PU	$y = -40.931 + 4.1273x - 3.0400e^{-2}x^2$	0.898	$y = -41.32 + 2.143x - 3.054e^{-2}x^2$	0.966
Rigid PU	$y = -81.276 + 6.0152x - 5.214e^{-2}x^2$	0.846	$y = -81.748 + 4.0335x - 5.2306e^{-2}x^2$	0.989
RIM-PU	$y = -45.202 + 4.5531x - 3.7445e^{-2}x^2$	0.866	$y = -45.523 + 2.5664x - 3.7565e^{-2}x^2$	0.974
ISOFOAM-PU	$y = -146.54 + 8.637x - 7.6367e^{-2}x^2$	0.946	$y = -145.74 + 6.6131x - 7.6189e^{-2}x^2$	0.995
C196	$y = -28.908 + 3.6767x - 2.5507e^{-2}x^2$	0.988	$y = -28.496 + 1.6616x - 2.5376e^{-2}x^2$	0.991
C198	$y = -30.146 + 3.8493x - 3.2287e^{-2}x^2$	0.972	$y = -29.883 + 1.8367x - 3.2155e^{-2}x^2$	0.997
C199	$y = -25.347 + 3.6962x - 3.2969e^{-2}x^2$	0.979	$y = -25.434 + 1.6992x - 3.2994e^{-2}x^2$	0.999

TABLE 8.6: Quadratic equations for  $W_A$  and  $S_C$  for different substrates

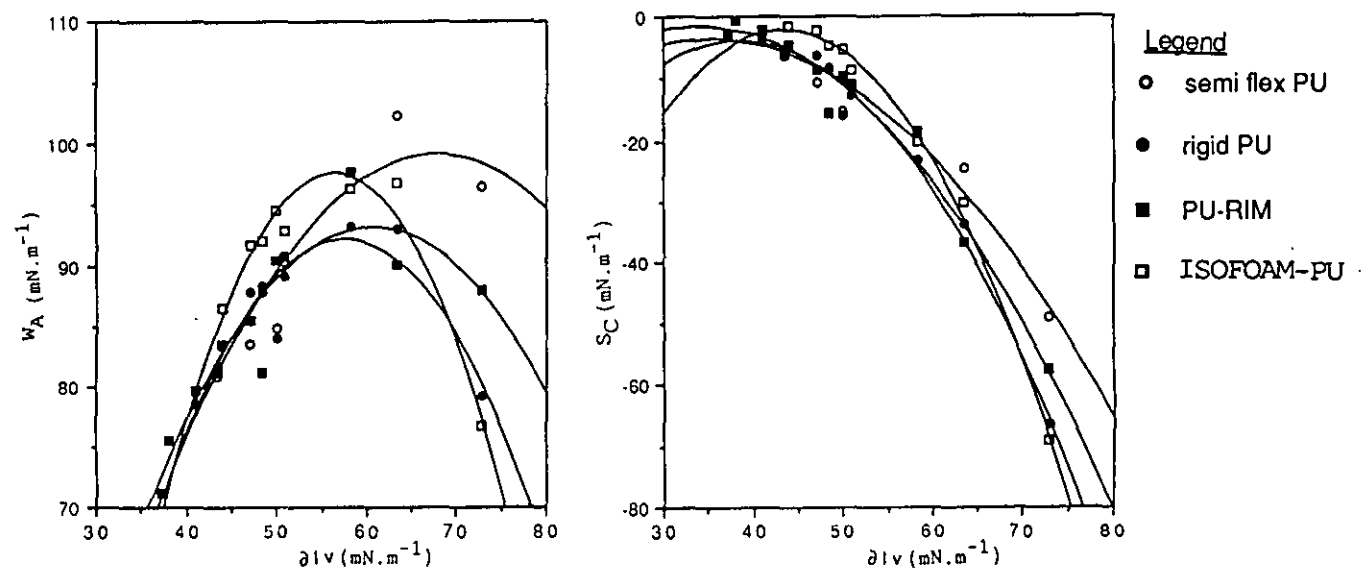


FIGURE 8.7:  $W_A$  and  $S_C$  relationships for PU substrates

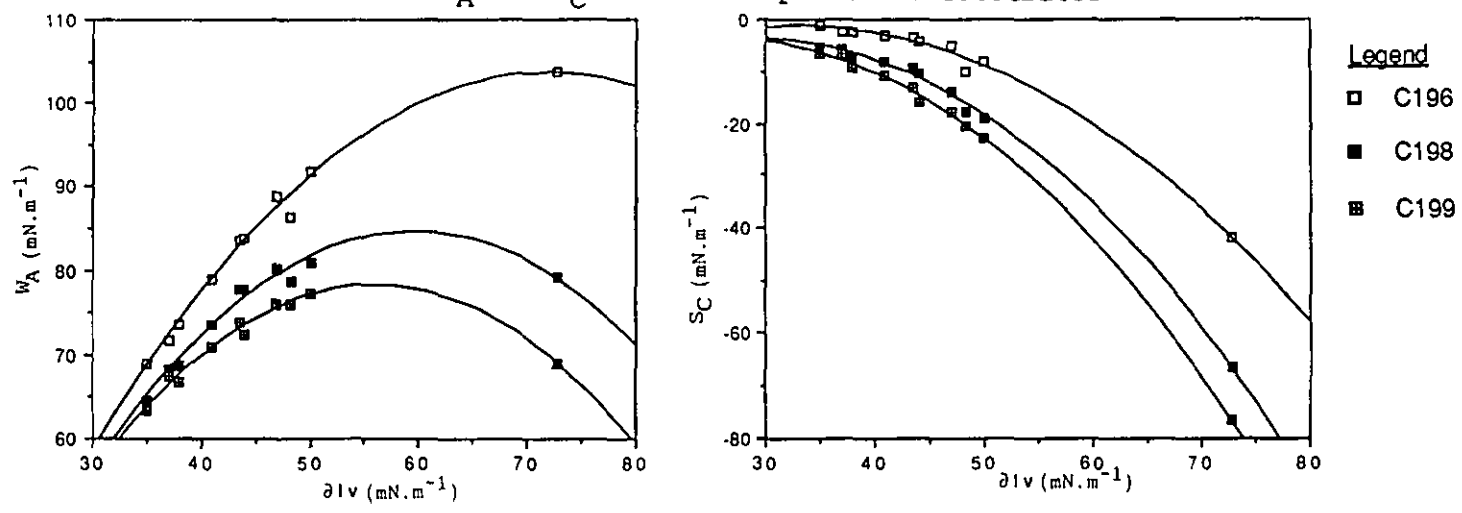


FIGURE 8.8:  $W_A$  and  $S_C$  relationships for polyester substrates

Method	Water Ethan-1 2-diol	Water DMSO	Ethan-1 2-diol DMSO	Glycerol Formamide	Glycerol Methylene iodide	Formamide Methylene iodide
Harmonic	D = 23.1 P = 17.3 $\gamma_s$ = 40.4	D = 24.9 P = 16.6 $\gamma_s$ = 41.5	D = 25.5 P = 14.8 $\gamma_s$ = 40.3	D = 25.0 P = 17.9 $\gamma_s$ = 42.9	D = 37.8 P = 9.4 $\gamma_s$ = 47.2	D = 37.9 P = 7.1 $\gamma_s$ = 45.0
Geometric	D = 16.1 P = 9.4 $\gamma_s$ = 25.5	D = 51.4 P = 11.4 Unaccepted	D = 32.4 P = 17.1 $\gamma_s$ = 49.5	D = 28.4 P = 16.3 $\gamma_s$ = 44.7	D = 1.3 P = 8.6 Unaccepted	D = 9.7 P = 6.8 $\gamma_s$ = 16.5
	Water Glycerol	Water Formamide	Water Methylene iodide	Ethan-1 2-diol Glycerol	Ethan-1 2-diol Formamide	Ethan-1 2-diol Methylene iodide
Harmonic	D = 27.6 P = 15.6 $\gamma_s$ = 43.2	D = 26.5 P = 16.0 $\gamma_s$ = 42.5	D = 37.7 P = 12.9 $\gamma_s$ = 50.6	D = 13.2 P = 39.9 $\gamma_s$ = 53.1	D = 34.0 P = 9.2 $\gamma_s$ = 43.2	D = 37.9 P = 7.6 $\gamma_s$ = 45.5
Geometric	D = 2.6 P = 7.8 Unaccepted	D = 13.5 P = 9.1 $\gamma_s$ = 22.6	D = 4.9 P = 8.2 Unaccepted	Unaccepted Value	D = 3.2 P = 7.8 Unaccepted	D = 6.2 P = 6.9 Unaccepted
	DMSO Glycerol	DMSO Formamide	DMSO Methylene iodide			
Harmonic	D = 24.2 P = 18.8 $\gamma_s$ = 43.0	D = 24.0 P = 19.5 $\gamma_s$ = 43.5	D = 38.7 P = 2.4 $\gamma_s$ = 41.1			
Geometric	D = 12.0 P = 20.7 $\gamma_s$ = 32.7	D = 30.2 P = 24.7 $\gamma_s$ = 54.9	D = 36.3 P = 1.6 $\gamma_s$ = 37.9			

TABLE 8.8: Surface tension,  $\gamma_s$  (mN.m<sup>-1</sup>) calculated by harmonic and geometric methods for semi-flexible polyurethane substrate

Method	Water Ethan-1 2-diol	Water DMSO	Ethan-1 2-diol DMSO	Glycerol Formamide	Glycerol Methylene iodide	Formamide Methylene iodide
Harmonic	D = 44.7 P = 5.7 $\gamma_s$ = 50.4	D = 30.1 P = 8.3 $\gamma_s$ = 38.4	D = 26.2 P = 14.5 $\gamma_s$ = 40.7	D = 32.5 P = 7.7 $\gamma_s$ = 40.2	D = 37.1 P = 5.8 $\gamma_s$ = 42.9	D = 37.2 P = 5.3 $\gamma_s$ = 42.5
Geometric	D = 67.0 P = 0.2 Unaccepted	D = 71.2 P = 0.02 Unaccepted	D = 27.2 P = 16.6 $\gamma_s$ = 43.8	D = 31.9 P = 2.4 $\gamma_s$ = 34.3	D = 20.1 P = 3.8 $\gamma_s$ = 23.9	D = 20.3 P = 4.2 $\gamma_s$ = 24.5
	Water Glycerol	Water Formamide	Water Methylene iodide	Ethan-1 2-diol Glycerol	Ethan-1 2-diol Formamide	Ethan-1 2-diol Methylene iodide
Harmonic	D = 32.4 P = 7.8 $\gamma_s$ = 40.2	D = 32.4 P = 7.8 $\gamma_s$ = 40.2	D = 37.0 P = 6.9 $\gamma_s$ = 43.9	No real value	D = 19.1 P = 23.5 $\gamma_s$ = 42.6	D = 34.9 P = 8.2 $\gamma_s$ = 43.1
Geometric	D = 39.6 P = 1.4 $\gamma_s$ = 41.0	D = 36.6 P = 1.6 $\gamma_s$ = 38.2	D = 22.3 P = 2.4 $\gamma_s$ = 24.7	Unaccepted Value	Unaccepted Value	D = 2.8 P = 8.0 Unaccepted
	DMSO Glycerol	DMSO Formamide	DMSO Methylene iodide			
Harmonic	D = 29.1 P = 9.5 $\gamma_s$ = 38.6	D = 28.2 P = 10.8 $\gamma_s$ = 39.0	D = 37.6 P = 3.2 $\gamma_s$ = 40.8			
Geometric	D = 21.0 P = 4.7 $\gamma_s$ = 25.7	D = 11.3 P = 7.1 $\gamma_s$ = 18.4	D = 29.7 P = 2.9 $\gamma_s$ = 32.6			

TABLE 8.9: Surface tension,  $\gamma_s$  ( $\text{mN}\cdot\text{m}^{-1}$ ) calculated from harmonic and geometric methods for rigid polyurethane substrate



Method	Water Ethan-1 2-diol	Water DMSO	Ethan-1 2-diol DMSO	Glycerol Formamide	Glycerol Methylene iodide	Formamide Methylene iodide
Harmonic	D = 20.3 P = 14.8 $\gamma_s$ = 35.1	D = 27.0 P = 12.3 $\gamma_s$ = 39.3	D = 30.7 P = 7.4 $\gamma_s$ = 37.1	No real value	D = 38.7 P = 4.2 $\gamma_s$ = 42.9	D = 38.4 P = 6.8 $\gamma_s$ = 45.2
Geometric	D = 1.6 P = 7.0 Unaccepted	D = 0.02 P = 6.1 Unaccepted	D = 17.3 P = 4.1 $\gamma_s$ = 21.4	D = 6.7 P = 5.7 Unaccepted	D = 33.0 P = 6.4 $\gamma_s$ = 39.4	D = 11.3 P = 6.4 Unaccepted

	Water Glycerol	Water Formamide	Water Methylene iodide	Ethan-1 2-diol Glycerol	Ethan-1 2-diol Formamide	Ethan-1 2-diol Methylene iodide
Harmonic	D = 20.1 P = 14.9 $\gamma_s$ = 35.0	D = 31.5 P = 11.1 $\gamma_s$ = 42.6	D = 38.2 P = 9.6 $\gamma_s$ = 47.8	D = 30.6 or 21.6 P = 13.6 or 7.4 $\gamma_s$ = *	D = 60.6 P = 0.6 Unaccepted	D = 38.6 P = 4.5 $\gamma_s$ = 43.1
Geometric	D = 13.4 P = 8.5 $\gamma_s$ = 21.9	D = 13.6 P = 3.7 Unaccepted	D = 5.0 P = 4.7 Unaccepted	D = 10.7 P = 5.2 Unaccepted	D = 7.8 P = 5.8 Unaccepted	D = 28.7 P = 2.7 $\gamma_s$ = 31.4

	DMSO Glycerol	DMSO Formamide	DMSO Methylene iodide	Water DMF	Ethan-1 2-diol	DMSO DMF
Harmonic	D = 30.7 P = 7.4 $\gamma_s$ = 38.1	D = 24.5 P = 18.7 $\gamma_s$ = 43.2	D = 39.2 P = 2.4 $\gamma_s$ = 41.6	D = 25.8 P = 12.7 $\gamma_s$ = 38.5	D = 26.9 P = 9.4 $\gamma_s$ = 36.3	D = 25.0 P = 17.0 $\gamma_s$ = 42.0
Geometric	D = 32.4 P = 2.4 $\gamma_s$ = 34.8	D = 21.3 P = 23.0 $\gamma_s$ = 44.3	D = 37.0 P = 1.6 $\gamma_s$ = 38.6	D = 6.6 P = 7.8 Unaccepted	D = 0.6 P = 10.3 Unaccepted	D = 1112 P = 80.0 Unaccepted

	Glycerol DMF	Formamide DMF	Methylene iodide DMF
Harmonic	D = 23.6 P = 11.7 $\gamma_s$ = 35.3	D = 18.6 P = 32.0 $\gamma_s$ = 50.6	D = 39.9 P = 1.2 $\gamma_s$ = 41.1
Geometric	D = 4.1 P = 6.4 Unaccepted	Unaccepted value	D = 41.3 P = 0.2 $\gamma_s$ = 41.5

\*  $\gamma_s$  can be any of D+P combinations (i.e. 44.2, 38.0, 35.2 or 29.0).

TABLE 8.10: Surface Tension,  $\gamma_s$  ( $\text{mN.m}^{-1}$ ) calculated from harmonic and geometric methods for RIM polyurethane substrate

	Water Ethan-1 2-diol	Glycerol Formamide	Glycerol Methylene iodide	Formamide Methylene iodide	Water Glycerol	Water Formamide
Harmonic	D = 70.7 P = 2.6 Unaccepted	D = 32.5 P = 9.4 $\gamma_s = 41.9$	D = 40.1 P = 6.1 $\gamma_s = 46.2$	D = 40.2 P = 5.4 $\gamma_s = 45.6$	D = 43.4 P = 5.1 $\gamma_s = 48.5$	D = 39.4 D = 5.7 $\gamma_s = 45.1$
Geometric	D = 63.0 P = 0.2 Unaccepted	D = 22.7 P = 3.8 $\gamma_s = 26.5$	D = 20.9 P = 4.0 $\gamma_s = 24.9$	D = 23.5 P = 4.1 $\gamma_s = 27.6$	D = 64.5 P = 0.1 Unaccepted	D = 57.5 P = 0.4 Unaccepted

	Water Methylene iodide	Ethan-1 2-diol glycerol	Ethan-1 2-diol formamide	Ethan-1 2-diol methylene iodide
Harmonic	D = 40.2 P = 5.6 $\gamma_s = 45.8$	No real value	D = 17.8 P = 32.2 $\gamma_s = 50.0$	D = 39.9 P = 9.0 $\gamma_s = 48.9$
Geometric	D = 37.3 P = 1.4 $\gamma_s = 38.7$	Unaccepted value	Unaccepted value	D = 2.1 P = 8.7 Unaccepted

TABLE 8.11: Surface Tension,  $\gamma_s$  ( $\text{mN.m}^{-1}$ ) calculated from harmonic and geometric methods for ISOFOAM-PU substrate

Substrate	Method	Water Ethan-1, 2-diol	Water DMSO	Water DMF	Ethan-1 2-diol DMSO	Ethan-1, 2-diol DMF	DMSO DMF
C <sub>196</sub>	Harmonic	D = 17.8 P = 23.5 $\gamma_s$ = 41.3	D = 26.0 P = 19.3 $\gamma_s$ = 45.3	D = 25.0 P = 19.7 $\gamma_s$ = 44.7	D = 30.1 P = 10.4 $\gamma_s$ = 40.5	D = 26.1 P = 13.1 $\gamma_s$ = 39.2	D = 24.3 P = 27.2 $\gamma_s$ = 51.5
	Geometric	D = 295.0 P = 18.5 Unaccepted	D = 145.5 P = 15.0 Unaccepted	D = 365.0 P = 19.6 Unaccepted	D = 1.2 P = 8.5 Unaccepted	D = 105.0 P = 22.0 Unaccepted	D = 812.0 P = 203.0 Unaccepted
C <sub>198</sub>	Harmonic	D = 23.6 P = 10.1 $\gamma_s$ = 33.7	D = 26.2 P = 9.3 $\gamma_s$ = 35.5	D = 24.3 P = 9.9 $\gamma_s$ = 34.2	D = 27.5 P = 7.7 $\gamma_s$ = 35.2	D = 24.4 P = 9.6 $\gamma_s$ = 34.0	D = 22.7 P = 16.4 $\gamma_s$ = 39.1
	Geometric	D = 17.9 P = 2.8 $\gamma_s$ = 20.7	D = 11.4 P = 3.3 $\gamma_s$ = 14.7	D = 2.2 P = 4.6 Unaccepted	D = 11.1 P = 4.9 $\gamma_s$ = 16.0	D = 3.7 P = 11.4 $\gamma_s$ = 15.1	D = 1018 P = 77.0 Unaccepted
C <sub>199</sub>	Harmonic	D = 31.5 P = 4.7 $\gamma_s$ = 36.2	D = 26.0 P = 6.0 $\gamma_s$ = 32.0	D = 25.4 P = 6.2 $\gamma_s$ = 31.6	D = 23.8 P = 8.5 $\gamma_s$ = 32.3	D = 24.4 P = 8.1 $\gamma_s$ = 32.5	D = 24.7 P = 7.3 $\gamma_s$ = 32.0
	Geometric	D = 48.9 P = 0.2 $\gamma_s$ = 49.1	D = 30.4 P = 1.2 $\gamma_s$ = 31.6	D = 29.9 P = 1.3 $\gamma_s$ = 31.2	D = 3.6 P = 6.4 Unaccepted	D = 1.1 P = 7.4 Unaccepted	D = 36.8 P = 0.4 $\gamma_s$ = 37.2

TABLE 8.12: Surface tension,  $\gamma_s$  (mN.m<sup>-1</sup>), calculated from harmonic and geometric methods for polyester substrates

Substrate	Harmonic Mean Method	Geometric Mean Method	Equation of State Method
Semi-flexible PU	$\gamma_S^d = 29.2$ $\gamma_S^p = 15.0$ $\gamma_S = 44.2$	$\gamma_S^d = 22.3$ $\gamma_S^p = 13.2$ $\gamma_S = 35.5$	$\gamma_S = 41.3$
Rigid PU	$\gamma_S^d = 32.7$ $\gamma_S^p = 8.9$ $\gamma_S = 41.6$	$\gamma_S^d = 26.0$ $\gamma_S^p = 4.7$ $\gamma_S = 30.7$	$\gamma_S = 40.9$
RIM-PU	$\gamma_S^d = 29.6$ $\gamma_S^p = 11.0$ $\gamma_S = 40.6$	$\gamma_S^d = 28.0$ $\gamma_S^p = 6.1$ $\gamma_S = 34.1$	$\gamma_S = 41.1$
ISOFOAM-PU	$\gamma_S^d = 36.7$ $\gamma_S^p = 9.8$ $\gamma_S = 46.5$	$\gamma_S^d = 26.1$ $\gamma_S^p = 3.3$ $\gamma_S = 29.4$	$\gamma_S = 44.7$
C <sub>196</sub>	$\gamma_S^d = 24.9$ $\gamma_S^p = 18.9$ $\gamma_S = 43.8$	Unaccepted value	$\gamma_S = 42.2$
C <sub>198</sub>	$\gamma_S^d = 24.8$ $\gamma_S^p = 10.5$ $\gamma_S = 35.3$	$\gamma_S^d = 11.0$ $\gamma_S^p = 5.6$ $\gamma_S = 16.6$	$\gamma_S = 34.8$
C <sub>199</sub>	$\gamma_S^d = 26.0$ $\gamma_S^p = 6.8$ $\gamma_S = 32.8$	$\gamma_S^d = 36.5$ $\gamma_S^p = 0.8$ $\gamma_S = 37.3$	$\gamma_S = 31.3$

TABLE 8.13: Surface tension,  $\gamma_S$  (mN.m<sup>-1</sup>), calculated by different methods

Liquid surface tension, $\gamma_{LV}$ , $\text{mN.m}^{-1}$	$\gamma_C, \text{mN.m}^{-1}$						
	Semi-flexible PU	Rigid PU	RIM-PU	ISOFOAM-PU	C <sub>196</sub>	C <sub>198</sub>	C <sub>199</sub>
72.8	31.9	21.5	26.5	20.1	36.8	21.5	16.3
48.3	39.9	40.4	34.1	43.9	38.6	32.0	29.9
43.54	37.5	38.1	37.9	-	40.1	34.8	31.3
37.10	-	-	34.2	-	34.7	31.3	30.7
50.0	35.9	35.3	40.9	44.7	42.2	32.6	29.8
47.0	37.1	40.9	38.9	44.7	42.0	34.2	30.7
44.0	39.3	39.3	39.6	42.5	40.0	34.3	29.7
41.0	38.5	37.5	38.8	-	38.0	33.1	30.7
38.0	-	-	37.4	-	35.7	31.1	29.2
35.0	-	-	-	-	34.0	29.9	28.6
63.4	41.3	34.2	32.0	37.0	-	-	-
58.2	41.1	37.3	41.1	39.9	-	-	-
50.8	40.1	39.1	40.6	42.5	-	-	-

TABLE 8.14: Critical surface tension,  $\gamma_C$  ( $\text{mN.m}^{-1}$ ), of different substrates calculated by equation of state method

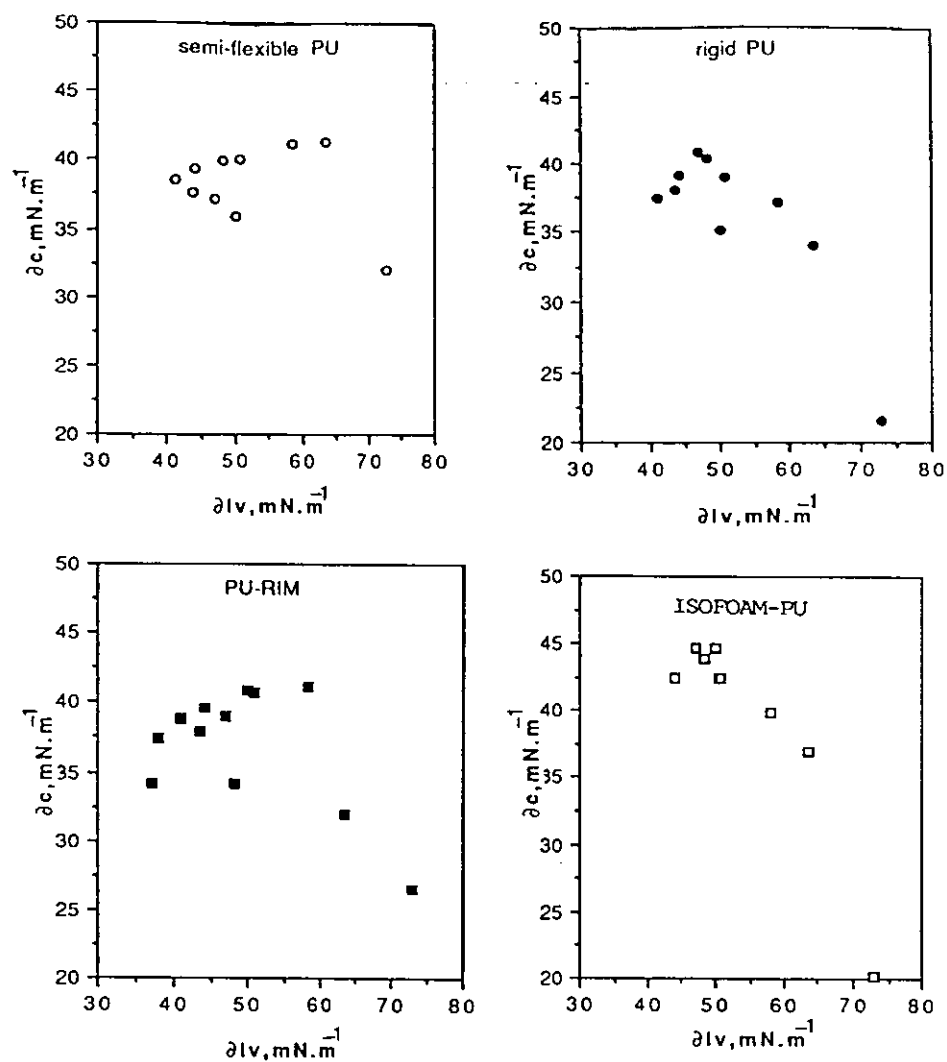


FIGURE 8.9: Equation of state plots for PU substrates

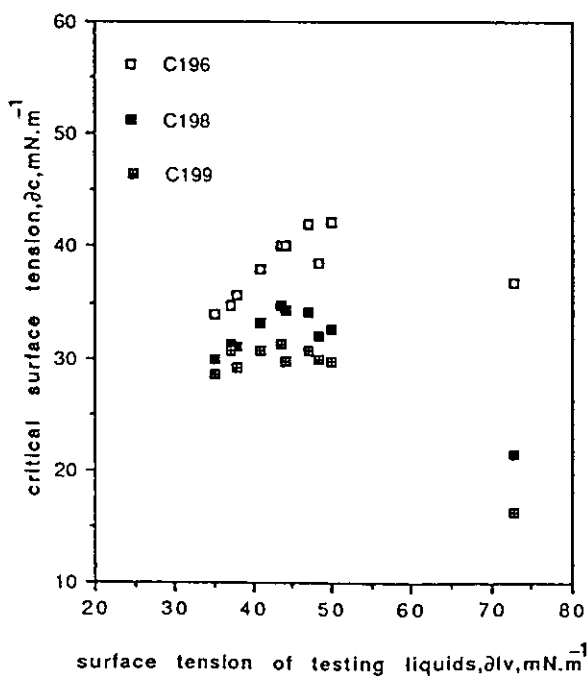


FIGURE 8.10: Equation of state plots for polyester substrates

### 8.2.7 Modification and Simplification of Some Thermodynamic Relationships

Considering the thermodynamic parameters and relationships already mentioned (see Chapter 5), some modification was carried out by applying some trigonometric relationships:

Work of adhesion:  $W_A = \gamma_{LV} (1 + \cos \theta)$

$$W_A = 2 \gamma_{LV} \cos^2 \theta/2 \quad (1)$$

(i.e.  $\cos^2 A = \frac{1+\cos 2A}{2}$ )

Spreading Coefficient:  $S_C = \gamma_{LV} (\cos \theta - 1)$

$$S_C = -2\gamma_{LV} \sin^2 \theta/2 \quad (2)$$

(i.e.  $\sin^2 A = \frac{1-\cos 2A}{2}$ )

Using the relationship for work of cohesion ( $W_C = W_A - S_C$  or  $W_C = 2 \gamma_{LV}$ ) in relationships (1) and (2) above gives:

$$\frac{W_A}{W_C} = \cos^2 \theta/2$$

$$\frac{S_C}{W_C} = -\sin^2 \theta/2$$

$$\frac{S_C}{W_A} = -\tan^2 \theta/2$$

The ratios obtained above are useful when surface tension of liquids,  $\gamma_{LV}$  is plotted against  $\cos^2 \theta/2$  and  $\sin^2 \theta/2$  on the same graph as x, y and y' ordinates respectively. As a result for all substrates whose contact angles have been measured under the same conditions, the model shown in Figure 8.11 will result in a direct measurement of two important thermodynamic parameters:  $W_A$  and  $S_C$ . Furthermore, the intercept of  $\cos^2 \theta/2$  against  $\gamma_{LV}$  relationship with  $\cos^2 \theta/2 = 1$  (i.e.  $\theta/2$  or  $\theta = 0$ ) will give the critical surface tension,  $\gamma_C$ , of the corresponding surface.

#### 8.2.7.1 Results and Discussion

The  $\cos^2 \theta/2$  against  $\gamma_{LV}$  results for all substrates are shown in Figures 8.12 and 8.13 and Table 8.15. The relationships between  $\cos \theta$  and  $\cos^2 \theta/2$  against  $\gamma_{LV}$  for PE and PTFE substrates investigated in this research and the works carried out by others are compared in Figures 8.14 and 8.15 respectively. As expected, the critical surface tensions calculated using  $\cos^2 \theta/2$  substitution showed good agreement with those obtained using  $\cos \theta$  (i.e. since  $\cos^2 \theta/2 = 0.5 + \frac{\cos \theta}{2}$ , this substitution changes the slope and intercept of any line plotted against  $\cos \theta$ ) for all substrates.

It can be considered that the surface tension,  $\gamma_{LV}$ , for most wetting liquids applied on many polymeric substrates has the value  $10 < \gamma_{LV} < 100 \text{ mN}\cdot\text{m}^{-1}$  and that  $-1 \leq \cos \theta \leq 1$  and  $0 \leq \cos^2 \theta/2$  (or  $\sin^2 \theta/2$ )  $\leq 1$  (for  $0 \leq \theta \leq 180$ ). As a result for each substrate a linear relationship between  $\cos \theta$  or  $\cos^2 \theta/2$  and  $\gamma_{LV}$  would result in determining the  $\gamma_C$  and finding the  $W_A$ ,  $S_C$  and  $W_C$  for any point on the corresponding graph:



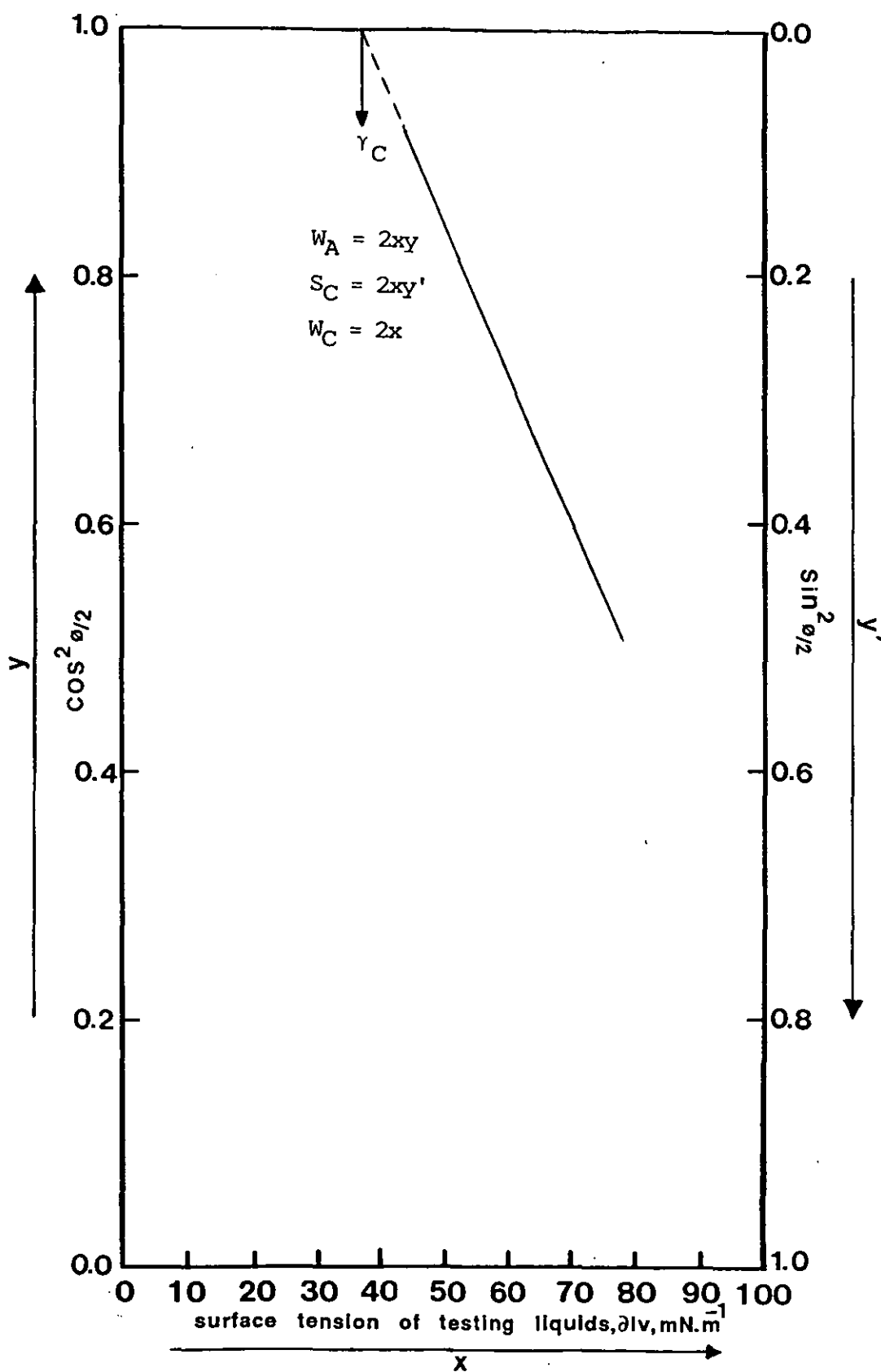


FIGURE 8.11: A schematic diagram representing the modified thermodynamic model

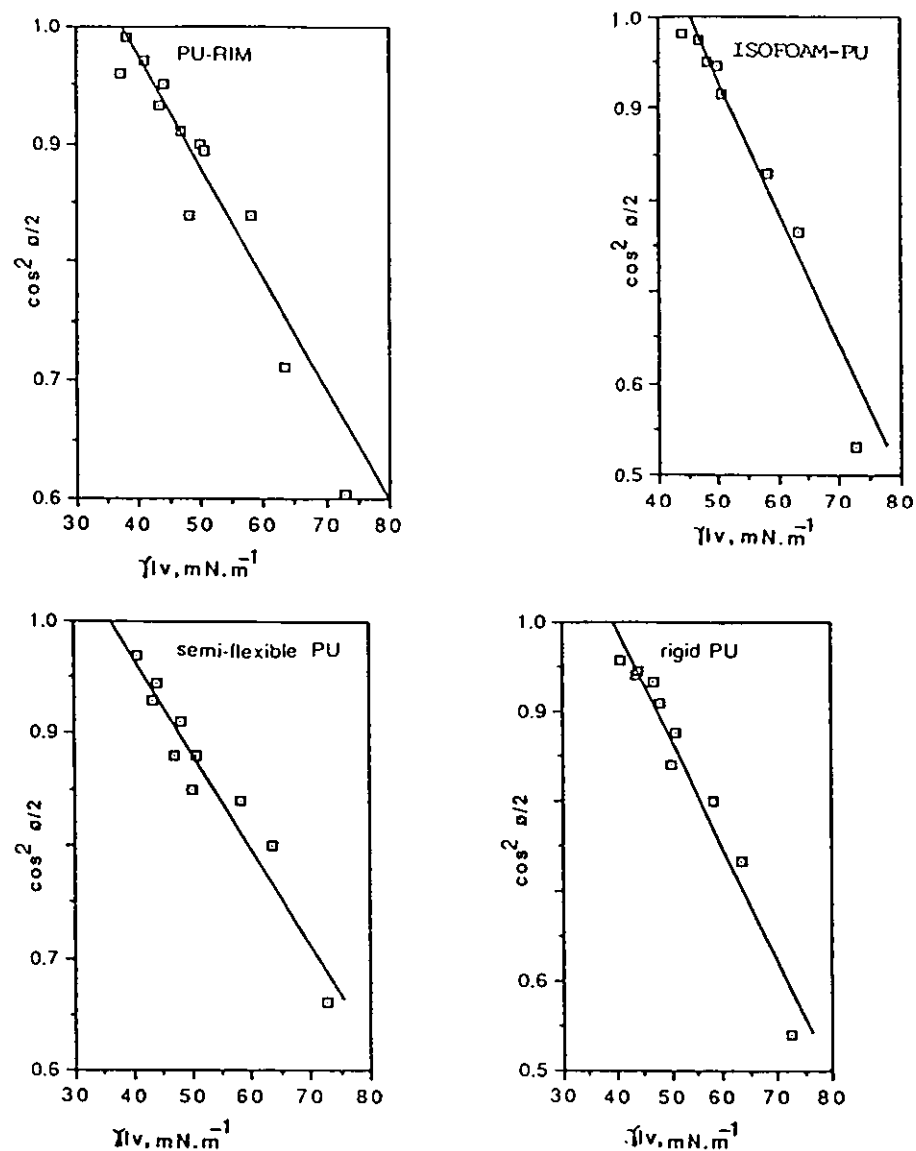


FIGURE 8.12:  $\cos^2 \frac{\theta}{2} \text{ v } \gamma_{LV}$  for PU substrates

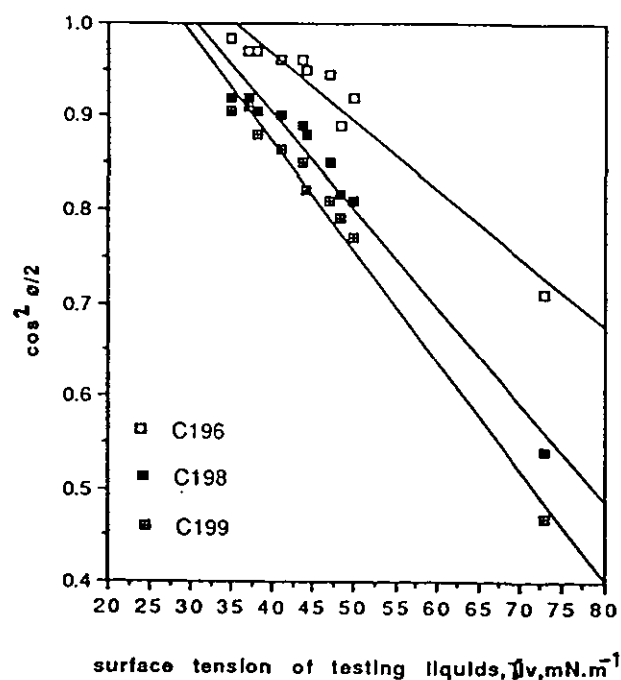


FIGURE 8.13:  $\cos^2 \frac{\theta}{2} \text{ v } \gamma_{LV}$  for polyester substrates

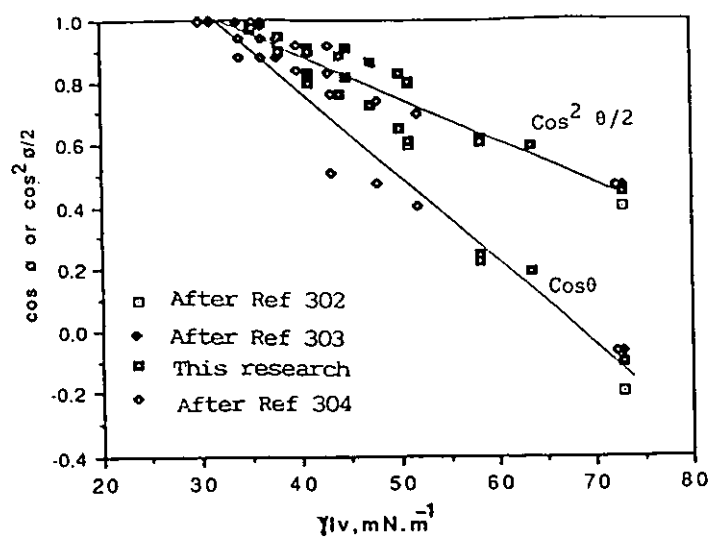


FIGURE 8.14:  $\cos\theta$  and  $\cos^2 \frac{\theta}{2}$  vs  $\gamma_{LV}$  for PE Substrates Using Various Data

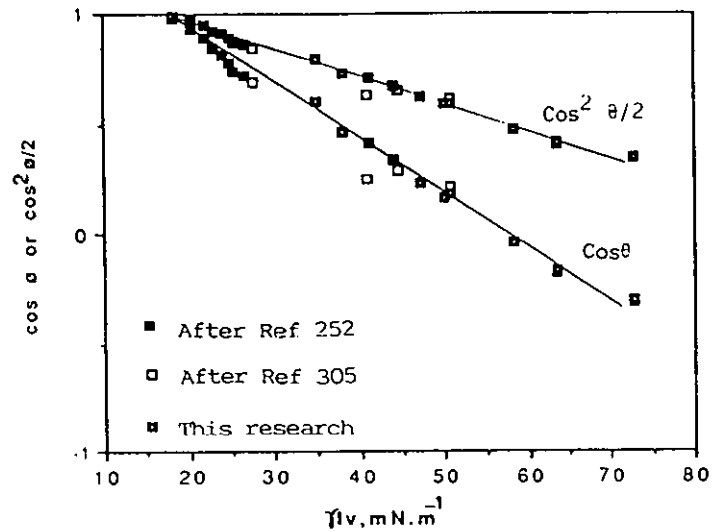


FIGURE 8.15:  $\cos\theta$  and  $\cos^2 \frac{\theta}{2}$  vs  $\gamma_{LV}$  for PTFE Substrates Using Various Data

Substrate	$\cos^2 \frac{\theta}{2}$ v $\gamma_{LV}$	Correlation Coefficient	$\gamma_C$ $\text{mN.m}^{-1}$
Semi-flexible PU	$y = 1.3117 - 8.5765e^{-3}x$	0.931	36.3
Rigid-PU	$y = 1.5049 - 1.2665e^{-2}x$	0.954	39.8
RIM-PU	$y = 1.3868 - 1.0335e^{-2}x$	0.924	37.4
ISOFOAM-PU	$y = 1.6981 - 1.5417e^{-2}x$	0.960	45.3
C196	$y = 1.2569 - 7.2344e^{-3}x$	0.940	35.5
C198	$y = 1.3179 - 1.0376e^{-2}x$	0.967	30.6
C199	$y = 1.3368 - 1.1614e^{-2}x$	0.984	29.0

TABLE 8.15: Wettability Equations and Critical Surface Tensions for Different Substrates

General linear equation:	$y = a-bx$ or $y'' = a''-b''x$
Work of adhesion:	$W_A = 2xy$ or $W_A = x(1+y'')$
Spreading coefficient:	$S_C = 2xy'$ or $S_C = x(y''-1)$
Work of cohesion:	$W_C = 2x$

where  $y = \cos^2 \theta/2$ ,  $x = \gamma_{LV}$ ,  $y' = \sin^2 \theta/2$ , and  $y'' = \cos \theta$ .

Furthermore, the surface tension,  $\gamma_S$ , of various substrates described by different methods (see Chapter 5) may be calculated using the plots of  $\cos \theta$  or  $\cos^2 \theta/2$  against  $\gamma_{LV}$ . At any point on the corresponding graph for a substrate it can be written that:

$$xy \text{ (or } \frac{x}{2} (1+y'')) = (\gamma_S^d \gamma_{LV}^d)^{1/2} + (\gamma_S^p \gamma_{LV}^p)^{1/2}$$

(for geometric mean method)

$$xy \text{ (or } \frac{x}{2} (1+y'')) = 2 \left( \frac{\gamma_{LV}^d \gamma_S^d}{\gamma_{LV}^d + \gamma_S^d} + \frac{\gamma_{LV}^p \gamma_S^p}{\gamma_{LV}^p + \gamma_S^p} \right)$$

(for harmonic mean method)

$$xy^2 \text{ (or } \frac{x}{4} (1+y'')^2) = \gamma_C$$

(for equation of state method)

### 8.2.8 Wettability of Polyurethane Substrates

Some preliminary wetting testing indicated that for most of the PU substrates, the liquids having surface tensions below  $38 \text{ mN.m}^{-1}$  had difficulty forming a true droplet on these surfaces and the contact angles observed were small or near zero (complete wetting). Therefore, three additional wetting liquids: glycerol, formamide and methylene-iodide having  $\gamma_{LV}$  values larger than  $50 \text{ mN.m}^{-1}$  were employed to provide more information on the wettability of PU substrates. The wettability equations derived from  $\cos \theta$  and  $\cos^2 \theta/2$  plotted against  $\gamma_{LV}$  for all PU surfaces showed a linear relationship of the type,  $y = a-bx$ . The work of adhesion,  $W_A$ , and the spreading coefficient  $S_C$ ,

equations (see Table 8.6) for all PU substrates demonstrated a quadratic equation of the type,  $y = -ax^2 + bx - c$ . The critical surface tension,  $\gamma_C$ , values obtained for  $\cos\theta$  and  $\cos^2 \theta/2$  graphs (see Tables 8.5 and 8.15) ranged from 36.3 to 45.4 mN.m<sup>-1</sup>. The corresponding surface tension,  $\gamma_S$ , values measured by different methods (see Table 8.13) showed a satisfactory agreement between the results obtained by harmonic mean and the equation of state methods. However in all cases the results obtained by the geometric mean method showed much lower values than the other two methods.

For all polyurethane substrates the  $\gamma_S^d$ , the dispersive component of surface tension, had a higher value than the corresponding  $\gamma_S^p$ , the polar component of  $\gamma_S$ .

#### 8.2.9 Wettability of Polyester Substrates

The relationship between surface tension of liquids,  $\gamma_{LV}$ , and  $\cos\theta$  and  $\cos^2 \theta/2$  showed a linear relationship (i.e.  $y = a - bx$ ) for polyester substrates. The work of adhesion,  $W_A$ , and the spreading coefficient,  $S_C$ , indicated a quadratic equation (i.e.  $y = -ax^2 + bx - c$ ). The critical surface tension,  $\gamma_C$ , values ranged from 29 to 35.5 mN.m<sup>-1</sup>. The corresponding surface tension,  $\gamma_S$ , values obtained by different methods showed good agreement between the results from harmonic mean and the equation of state methods but with unaccepted and scattered results from the geometric mean method. Generally,  $\gamma_S^d$  for all three types of polyester substrate showed a larger value than the corresponding  $\gamma_S^p$  value.

The results from Figures 8.6 and 8.8 indicate that there is a decreased adhesion of liquids to the polyester substrate from C196 to C199. In effect the maximum work of adhesion,  $\text{Max } W_A$ , and  $\gamma_C$  are directly related.

### 8.3 SURFACE ANALYSIS: CHEMICAL TECHNIQUES

To date, the most widely used techniques in the analysis of surfaces and interfaces are infra-red spectroscopy (IR) including Fourier transform spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS or ESCA), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS) and ion scattering spectrometry (ISS). These techniques have been reviewed in detail in the related literature [45,287,306-311]. The applications, limitations and usefulness of these techniques with the special relevance to this research will be followed.

#### 8.3.1 Applications and Limitations

IR spectroscopy is a rapid, direct, non-destructive technique that can be used for the identification of polymers and individual components in polymer compositions and for certain detection of the thermal and UV degradation of polymers. However, chemical analysis of coated polymeric substrates, using IR, is not quite as clear cut as with pure organic compounds. IR spectroscopy relies on individual chemical groups in a sample absorbing electromagnetic radiation at different wavelengths within the range  $400$  to  $4600\text{ cm}^{-1}$  [309].

Attenuated total reflectance (ATR) and multiple internal reflectance (MIR) techniques have been used successfully to provide information to identify not only a single polymer, but also to give chemical information about the various functional groups in laminated and composite systems. Both ATR and MIR techniques require the radiation to be internally reflected at the interface between a prism and the sample under investigation. The prisms used in ATR and MIR are normally based on a mixture of thallium bromide and iodide, commonly known as KRS-5.

The introduction of FT-IR, operable over the entire infra-red frequency range, has led to an increase in the sensitivity of the technique such that both extremely small samples and optically dense materials (e.g. heavily carbon black filled samples) can be successfully analysed.

The four relatively modern surface analysis techniques (i.e. XPS, AES, SIMS and ISS) all depending on ultra-high vacuum (UHV) technology, are presented schematically in Figure 8.16. These techniques can provide useful chemical information on the structure and composition of many surfaces (Table 8.16). However, because of their surface sensitivity and ability to differentiate between surface and bulk phases, these techniques are particularly suitable for the investigation of interfaces between metal-metal and polymer-metal systems. For example, XPS has been used to chemically characterise polymeric surfaces, however the technique can only be used to study interfacial interactions provided the coating on the substrate is thin ( $< 5$  nm) [287].

The surface and interface analysis of polymer-polymer systems is not as simple as those of metal-metal or polymer-metal systems because of the fact that polymer-polymer interfaces are not sharply separated but are rather intermixed and diffuse (see Chapter 11). In particular, the problem facing the interfacial analysis of samples in this research has been shown (see Section 8.3.2) to be more complex because of near chemical composition of urethane/urethane systems.

The major disadvantage of AES for adhesive bonding investigation, in general and interfacial formation studies in ICM and PMC samples reported in this research is that organic compounds are very unstable and easily decomposed by the electron beam due to localised heating. This limitation does not exist with metal composites. SIMS is the most

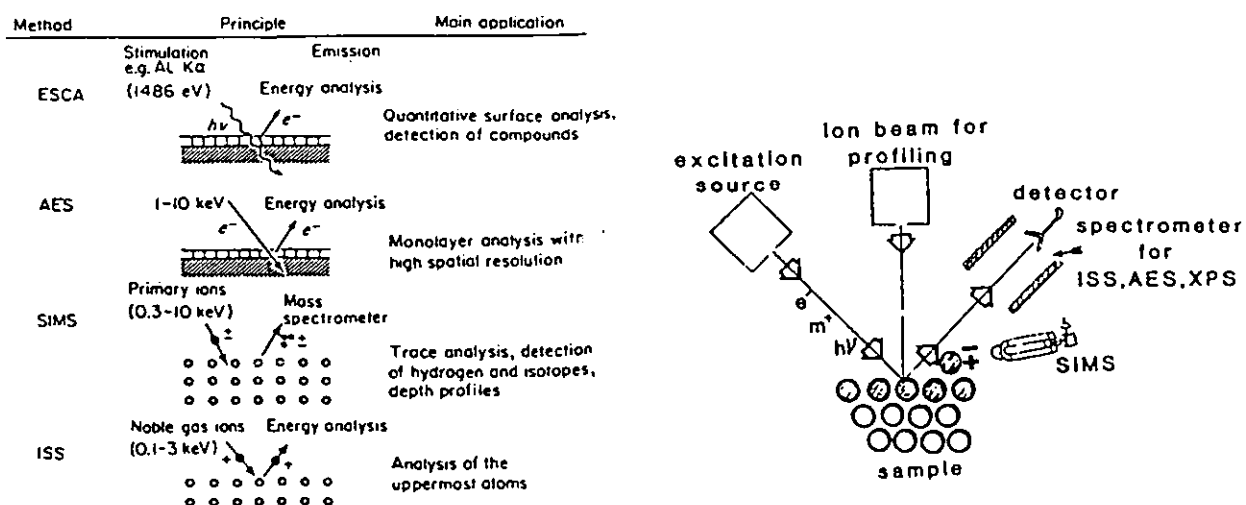


FIGURE 8.16: Schematic representation of surface analysis methods (after refs 307 and 311)

Parameter	Technique			
	Ion Scattering Spectrometry (ISS)	Secondary Ion Mass Spectrometry (SIMS)	Auger Electron Spectrometry (AES)	X-Ray Photoelectron Spectrometry (XPS)
Principle	elastic binary collision with surface ion	sputtering of surface atoms by ion beam	ejection of Auger electron upon recombination	ejection of photoelectrons by photon
Probe	~ 1 to 3 keV ions	~ 1 to 3 keV ions	~ 1 to 3 keV electrons	0 to 2 keV photons
Signal	ion current versus energy	ion current versus mass	derivation $e^+$ emission versus energy	electron emission versus energy
Applicable elements	$Z \geq 3$	all (if positive and negative SIMS)	$Z \geq 3$	$Z \geq 3$
Surface sensitivity	high	variable	variable	high
Elemental profiling	yes	yes	yes, with ion beam	yes, with ion beam
Image-spatial analysis	yes	yes	yes	no
Spectral shift	possible, but generally no	no	yes	yes
Information on chemical combination	yes, in fine features but generally no	in some cases (fingerprint spectra)	yes	yes
Quantitative analysis	yes	probably no, maybe with similar standards	yes, in principle but difficult	yes
Influence of operating conditions and matrix	no	yes	yes	yes
Isotopic analysis	yes, in principle but generally no because of resolution limits	yes	no	no
Beam induced surface changes	yes, sputtering damage	yes, sputtering damage	yes, due to sputtering and electron beam heating	no, (except when profiling)

TABLE 8.16: Comparison of primary elemental surface characterisation techniques to determine locus of failure (after refs 310 and 311)



sensitive method for surface analysis and unlike XPS and AES is capable of detecting hydrogen and its compounds and isotopes. The information depths are  $\leq 10$  nm with XPS,  $\leq 5$  nm with AES, and  $\leq 1$  nm with SIMS [307]. The ISS technique gives the least information depth where only elements in the first atomic layer at the surface are detected.

### 8.3.2 Results and Discussion

Some preliminary studies using the analysis techniques mentioned above were carried out. A number of IR results on substrate and coating materials used in this research are shown in Figure 8.17. It may be noted that although some information about the presence of the urethane structure can be found with the examination of the IR spectrum for particular bands, this data cannot be used in investigation of adhesion properties of coated systems and is of little significance in this work. Furthermore, the close resemblance of IR results for coating and substrate materials (i.e. due to similar chemical constituents in their formulations), highlights the main difficulty associated with understanding and application of adhesion/interfacial bonding theories to IMC and PMC systems. IR results for IMC and PMC specimens were misleading and no valid information could be gained.

The FT-IR results with X-226/C2885, a flexible fully reacted polyether PU coating, and MRC (600) a self releasing PU barrier coating, are presented in Figure 8.18. The presence of free-NCO in low levels in the wet film of X-226/C2885 and in the paint film at different time intervals up to five minutes at 20°C is observed. This important finding indicates the strong chemical and physical activity of IMC surfaces and shows some potential for chemisorptive bonding (see Chapter 12).

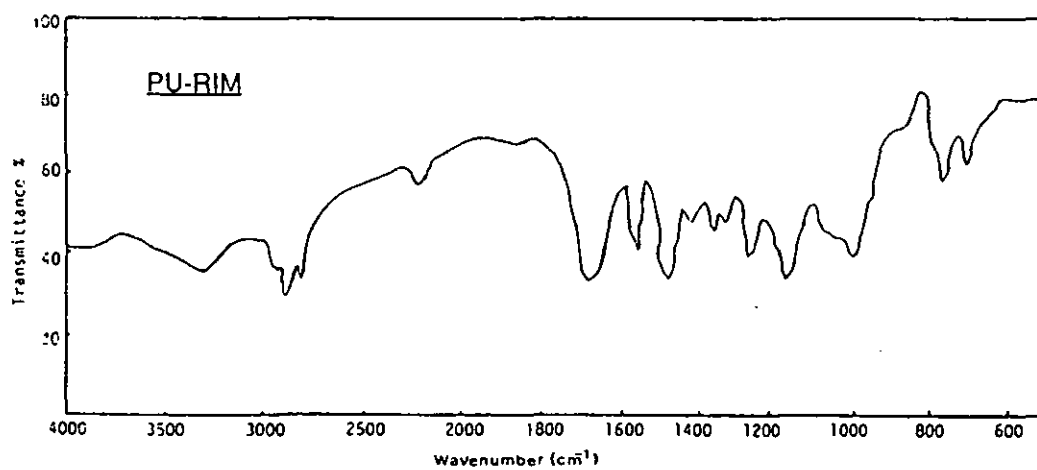
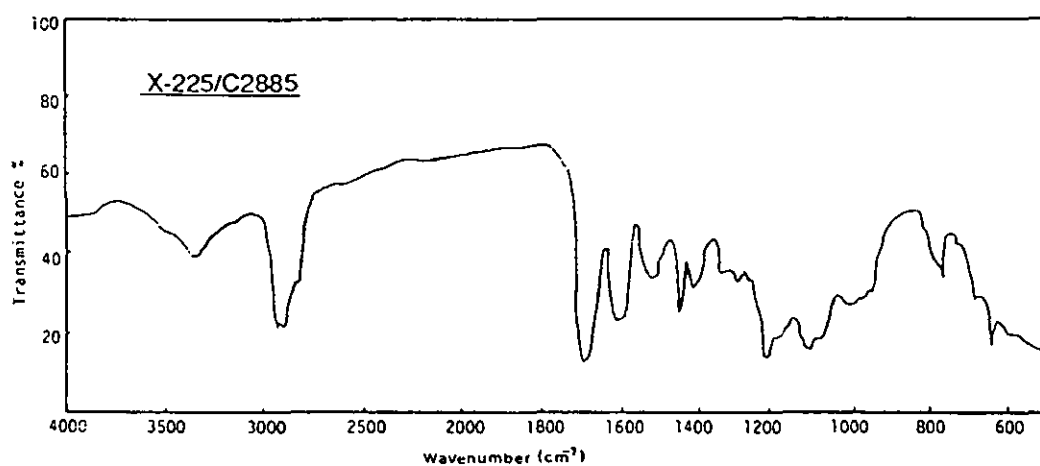
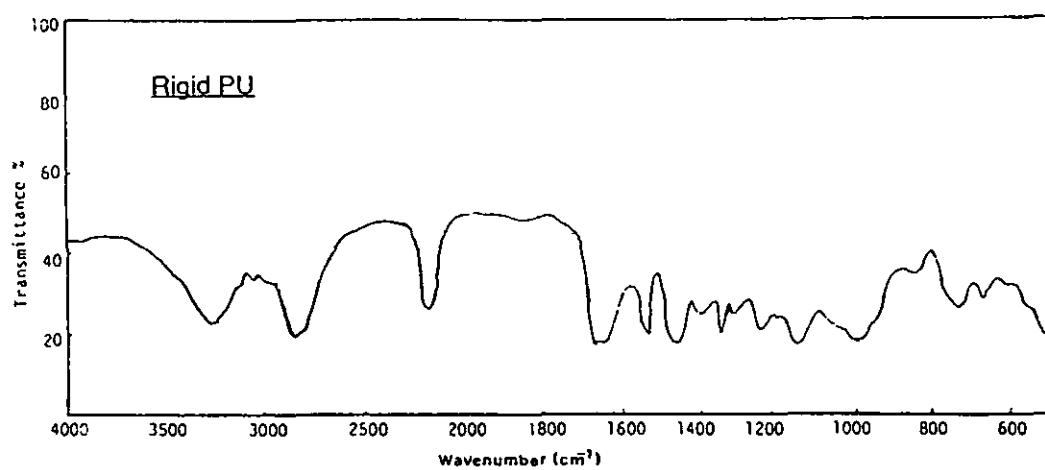


FIGURE 8.17: IR results for some substrate and coating materials

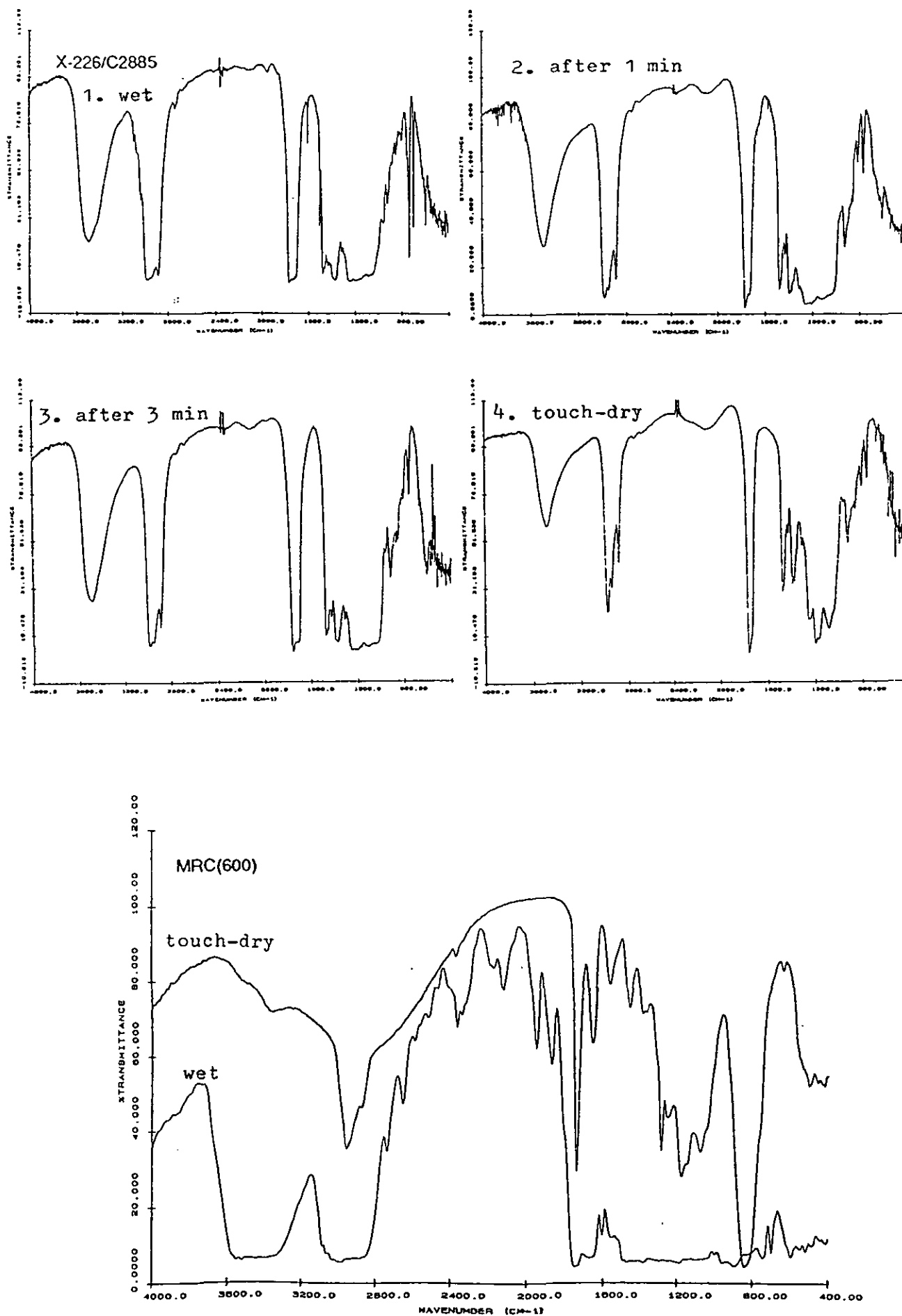


FIGURE 8.18: FT-IR results for X-226/C2885 and MRC (600) coatings at different time intervals

The FT-IR studies on these two PU based one pack coatings may be used to explain various adhesion properties of coated systems shown by a number of quantitative test results (see Chapter 9).

Similarly, Merten et al and Murphy and O'Neil [312,313] have applied the IR technique to develop a method for the determination of the unreacted-NCO group in PU foams. TDI-based foams were found to contain less free-NCO than MDI-based foams and the isocyanate content dropped more rapidly over a four week ageing period with the greatest improvement occurring in the first two weeks. This was explained on the basis of the greater reactivity of TDI. The considerable amount of free isocyanate (i.e. varying between 0.15 to 0.92 wt%-NCO) remaining in the various PU foams was available for additional reactions, such as with moisture from the air during production and handling.

The analysis of original and coated specimens with chemical analysis techniques reviewed above proved problematic and the results were not trustworthy. For example, XPS results of a dry IMC film of X-225/C2885 gave elemental mass ratios of C:O:Si of 63:25:12 and 59:24:17 (surface and interior respectively), with nitrogen and hydrogen levels below the minimum sensitivity of 1% [314]. The silicon content may be derived from flow aids or silicate fillers. However, for a flexible PU paint film, based on a polyester polyol (2000 molecular weight minimum) with MDI, the theoretical atomic mass ratio of C:O:H:N would be approximately 65:24:1:<0.01. Therefore it may be noted that the type of information obtained above by XPS is not useful in the interfacial studies of coated polymers in this work. SIMS was used to scan across the interface of several IMC and PMC PU systems. However, it was not possible to discern between the aromatic isocyanate related structure of the substrate and the isocyanate related structure (normally non-aromatic) of the coating.

**CHAPTER 9**  
**MECHANICAL TESTING TECHNIQUES**

**9.1 INTRODUCTION**

The knowledge in the science of adhesion is important not only in the practical application of polymer coating but also for understanding the bonding phenomenon and its effects at interfaces in general. Serious attempts to measure paint adhesion have been made only in the last fifty years, with most of the development of the techniques being in the 1950s and 1960s [308,315,316]. The tensile adhesion pull-off, impact properties and non-quantitative adhesion tests are the mechanical testing techniques used in this research. The test methods, experimental devices and designs, classification of expected types/modes of failure and a report of the results and discussion of these techniques will be reviewed in this Chapter respectively.

**9.2 TENSILE ADHESION PULL-OFF: MEASUREMENTS, RESULTS AND DISCUSSION**

**9.2.1 Introduction**

In order to achieve meaningful data about the strength of adhesion, the system of measurement used should allow the calculation or at least the estimation of the stress at the coating/polymer interface. For instance, the pull-off tensile test, an established method in which the applying forces are acting perpendicularly at the interface, is a favourable method to measure paint adhesion. The two most practised methods: the direct and the sandwich method of pull-off test are shown schematically in Figures 9.1(a) and 9.1(b) respectively

[317]. Some preliminary research was carried out in order to find a suitable method of pull-off tensile testing for our need and is reviewed here.

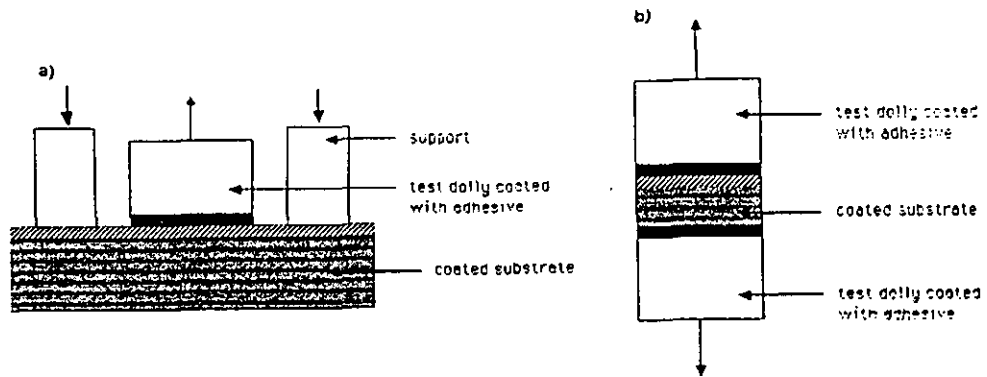


FIGURE 9.1: Schematic Drawing of the Direct (a) and the Sandwich (b) Methods of Tensile Pull-Off Test

### 9.2.2 The Choice of Test Method

Although some earlier studies had shown that the adhesion as determined by the direct method is much lower than the adhesion determined by the sandwich method, the difference between the two methods have only become clear by some studies to the field of forces existing in each method [317,318]. The fields of forces are shown schematically in Figures 9.2(a) and 9.2(b).

Hopman [317] studying the differences between these two methods concluded that in order to achieve a better agreement between the two methods the following requirements have to be met:

1. the diameter of the dolly (test cylinder) should be much smaller than the thickness of the substrate;

2. the distance between the edge of the dolly and the support (cylinders) should be larger than the diameter of the dolly.

As a result the field of force existing in a direct pull-off test almost equal to the sandwich method (shown in Figure 9.2(c)), can be achieved.

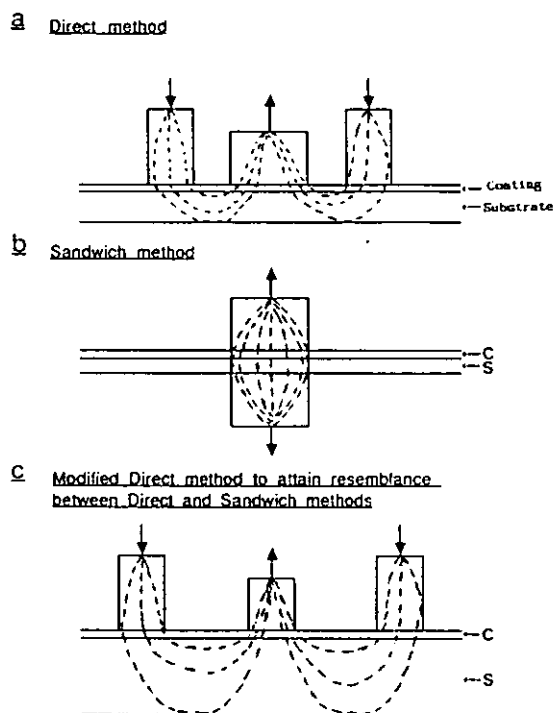


FIGURE 9.2: Schematic Drawing of Lines of Force Existing During Pull-off Test

In order to demonstrate further the differences in stress distribution between these two methods, the isopachic and isochromatic patterns are shown in Figures 9.3(a) and 9.3(b).

Sickfeld and others [318,319] investigating the influences on the test results of the two direct and sandwich pull-off methods concluded that the results obtained with a test assembly consisting of only one test

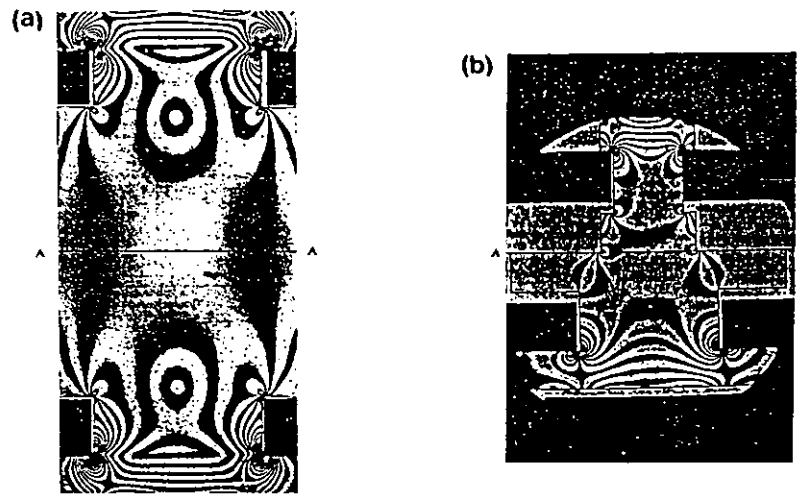


FIGURE 9.3: Isochromatic (a) and Isopachic (b) patterns representing stress distribution in a sandwich and in a direct method of pull-off test assembly respectively. Section A-A indicates the position of coating used for testing (After Ref 318)

cylinder (i.e. direct pull-off) applied on a rigid substrate are about 20 to 60 per cent lower than the values obtained with the sandwich test assembly consisting of two coaxially aligned test cylinders. The reason being a less uniform stress distribution in the direct pull-off test assembly. The sandwich method of pull-off test measuring the adhesion of a coating to a substrate standardised in BS 3900: Part E10: 1979 and also as ISO 4624 [320] was preferred to the direct pull-off method and applied in this research.

### 9.2.3 Expected Modes of Failure

In conjunction with the numerical data gathered from a pull-off adhesion test, it is important to examine the fracture surfaces and record the visual observations. In general, four modes of failure could be observed in this work:

- A. Complete cohesive failure through the bulk phase of either the substrate or dry coating. For best adhesive properties of a joint, the strength of the bond must be greater than the higher cohesive strength.
- B. Mixed cohesive and adhesive failure, which may move across the interface from substrate to adherent or vice versa.



- C. Interfacial failure between substrate and dry coating. This is a special type of adhesive failure where the fracture at the interfacial region between substrate and coating is considered more important.
- D. Adhesive failure which is either an apparent (D') or a true complete failure (D). Although both of these failures may show a clear delamination of one surface from the other with the naked eye, a close observation of the exposed surfaces usually with the aid of an optical microscope and other surface analysis equipment will reveal cross-contamination with the apparent adhesive failure.

The above modes of failure are shown schematically in Figure 9.4.

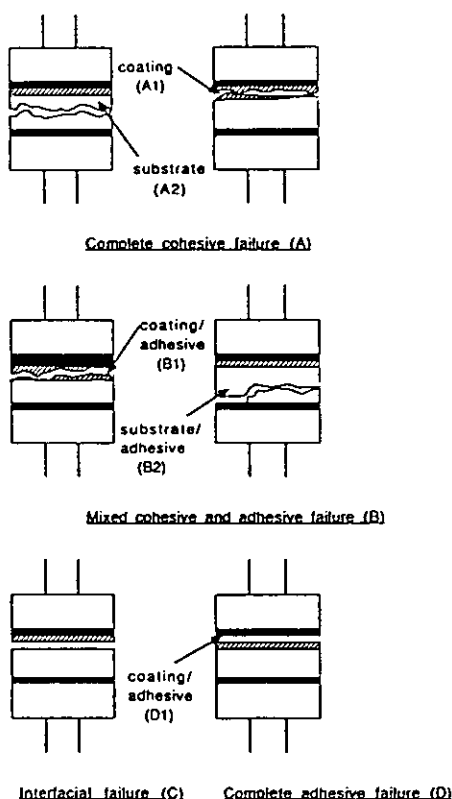


FIGURE 9.4: Modes of failure of adhesion pull-off samples

#### 9.2.4 Experimental Procedure

##### a) Specimens Preparation

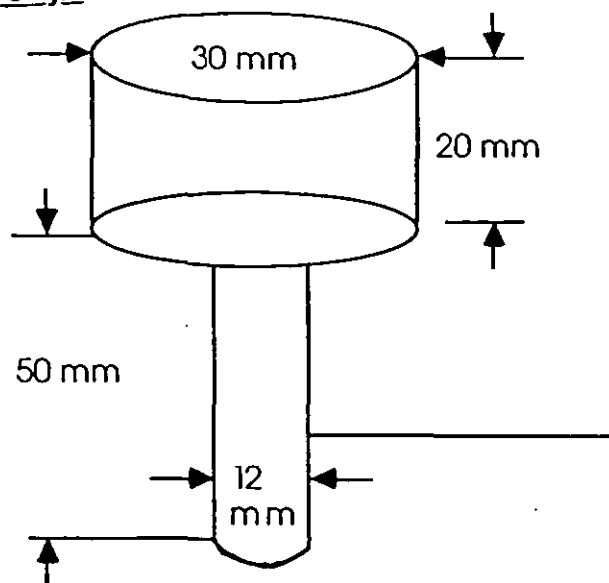
The test piece or dollies used in this work (Figure 9.5(a)) were made of mild rolled steel shaped into cylinders of 30 mm diameter and a 20 mm length having thinner cylinders (pull-rods) of 12 mm diameter and 50 mm length.

All the coated specimens under the test (i.e. being preconditioned for about one week at  $20 \pm 1^{\circ}\text{C}$  and  $50 \pm 5\%$  relative humidity, unless otherwise stated) were cut into the squares of minimum side of 30 mm ( $30 < l < 35$  mm). Prior to any testing, the 30 mm diameter faces of steel cylinders, were glass bead blasted to remove dirt, dust and other contaminations, then washed in acetone and rinsed in trichloroethane. The appropriate adhesive (see Section 9.2.4(b)) was then evenly applied to the surfaces of two freshly cleaned cylinders. The coated specimen was then placed on one the of glued surfaces allowing it to reach a reasonable strength, and then with the help of a special aligning device (Figure 9.5(b)) the other cylinder was attached to the specimen.

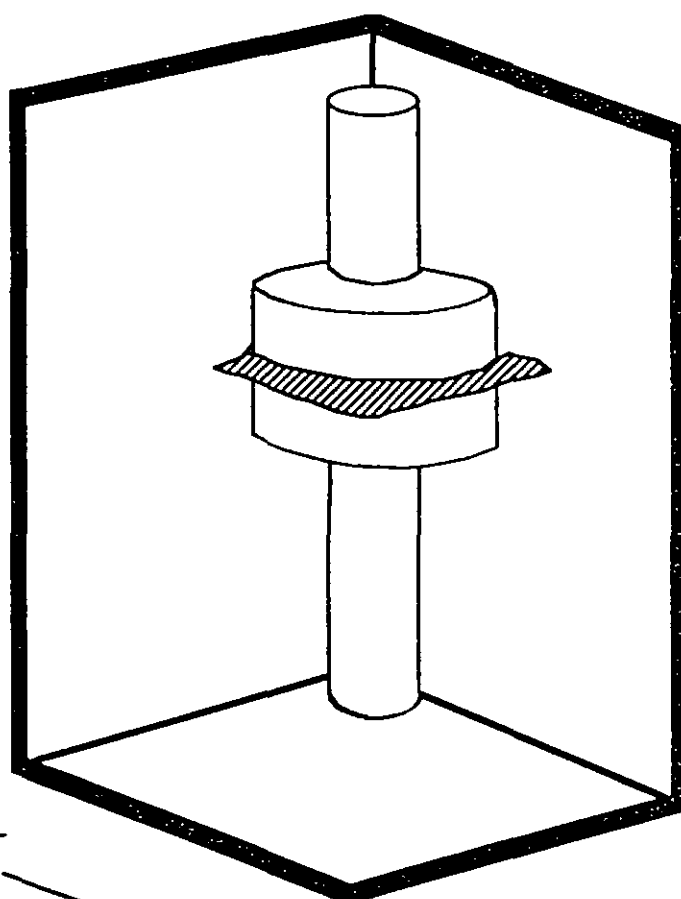
During the adhesive application, sufficient pressure was applied on the specimen/cylinder to ensure a uniform layer of adhesive leaving no air bubbles. The test cylinders were then transferred to a horizontal surface in an upright position to reach full cure.

The cured test specimens were then cut down to the same diameter as the test cylinders in order to get rid of excess adhesive and also have the same coated area of contact for all the samples under the test (Figure 9.5(c)).

**a** Test piece (dolly)



**b** Aligning device



**c** Prepared test assembly

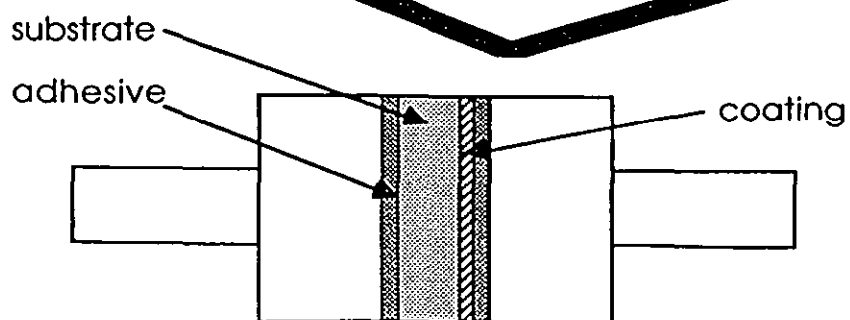


FIGURE 9.5: Schematic drawing of specimens preparation for sandwich pull-off test

#### b) Adhesives

Initially five different adhesives were used to glue the test specimens to the steel cylinders (Table 9.1). The adhesive Araldite 2002 having a short pot life was discarded. Also some preliminary results showed that results obtained with Loctite 496 were not reliable as the coefficients of variation were too scattered. Although the adhesives Araldite M750 with HY951 and Araldite DIY were suitable, the adhesive Araldite 2001 proved to give a better consistency in results with all different types of coating/substrate combinations. It seems reasonable to assume that, provided a suitable adhesive is selected and used according to the manufacturer's specifications and test requirements, interference from the adhesive (i.e. affecting the interfacial region) applied in very thin layers will be negligible.

Unless otherwise stated, all the samples preparation in the pull-off test for adhesion used Araldite 2001 in order to achieve repeatable results and avoid any possible effect by using a variation of adhesives.

#### c) Testing

After the test specimens were prepared and preconditioned (i.e. at  $t = 20 \pm 1^\circ\text{C}$  and  $\text{RH} = 50 \pm 5\%$  for an average 24 hours prior to testing), the adhesion pull-off (sandwich method) test was carried out on a tensile tester (Instron type TT-DML) using two load cells: DM type (maximum 500 kgf) and GRM type (maximum 10,000 kgf) according to the required force needed to break different test specimens.

The test cylinder was placed between the jaws of a specially designed jig (having one flat and the other an angled corrugated surface) to give a better grip than ordinary jaws. The pull-off rods were

Adhesive	Manufacturer	Type and Application Recommendation	Full Curing Time (20°C)
"Araldite" DIY	Ciba-Geigy	Two pack epoxy adhesive. Mix 1:1 by volume. Pot life ~ 20 mins. Apply to both surfaces.	24 hours
"Araldite" M750 with HY951	Ciba-Geigy	Epoxy coating compound. Mix 10:1 by weight resin to hardener. Pot life 20 to 30 mins. Apply to both surfaces. Bring together, apply pressure, squeeze out excess.	>24 hours
"Loctite" 496	Loctite	Cyanoacrylate adhesive. Apply a small amount to one surface only. Join the two surfaces immediately, applying pressure.	12 hours
"Araldite" 2001	Ciba-Geigy	Two pack epoxy paste. Mix 10:8 by weight resin to hardener. Pot life ~ 2 hours. Apply to both surfaces.	24 hours
"Araldite" 2002	Ciba-Geigy	Two pack epoxy paste. Mix 1:1 by weight. Pot life <10 mins. Apply to both surfaces.	4 hours

TABLE 9.1: Typical adhesives used in tensile adhesion pull-off test

carefully aligned so that a tensile force was uniformly applied through the test area, without imparting a bending moment. It has been assumed that cylinders are pulled-off perpendicularly to the substrate. Sickfeld and Raabe [321] showed that even if the test cylinder is pulled off at an angle of  $88^{\circ}$  the measured adhesion does not vary significantly.

A cross-head speed of 0.05 cm/min was chosen since it gave the necessary force loading rate for the failure of the test assembly within 90 seconds of initial application of the stress specified by BS 3900: Part E10: 1979. This slow extension speed was also beneficial since it provided enough time to observe and record the initiating mode of failure and assess the effect of stress on different specimens under the test.

A minimum of eight samples were tested for each specimen. All the tests were carried out at  $20 \pm 1^{\circ}\text{C}$  and  $50 \pm 5\%$  relative humidity. The chart speed on the test recorder was kept at 1.0 cm/min for all the tests.

#### 9.2.5 Results and Discussion

Results obtained from the tensile adhesion testing of all samples are presented in Tables 9.2 to 9.8 and Figures 9.6 to 9.11. These results may be compared according to the three main influencing factors. These are:

1. Effect of substrate materials
2. Effect of coating materials
3. Effect of coating processes (i.e. IMC and PMC).

Coating Type	Mean Failure Load (kg)		Mean Failure Stress (MNm <sup>-2</sup> )		No and Type of Failure								Standard Deviation		Coefficient of Variation (%)	
	IMC	PMC	IMC	PMC	IMC				PMC				IMC	PMC	IMC	PMC
					A	B	C	D	A	B	C	D				
MRC (120N)	78.1	48.1	1.09	0.67	6A <sub>2</sub>	2B <sub>1</sub>	-	-	1A <sub>2</sub>	2B <sub>1</sub> 5B <sub>3</sub>	-	-	0.33	0.39	30	58
X-226/C2885	24.5	33.0	0.34	0.46	3A <sub>2</sub>	4B <sub>3</sub> 1B <sub>1</sub>	-	-	-	6B <sub>3</sub>	2	-	0.16	0.18	49	40
X-225/C2885	29.3	27.6	0.41	0.38	2A <sub>2</sub>	4B <sub>3</sub> 2B <sub>2</sub>	-	-	3A <sub>2</sub>	3B <sub>1</sub> 2B <sub>3</sub>	-	-	0.17	0.17	41	46
X-220/C075/ C770	58.5	42.5	0.82	0.59	5A <sub>2</sub>	2B <sub>2</sub>	-	1D <sub>1</sub>	2A <sub>2</sub>	5B <sub>3</sub>	1	-	0.22	0.24	27	42
MRC(600)	98.8	38.2	1.38	0.53	6A <sub>2</sub>	1B <sub>3</sub> 1B <sub>1</sub>	-	-	5A <sub>2</sub>	2B <sub>3</sub>	1	-	0.42	0.24	30	45
MRC(200)	158.3	43.6	2.21	0.61	7A <sub>2</sub>	1B <sub>2</sub>	-	-	5A <sub>2</sub>	2B <sub>2</sub>	-	1D <sub>2</sub>	0.36	0.29	16	47

TABLE 9.2: Tensile adhesion results for IMC and PMC semi-flexible PU substrate

Coating Type	Mean Failure Load (kg)		Mean Failure Stress (MNm <sup>-2</sup> )		No and Type of Failure								Standard Deviation		Coefficient of Variation (%)	
	IMC	PMC	IMC	PMC	A	IMC				PMC				IMC	PMC	IMC
						B	C	D	A	B	C	D				
MRC (120N)	83.0	57.6	1.16	0.8	8A <sub>2</sub>	-	-	-	4A <sub>2</sub>	2B <sub>1</sub> 2B <sub>3</sub>	-	-	0.18	0.23	15	28
X-226/C2885	20.5	25.5	0.28	0.36	-	4B <sub>3</sub> 1B <sub>1</sub>	3	-	2A <sub>2</sub>	3B <sub>3</sub>	3	-	0.11	0.15	40	42
X-225/C2885	42.4	37.5	0.59	0.52	5A <sub>2</sub>	2B <sub>2</sub> 1B <sub>3</sub>	-	-	1A <sub>2</sub>	2B <sub>1</sub> 5B <sub>3</sub>	-	-	0.24	0.15	41	29
X-220/C075/ C770	58.7	57.4	0.82	0.80	6A <sub>2</sub>	2B <sub>3</sub>	-	-	3A <sub>2</sub>	4B <sub>3</sub>	-	1D <sub>2</sub>	0.22	0.23	26	29
MRC(600)	34.0	37.5	0.47	0.52	2A <sub>2</sub>	4B <sub>3</sub> 2B <sub>1</sub>	-	-	3A <sub>2</sub>	4B <sub>3</sub>	1	-	0.15	0.18	32	35
MRC(200)	78.5	65.7	1.09	0.92	5A <sub>2</sub>	1B <sub>1</sub> 2B <sub>2</sub>	-	-	5A <sub>2</sub>	3B <sub>3</sub>	-	-	0.23	0.23	21	25

TABLE 9.3: Tensile adhesion results for IMC and PMC rigid PU substrate



Coating Type	Mean Failure Load (kg)		Mean Failure Stress ( $\text{MNm}^{-2}$ )		No and Type of Failure								Standard Deviation		Coefficient of Variation (%)	
	IMC	PMC	IMC	PMC	A	IMC			PMC				IMC	PMC	IMC	PMC
MRC (120N)	235.9	126.5	3.30	1.77	3A <sub>1</sub>	1B <sub>2</sub> 4B <sub>3</sub>	-	-	-	3B <sub>1</sub> 5B <sub>3</sub>	-	-	0.75	0.33	23	19
X-226/C2885	254.5	196.0	3.56	2.74	-	3B <sub>1</sub> 4B <sub>3</sub>	-	1D <sub>2</sub>	2A <sub>1</sub>	1B <sub>1</sub> 5B <sub>3</sub>	-	-	0.61	0.46	17	17
X-225/C2885	354.2	199.0	4.95	2.78	2A <sub>1</sub>	1B <sub>1</sub> 2B <sub>2</sub> 3B <sub>3</sub>	-	-	1A <sub>1</sub>	1B <sub>2</sub> 6B <sub>3</sub>	-	-	0.71	0.54	14	19
X-220/C075/ C770	443.5	254.0	6.20	3.55	2A <sub>1</sub>	2B <sub>1</sub> 3B <sub>2</sub> 1B <sub>3</sub>	-	-	-	2B <sub>2</sub> 4B <sub>3</sub> 1B <sub>1</sub>	-	1D <sub>2</sub>	2.0	0.56	32	16

TABLE 9.4: Tensile adhesion results for IMC and PMC RIM-PU substrate

Coating Type	Mean Failure Load (kg)		Mean Failure Stress (MNm <sup>-2</sup> )		No and Type of Failure								Standard Deviation		Coefficient of Variation (%)			
	IMC	PMC	IMC	PMC	A	IMC		C	D	A	PMC		C	D	IMC	PMC	IMC	PMC
						B					B	C						
MRC (120N)	132.1	108.7	1.84	1.52	-	4B <sub>3</sub> 1B <sub>2</sub>	2	1D <sub>2</sub>	-	8B <sub>3</sub>	-	-	0.4	0.27	22	18		
X-226/C2885	248.0	211.2	3.47	2.95	1A <sub>1</sub>	5B <sub>3</sub> 1B <sub>2</sub>	-	1D <sub>2</sub>	-	6B <sub>3</sub> 1B <sub>1</sub>	1	-	0.73	1.0	21	36		
X-225/C2885	342.4	233.1	4.80	3.26	-	5B <sub>1</sub> 3B <sub>3</sub>	-	-	-	6B <sub>3</sub>	1	1D <sub>1</sub>	1.5	0.44	32	13		
X-220/C075/ C770	349.7	259.2	4.90	3.62	2A <sub>1</sub>	4B <sub>1</sub> 2B <sub>3</sub>	-	-	1A <sub>2</sub>	7B <sub>3</sub>	-	-	0.64	0.46	13	12		

TABLE 9.5: Tensile adhesion results for IMC and PMC C<sub>196</sub> substrate

Coating Type	Mean Failure Load (kg)		Mean Failure Stress (MNm <sup>-2</sup> )		No and Type of Failure								Standard Deviation		Coefficient of Variation (%)		
	IMC	PMC	IMC	PMC	A	IMC				PMC			IMC	PMC	IMC	PMC	
MRC (120N)	111.4	92.5	1.55	1.3	2A <sub>2</sub>	3B <sub>3</sub>	3	-	-	-	5B <sub>3</sub>	3	-	0.24	0.23	16	17
X-226/C2885	200.2	217.6	2.8	3.0	1A <sub>1</sub>	7B <sub>3</sub>	-	-	-	-	6B <sub>3</sub>	2	-	0.41	1.0	14	33
X-225/C2885	231.3	166.7	3.23	2.33	-	8B <sub>3</sub>	-	-	-	-	5B <sub>3</sub> 1B <sub>1</sub>	2	-	0.47	0.47	15	20
X-220/C075/ C770	274.5	207.1	3.84	2.9	-	6B <sub>3</sub> 2B <sub>2</sub>	-	-	-	-	7B <sub>3</sub> 1B <sub>1</sub>	-	-	0.35	0.25	9	8

TABLE 9.6: Tensile adhesion results for IMC and PMC C<sub>198</sub> substrate

Coating Type	Mean Failure Load (kg)		Mean Failure Stress ( $\text{MNm}^{-2}$ )		No and Type of Failure								Standard Deviation		Coefficient of Variation (%)	
	IMC	PMC	IMC	PMC	A	IMC			PMC				IMC	PMC	IMC	PMC
MRC (120N)	120.4	104.6	1.68	1.46	-	7B <sub>3</sub>	1	-	-	5B <sub>3</sub>	2	1D <sub>1</sub>	0.2	0.2	12	14
X-226/C2885	221.6	192.5	3.10	2.7	1A <sub>1</sub>	5B <sub>3</sub>	-	1D <sub>1</sub> 1D <sub>1</sub>	-	6B <sub>3</sub>	2	-	0.77	0.91	25	34
X-225/C2885	191.4	173.6	2.67	2.43	-	1B <sub>1</sub> 4B <sub>3</sub>	1	2D <sub>1</sub>	-	5B <sub>3</sub>	3	-	0.25	0.27	9	11
X-220/C075/ C770	262.6	192.0	3.67	2.68	2A <sub>1</sub>	2B <sub>2</sub> 3B <sub>3</sub>	1	-	1A <sub>2</sub>	5B <sub>3</sub> 1B <sub>2</sub>	1	-	0.38	0.2	10	7

TABLE 9.7: Tensile adhesion results for IMC and PMC C<sub>199</sub> substrate

Coating Condition	Mean Failure Load (kg)	Number and Type of Failure				Mean Failure Stress $\text{MN}\cdot\text{m}^{-2}$	Standard Deviation	Coefficient of Variation (%)
		A	B	C	D			
+ 30 sec	100.1	5A <sub>2</sub>	2B <sub>2</sub>	-	1D' <sub>2</sub>	1.4	0.27	19
+ 30 min	74.0	4A <sub>2</sub>	4B <sub>3</sub>	-	-	1.03	0.08	8
+ 45 min	78.0	5A <sub>2</sub>	2B <sub>3</sub> 1B <sub>2</sub>	-	-	1.1	0.22	20
+ 60 min	72.6	2A <sub>2</sub>	3B <sub>3</sub> 2B <sub>2</sub>	-	1D <sub>1</sub>	1.01	0.09	9
+ 24 hr (outdoor)	54.6	1A <sub>2</sub>	6B <sub>3</sub>	-	1D' <sub>1</sub>	0.76	0.09	12
+ 48 hr (indoor)	56.0	3A <sub>2</sub>	5B <sub>3</sub>	-	-	0.78	0.07	9
+ 3 day (indoor)	39.1	1A <sub>2</sub>	6B <sub>3</sub>	-	1D' <sub>2</sub>	0.54	0.12	23
+ 3 day (outdoor)								
+ 20 day (indoor)	46.6	1A <sub>2</sub>	1B <sub>2</sub>	-	-	0.65	0.12	20
+ 3 day (outdoor)			6B <sub>3</sub>					

TABLE 9.8: Tensile adhesion results for coated PU spray foam substrate

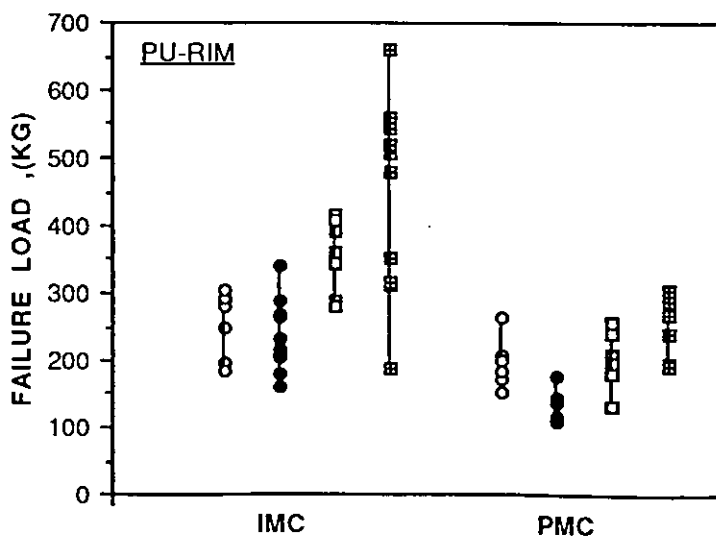
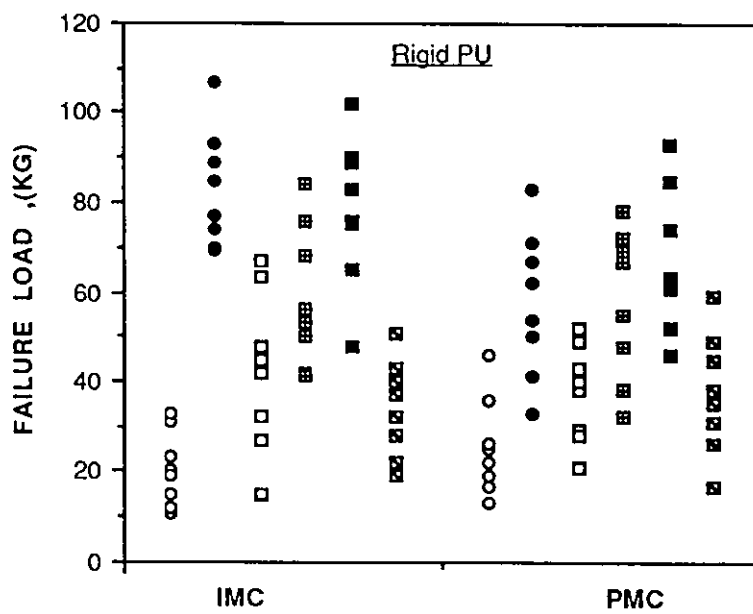
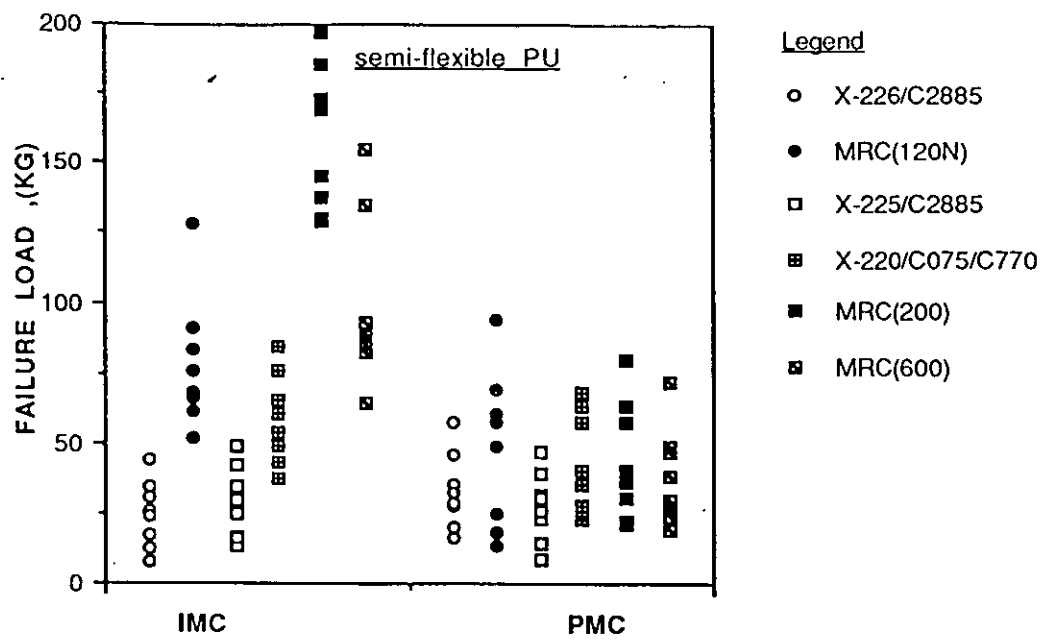


FIGURE 9.6: Bond failure load for IMC and PMC PU substrates (kg)

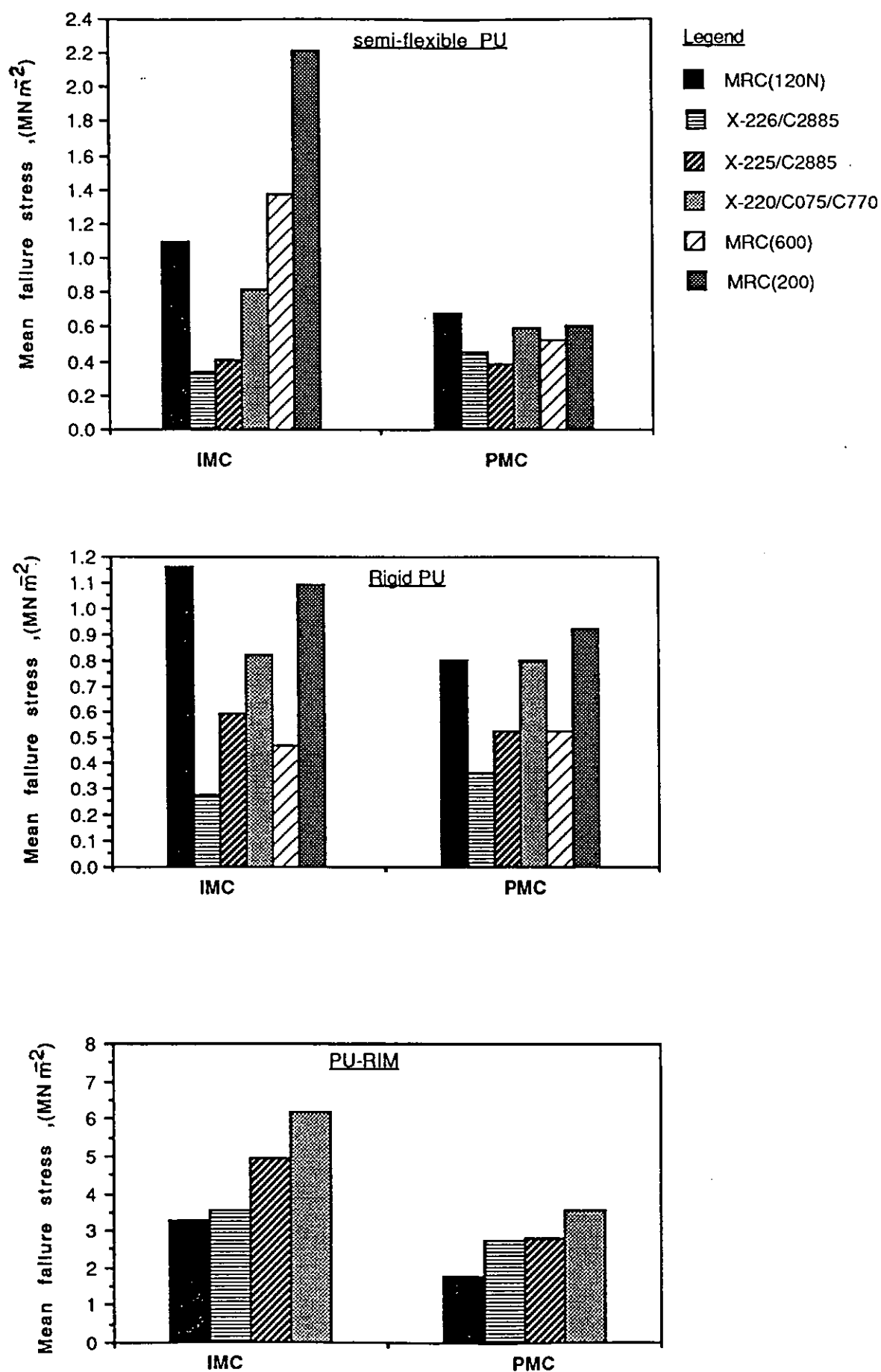


FIGURE 9.7: Mean failure stress for IMC and PMC PU substrates ( $\text{MNm}^{-2}$ )

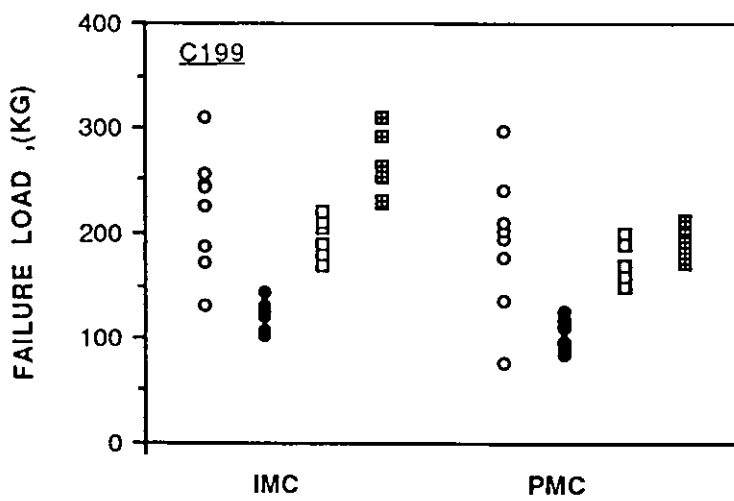
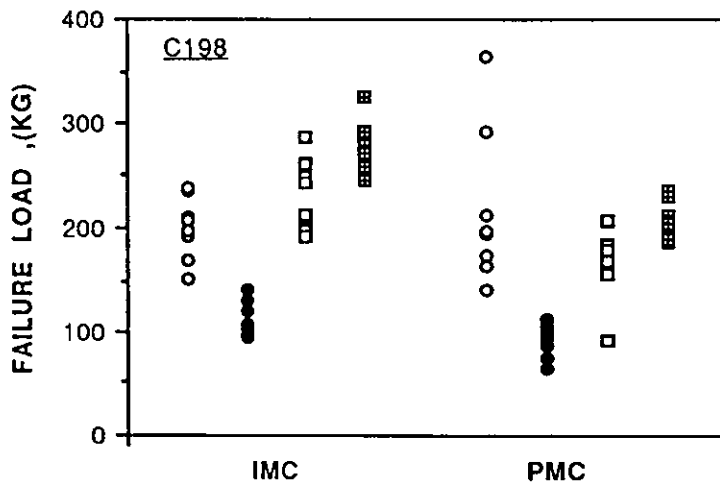
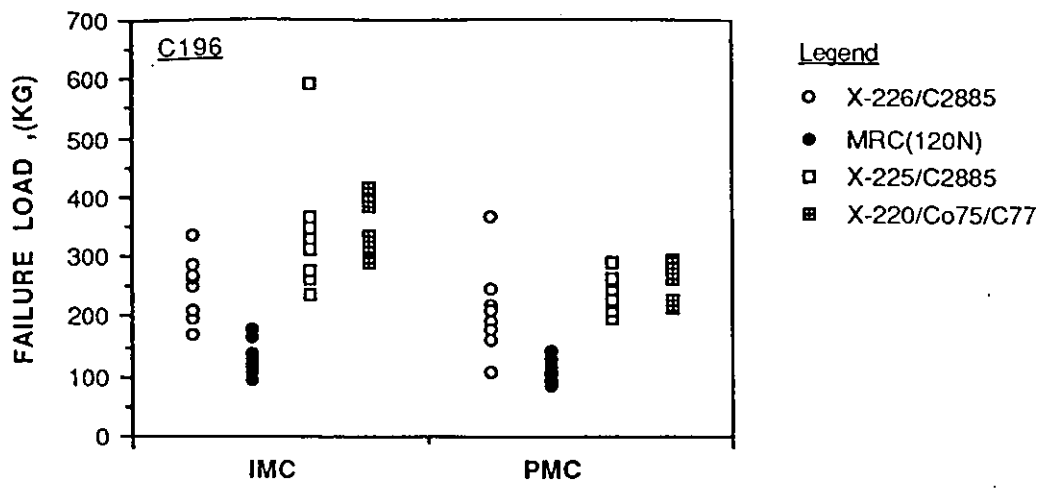


FIGURE 9.8: Bond failure for IMC and PMC polyester substrates (kg)



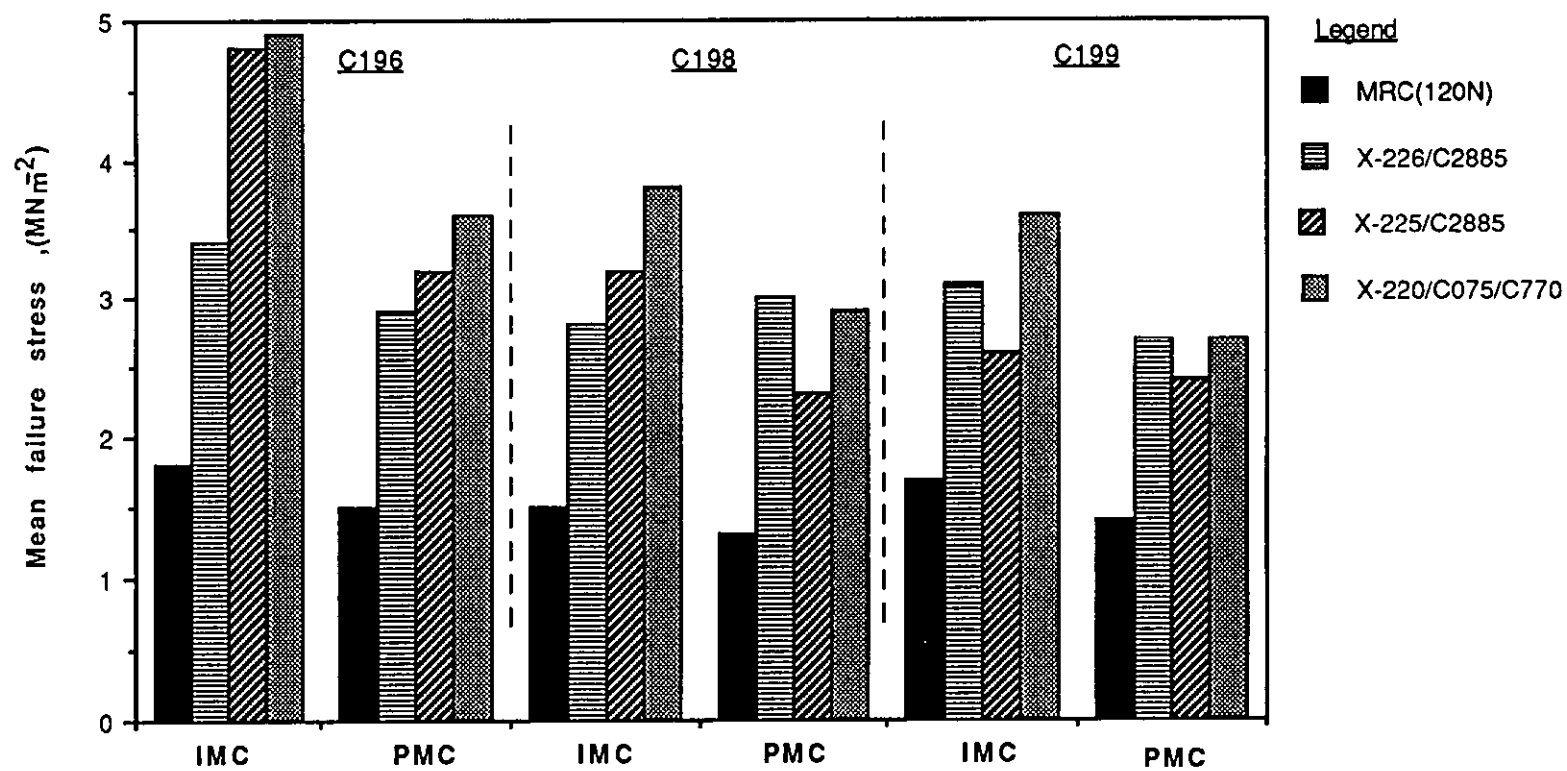


FIGURE 9.9: Mean failure stress for IMC and PMC polyester substrates ( $\text{MNm}^{-2}$ )

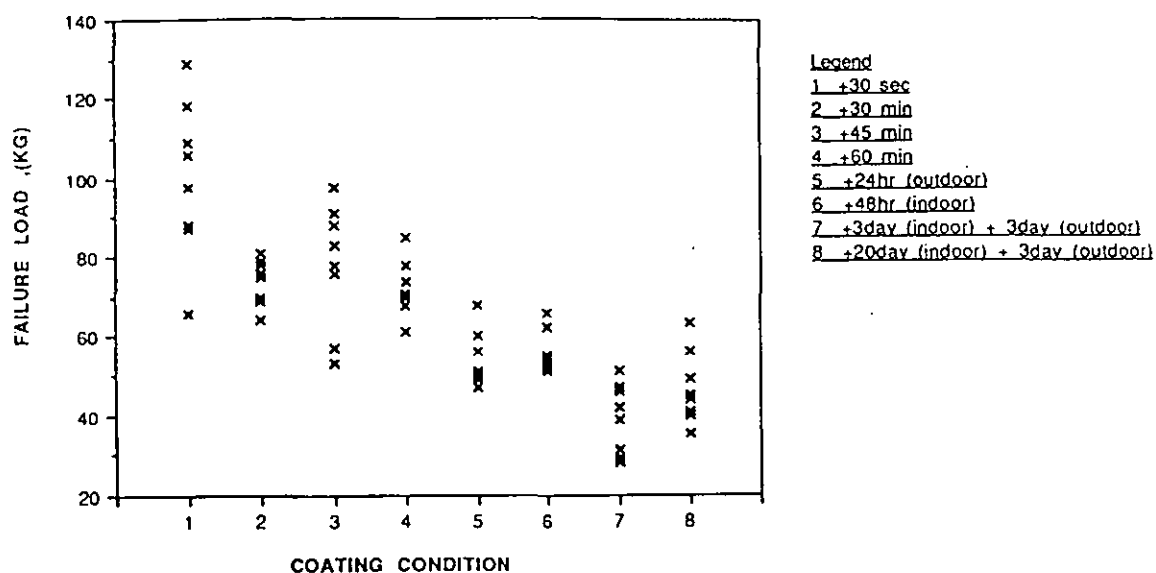


FIGURE 9.10: Bond failure load for coated PU spray foam substrates (kg)

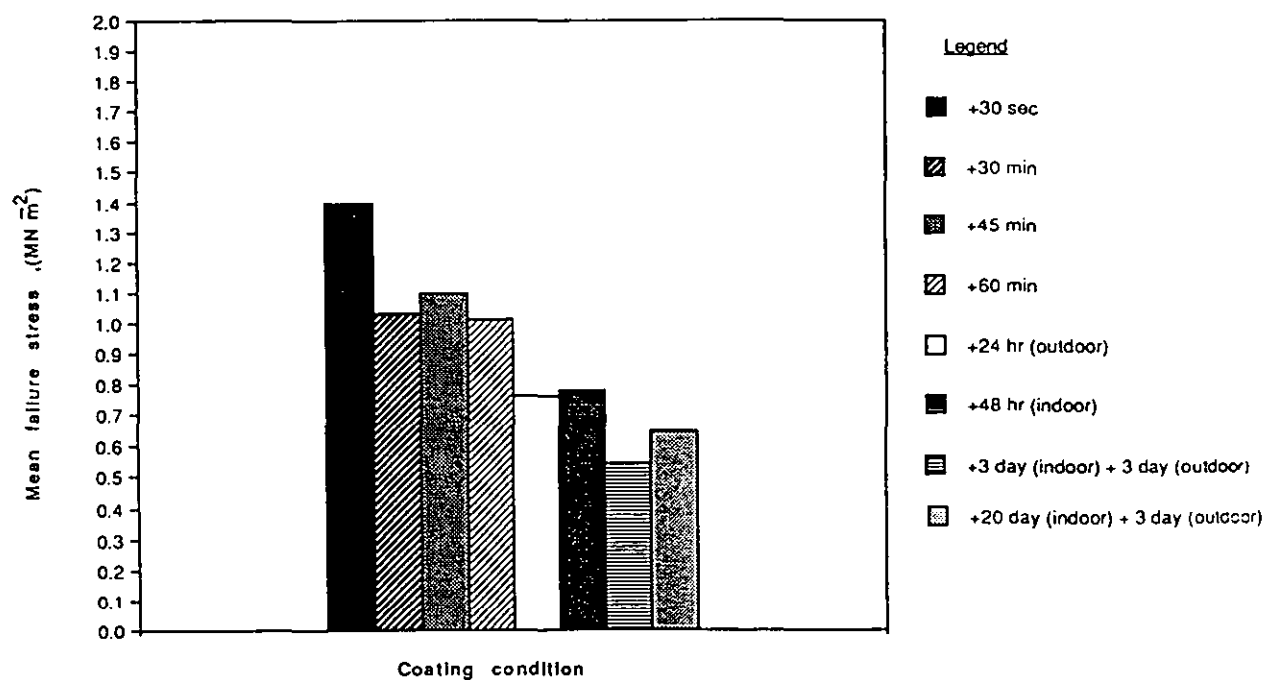


FIGURE 9.11: Mean failure stress for coated PU spray foam substrates (MNm<sup>-2</sup>)

It has also been found useful to study and report on the number and type of joint failures. This observation is particularly informative where IMC and PMC specimens seem to fail similarly and the stress failures of test samples are numerically identical.

The results for rigid PU spray foam systems coated with urethane elastomer where the effect of coating conditions are important are discussed separately.

It may be noted that the term "good adhesion" used throughout this work is indicative of the fact the the coating could not be removed from the substrate easily (i.e. no failure at unacceptably low stress levels). Also, adhesion strength is referred to the minimum tensile stress necessary to break the weakest interface (adhesive failure) or the weakest component (cohesive failure) of the test assembly. Mixed adhesive/cohesive failure may also occur (see Section 9.2.3).

#### Effect of Substrate Materials

##### a) Polyurethane substrates

The bond strengths achieved with IMC and PMC samples of RIM PU substrate were superior to those of semi-flexible and rigid PU surfaces. Generally, the failure stresses for the latter substrates were approximately similar to the semi-flexible samples showing some advantage in IMC and the rigid samples having improved PMC values.

##### b) Polyester substrates

The bond strengths achieved with IMC and PMC samples of C<sub>196</sub> polyester substrate were generally higher than those for corresponding C<sub>198</sub> and C<sub>199</sub> coated surfaces. The only exception was the PMC sample of C<sub>198</sub> substrate coated with X-226/C2885 coating that showed slightly higher

failure stress than PMC for C<sub>196</sub>. In a generalised form it can be written that:

$$\frac{C_{199} < C_{198} < C_{196}}{\text{failure stress increase}}$$

### Effect of Coating Materials

#### a) For polyurethane substrates

The two pack acrylic/urethane coating (X-220/C075/C770) gave the best tensile results for both IMC and PMC samples of RIM polyurethane. The one pack PU coating, MRC (120N) showed the lowest adhesion strength for RIM PU, whereas X-226/C2885 and X-225/C2885 resulted in similar bond strengths for PMC but with improved values for X-225/C2885 used in IMC.

For semi-flexible and rigid substrates the two pack acrylic/urethane coating (X-220/C075/C770), the two pack PU coating (MRC 200) and the one pack PU (MRC 120N) performed more satisfactorily than the others resulting in higher bond strengths for IMC and PMC coated samples.

#### b) For polyester substrates

The combination of X-220/C075/C770, a two pack acrylic/urethane coating with all polyester substrates gave the best overall tensile adhesion results both for IMC and PMC.

The bond strengths resulted from C<sub>196</sub> and C<sub>198</sub> substrates coated with X-225/C2885 coating were generally superior to those of X-226/C2885 but this effect was reversed with C<sub>199</sub> substrate. One pack PU coating, MRC (120N), showed the lowest adhesion strength values for all coating/substrate combinations.

## Effect of Coating Processes

### a) For PU substrates

In general, the adhesion strengths were greater for IMC PU substrates than those for PMC samples. This effect was more evident in the case of RIM-PU and semi-flexible PU than for rigid substrates. In-mould and post-mould coated materials may be regarded as a special form of polymer blends (see Section 10.2.3). By applying the interaction parameter equation [322], given below, to these systems it can be argued that as the solubility parameters of the two phases (i.e. substrate and coating) become closer, there will be less interaction and the substances will become more miscible.

$$\chi_{AB} = \left( \frac{V_r}{RT} \right) (\delta_A - \delta_B)^2$$

where:  $\chi_{AB}$  = interaction parameter

$V_r$  = reference volume

$R$  = gas constant

$T$  = temperature (Kelvin)

$\delta_A$  and  $\delta_B$  = solubility parameters of A (i.e. substrate) and B (i.e. coating systems).

It can be argued that for IMC samples where substrate ingredients (i.e. isocyanate and polyol) are in a liquid, more mobile state and in contact with a fresh layer of coating (i.e. possibly with some free functional groups) then the possibility of  $\delta_A$  and  $\delta_B$  to become closer is much more than PMC. As a result, it can be postulated that the interaction parameter,  $\chi_{AB}$  would be smaller for IMC and hence a more miscible system is achieved at the local level at the interface. This view has been visually supported by SEM micrographs of some IMC

systems where the miscibility phenomena in the form of more diffused interfacial regions are observed (see Chapter 11).

b) For polyester substrates

Generally, IMC samples of all substrates showed superiority over their corresponding PMC. On the whole, the PMC samples showed greater scattering of results and hence higher coefficient of variation.

Type of Failure

The numbers and types of failure for each coated substrate are shown in Tables 9.2 to 9.8. This information was based on expected modes of failure (see 9.2.3) where the following specifications have been included:

1. the number of failures in each case is shown by the figure preceding the type of failure.
2. types of failure are shown by A, B, C and D characters and followed by the position of each failure so that:
  - $A_1$  = cohesive within coating
  - $A_2$  = cohesive within substrate
  - $B_1$  = mixed failure between coating/adhesive
  - $B_2$  = mixed failure between substrate/adhesive
  - $B_3$  = mixed failure between coating/substrate
  - $B_4$  = mixed failure between adhesive/metal rod
  - $D_1$  = adhesive failure between coating/adhesive
  - $D_2$  = adhesive failure between substrate/adhesive.

It must be noted that in the case of mixed failure between adhesive/metal rod (i.e. type  $B_4$ ) the results were discarded and properly assembled test pieces were tested.

a) For polyurethane substrates

For semi-flexible PU, there was some 55% increase on mixed failure ( $B_3$  type) for PMC than IMC samples, but the cohesive failure within substrate ( $A_2$  type) was about 45% higher for IMC than PMC specimens. There were no interfacial failures between substrate and coating for the IMC sample whereas four failures of this type occurred for PMC.

For rigid PU, there was some 48% increase on mixed failure ( $B_3$  type) for PMC than IMC samples. The cohesive failure within substrate ( $A_2$  type) showed a 38% increase for IMC specimens.

For RIM-PU there was some 40% increase on mixed failure ( $B_3$  type) for PMC than IMC samples. The cohesive failure within coating ( $A_1$  type) showed 57% increase for IMC specimens.

b) For polyester substrates

Polyester substrates  $C_{198}$  and  $C_{199}$  showed similar types of failure. The total number of mixed failures between substrate and coating ( $B_3$  type) for IMC and PMC specimens of each substrate were almost equal. There was some 60% increase on the total number of interfacial failure for PMC samples.

In the case of the  $C_{196}$  substrate, the total number of mixed failures ( $B_3$  type) for PMC samples was about 48% higher than those of IMC.

Effect of Coating Conditions on Tensile Adhesion Properties of Coated PU Spray Foam

The results shown in Table 9.8 and Figures 9.10 and 9.11 showed that the coating conditions have had an effect on the degree of adhesion strength. In general, by increasing the time between the substrate

foam production and the application of the coating the failure stress decreased. The other factors such as relative humidity and temperature for indoor and outdoor environments seem to have some effect on the surface to be coated. The adverse outdoor conditions are likely to negatively affect the surface, making it more unsuitable for coating and giving rise to a poor adhesion between the coating and the PU foam surface. This decrease in adhesion is probably due to the PU substrate becoming less reactive as the residual active isocyanate and other polar groups (e.g. urethane) on the surface would pick up water molecules rapidly, especially in humid conditions and form more stable urethane linkages and hydrogen bonded structures respectively. As a result, the polarity of the PU surface would also be decreased.

The complete cohesive failure, in all cases, occurred within the foam substrate region. Only about 6% of the total specimens failed by complete and apparent adhesive failures. The majority of the samples (~ 60%) failed by mixed adhesive and cohesive failures. The mixed failure between coating and substrate constituted 50% of all failures.

An interesting observation was that although no true interfacial failure was recorded, the positions of mixed failures between substrate and coating were somewhat different for various specimens. For systems where severe conditions (i.e. prolonged ageing) had been applied to the substrate prior to the coating, this mixed failure showed some minor delamination of substrate from coating at some parts (approaching the interfacial failure). The UV degradation of the aged surfaces was shown by their darkened appearance. It is presumed that the random location and density of air traps (acting as stress areas) at interfaces of substrate and coating and also the presence of a WBL on these surfaces contributed to their poor adhesion strength (e.g. surface aged for six days).



### 9.3 IMPACT PROPERTIES: MEASUREMENTS, RESULTS AND DISCUSSION

#### 9.3.1 Introduction

With the increased use of plastics materials (see Section 3.1) the nature and characteristics of impact testing has changed over the last two decades. Initially impact testing was a relatively crude operation and the sensitivity of the impact resistance to certain factors had not been recognised. Today, with the new developments, particularly in relation to computer instrumentation, sensors and data processing, the technique and areas of application have improved, with results and the nature of fracture surfaces being better interpreted [323]. Nevertheless, the information on the impact properties of coated plastics is very scarce.

#### 9.3.2 Impact Properties of Coated Plastics

Jones et al [324] studied the application of instrumented falling weight impact (IFWI) technique in relation to the influence of paint on the toughness of plastics for automotive components. A rubber modified polypropylene compound where a combination of good paint adhesion and low temperature toughness were important, was chosen as the substrate. A traditional paint system (incorporating an adhesion-promoting primer, a surfacer and a top coat) and also a polyurethane coating (having an adhesion-promoting primer and a top coat) were used as the coating. The IFWI test on the polypropylene substrates was carried out at different temperatures in order to identify the ductile-brittle transition temperatures. Their findings shown in Table 9.9 clearly demonstrated that the traditional paint system reduced the impact toughness because the onset of embrittlement occurs at a temperature some 25°C higher. The PU top coat, on the other hand, had little effect on the overall toughness. It may be argued that solvent stress cracking due to the type and amount of solvents present

in coating systems used on some plastics like polypropylene will affect their impact properties.

TABLE 9.9: IFWI determination of ductile-brittle transition temperatures ( $5 \text{ m} \cdot \text{s}^{-1}$ ) (After Ref 324)

Material	Ductile-brittle transition temperature ( $^{\circ}\text{C}$ )
Unpainted polypropylene compound	-55
Polypropylene compound painted with traditional system	-30
Polypropylene compound painted with polyurethane top coat	-52

Dragovic [325] showed the effect of coating on the impact strength of a polycarbonate specimen using an unsuitable, very brittle paint and a specially formulated, very flexible two-pack PU paint. Considering the specimens after the falling weight test, he concluded that because of good adhesion of the paint film to the plastic's surface, the crack produced in the paint film is propagated in the plastics substrate in the form of a notch and, since the tear propagation resistance of plastics is generally less than their ultimate tear strength, the material breaks.

Mirgel and Kelso [326] reported on the impact properties of coated plastics being used in the exterior parts of cars. Specimen failure on impact, Figure 9.12(a), especially at low temperatures, have been associated with brittleness of the paint, and it has been recommended that flexible primers and top coats can eliminate the notch effect as shown in Figure 9.12(b). They also showed that due to coating flexibility, a decrease in the elasticity of the coated ABS samples

would result in a low impact failure (Figure 9.12(c)). Some studies [327] have expressed that the thermal history and moulding conditions of a plastic sample are more important in contributing to a meaningful impact result rather than some specific intrinsic material response. Nevertheless, to date, as far as we are concerned, there is no reported work concerning the differences in impact properties of in-mould and post-mould coated plastics materials having similar chemical ingredients for both coating and substrate but different coating applications.

In this section, the impact properties of polyurethane and polyester coated substrates have been studied in an attempt to distinguish how various factors (i.e. substrate and coating materials and coating processes) would influence the results.

### 9.3.3 Experimental Procedure

#### a) Sample Preparation

The test specimens for all substrate/coating combinations were cut into squares of 7.5 x 7.5 cm<sup>2</sup>. The IMC and PMC samples of moulded materials were tested having their original thickness. For coating spray PU foam specimens, the variation in thickness between different samples was corrected and the thickness for all coating combinations was kept the same throughout. The approximate thickness for various coated substrates are given in Table 9.10.

Substrate	Range of sample thickness for impact (mm)
Semi-flexible polyurethane	9.8-10.2
Rigid polyurethane	10.0-10.3
RIM-polyurethane	6.4- 6.6
Crystic polyesters	4.8- 5.0
Rigid spray polyurethane foam (Isofoam SS-0658)	16.5-18.0

TABLE 9.10: Sample thickness for impact testing

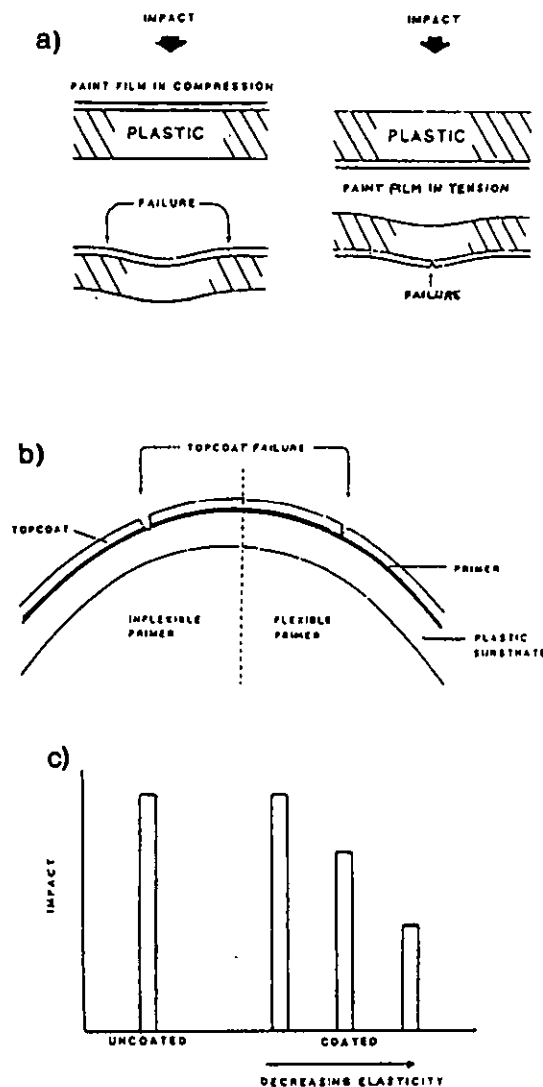


FIGURE 9.12: a) Impact failure of coated plastics  
b) Effect of primer flexibility on crack propagation  
c) Effect of coating flexibility on impact properties of ABS specimens (after ref 326)

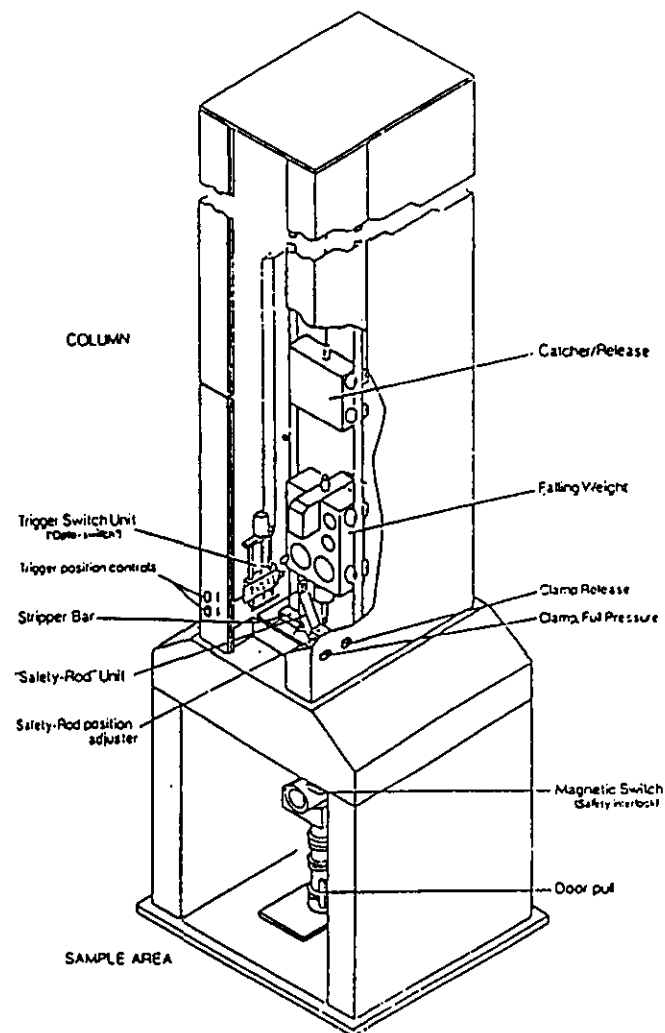


FIGURE 9.13: Instrumented Falling Weight Impact Tester (after ref 328)

b) Impact Testing

A Rosand instrumented falling weight impact tester (type 5A) was used to assess the impact properties of coated polyurethane and polyester specimens. A schematic diagram illustrating the Rosand impact tester is given in Figure 9.13 [328].

The impactor probe and the impact weight are fitted with a transducer. This assembly when released would accelerate, due to gravity, towards the sample holder. The falling impactor tip triggers a transient recorder just prior to striking sample. The transient recorder will then start collecting and storing data of the force-time during deformation and fracture. The impact assembly is equipped with a microcomputer which on receiving the force signals would process the data for force-time or force-deflection graphs. The stored data can also be analysed to give information about gradient and through integration of the force-time data, energy values at any given point are found. A force-deflection trace demonstrating the impact features is shown in Figure 9.14 [329].

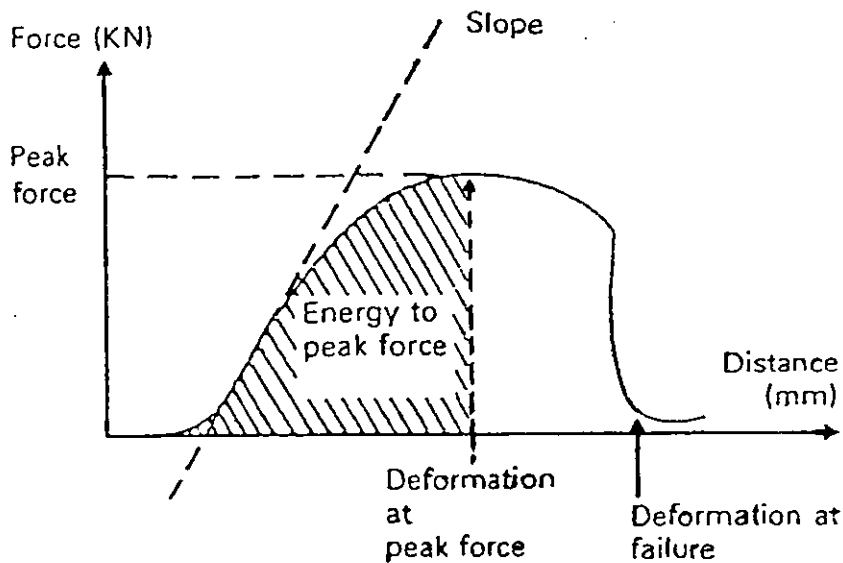


FIGURE 9.14: Impact force-deflection trace (after Ref 329)

### Testing Conditions

Details of the impact test conditions are given below:

Impact height	464 mm
Impact mass	25.35 kg
Impact speed	3.0 m/s
Impactor tip	10 mm hemispherical (ISO)
Sweep time	20 ms
Delay	10
Filter	3 kHz
Temperature	20 ± 1°C

Ten specimens were cut from each sample and tested so that average readings for a broad scatter of results could be found. The above conditions were selected after a number of preliminary tests and considering the following relationships [330]:

$$V = \sqrt{2gh}$$

$$E_O = mgh$$

$$m \geq \frac{3 \times E_{tot}}{gh}$$

where: V = Velocity (m/s)  
g = Acceleration due to gravity (9.81 m/s<sup>2</sup>)  
h = Test height (m)  
E<sub>O</sub> = Available impact energy (J)  
m = Impact mass (kg)  
E<sub>tot</sub> = Total energy available (J)

Using a sweep scan through preset times, from 2 ms to 8 seconds, a recording is taken after the data system has been triggered. Delay values indicate the number of points recorded after the trigger, so that a delay of 9 means that 90% of the points are to be taken after the trigger signal [328].

Filtering is applied in order to reduce undesired vibrations, especially for brittle samples. It must be noted that excessive filtering may result in hiding some of the important characteristics of the fracture behaviour [330].

### c) Types of Impact Failure

Various types of composite material response recorded from an instrumented impact test are shown in Figure 9.15. The first material (Figure 9.15(a)) is brittle which undergoes a linear elastic deformation and then shatters. The second material (Figure 9.15(b)) is ductile which, after an elastic deformation, the material passes through a yield point and undergoes plastic deformation before it breaks. The other two types (Figures 9.15(c) and 9.15(d)), brittle/ductile and ductile/brittle failures, respectively, are more specific and are mainly associated with more heterogeneous materials. Brittle/ductile failure takes place before peak force has been reached (i.e. prior to yield) whereas ductile/brittle failure takes place after peak force has been reached (i.e. beyond yield).

### 9.3.4 Results and Discussion

Results obtained from the impact testing of all samples are presented in Tables 9.11 to 9.13 and Figures 9.16 to 9.18. The peak energy was found to be the most reproducible calculated result and was therefore used to compare the different IMC and PMC samples. The effect of

different variables (see Section 9.2.5) on impact properties (i.e. peak energy) of coated samples are discussed here.

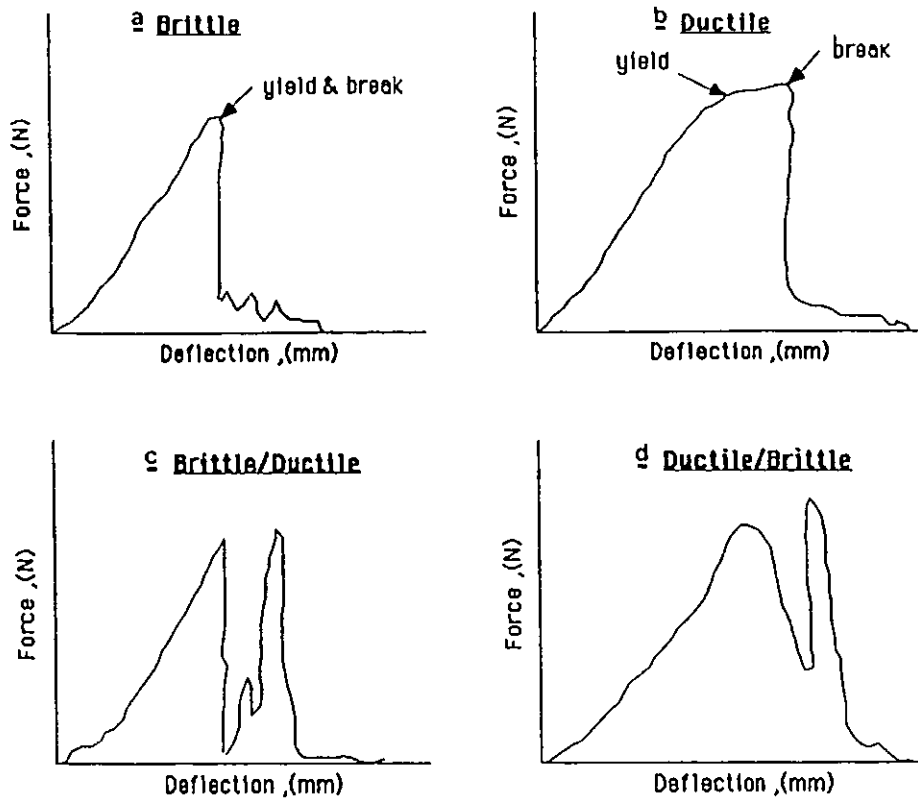


FIGURE 9.15: Different types of impact failure

Types of failure (see Section 9.3.3(c)) for all tested samples were also recorded and presented in Tables 9.11 to 9.13. This information was found particularly useful where a number of coated samples exhibited similar peak energy values and quantitative results could not easily be distinguished. The number and type of impact failures are reviewed as a separate issue in the last section. The results for rigid PU spray foam systems (Isofoam SS-0658) coated with urethane elastomer (Futura-thane 5000) where the effect of coating conditions are important are discussed separately.



Substrate	Coating Type	Peak Force (N/mm)		Peak Deflection (mm)		Peak Energy (J/mm)				Type of Failure*	
		IMC	PMC	IMC	PMC	IMC	PMC	IMC	S.d <sup>†</sup> PMC	IMC	PMC
Semi- flexi- ble PU	MRC(120N)	508	542	13.15	14.46	3.44	4.18	0.49	0.71	D	DB
	X-226/C2885	430	447	11.07	9.54	2.47	2.25	0.41	0.52	D/DB	DB
	X-225/C2885	511	660	10.76	13.26	2.89	4.60	0.39	0.96	DB	DB
	X-220/C075/C770	563	396	11.45	10.21	3.39	2.13	0.63	0.37	D	DB/D
	MRC(600)	624	670	12.23	9.31	4.01	3.26	0.52	0.5	D	DB/D
	MRC(200)	885	518	11.06	8.74	5.12	2.37	0.80	0.69	D	DB
Rigid	MRC(120N)	412	338	12.16	11.05	2.64	1.97	0.43	0.21	D	D
	X-226/C2885	267	308	10.73	10.85	1.28	1.76	0.22	0.31	DB	D
	X-225/C2885	298	279	9.45	6.36	1.39	0.93	0.27	0.25	D/DB	DB
	X-220/C075/C770	317	302	8.71	12.29	1.45	1.96	0.19	0.26	D	D
	MRC(600)	186	241	8.42	9.19	0.81	1.16	0.16	0.18	DB	DB
	MRC(200)	381	306	7.28	8.31	1.47	1.34	0.29	0.24	D	D
RIM-PU	MRC(120N)	1167	1302	10.43	11.22	6.33	7.78	0.87	1.24	D	D/DB
	X-226/C2885	1125	1211	10.21	9.62	6.07	6.13	0.76	0.94	DB	DB
	X-225/C2885	1460	1284	9.17	12.35	6.79	7.90	0.84	1.08	DB	DB
	X-220/C075/C770	1362	1029	12.68	13.15	8.63	6.91	1.10	1.0	D	DB

\* D = ductile, DB = ductile/brittle

† S.d = sample standard deviation

TABLE 9.11: Impact properties of coated polyurethane substrates

Substrate	Coating Type	Peak Force (N/mm)		Peak Deflection (mm)		Peak Energy (J/mm)				Type of Failure*	
		IMC	PMC	IMC	PMC	IMC	PMC	IMC	s.d <sup>†</sup> PMC	IMC	PMC
C <sub>196</sub>	MRC(120N)	970	1230	1.68	1.93	0.94	1.21	0.15	0.42	BD	B
	X-226/C2885	1305	1265	1.29	1.88	1.07	1.10	0.19	0.15	B	D/DB
	X-225/C2885	1138	1251	1.75	1.23	1.26	0.74	0.22	0.1	B	DB
	X-220/C075/C770	1640	1092	1.43	2.26	1.37	1.32	0.21	0.43	B	DB
C <sub>198</sub>	MRC(120N)	1099	853	1.37	1.17	0.81	0.52	0.31	0.18	BD	BD
	X-226/C2885	921	960	1.33	1.60	0.58	0.93	0.14	0.26	BD/B	BD
	X-225/C2885	952	762	1.94	2.18	1.05	1.02	0.17	0.22	D/DB	DB/D
	X-220/C075/C770	1032	942	1.85	1.51	1.16	0.97	0.22	0.15	B	D/DB
C <sub>199</sub>	MRC(120N)	845	593	1.37	2.44	0.63	0.85	0.11	0.21	BD/B	BD
	X-226/C2885	938	991	1.28	1.35	0.76	0.80	0.15	0.17	BD	BD
	X-225/C2885	842	920	1.81	1.46	0.92	0.83	0.26	0.31	DB	DB
	X-220/C075/C770	878	722	1.95	2.04	1.05	0.94	0.23	0.34	BD/B	DB

\* B = brittle, D = ductile, BD = brittle/ductile, DB = ductile/brittle

† S.d = sample standard deviation

TABLE 9.12: Impact properties of coated polyester substrates

Coating Conditions	Peak Force (N/mm)	Peak (mm)	Peak Energy (J/mm)	Energy S.d <sup>/</sup>	Type of Failure*
+ 30 sec	545	13.12	3.64	0.36	D
+ 30 min	528	12.24	3.32	0.51	D/DB
+ 45 min	567	13.59	3.90	0.53	D
+ 60 min	541	11.07	3.06	0.40	D/DB
+ 24 hr (outdoor)	491	10.12	2.56	0.17	DB/D
+ 48 hr (indoor)	485	10.58	2.63	0.22	DB
+ 3 day (indoor) + 3 day (outdoor)	291	6.52	1.02	0.30	DB
+ 20 day (indoor) + 3 day (outdoor)	447	9.17	2.16	0.23	DB

TABLE 9.13: Impact properties of coated PU spray foam

\* D = ductile  
DB = ductile/brittle

<sup>/</sup> S.d = sample standard deviation

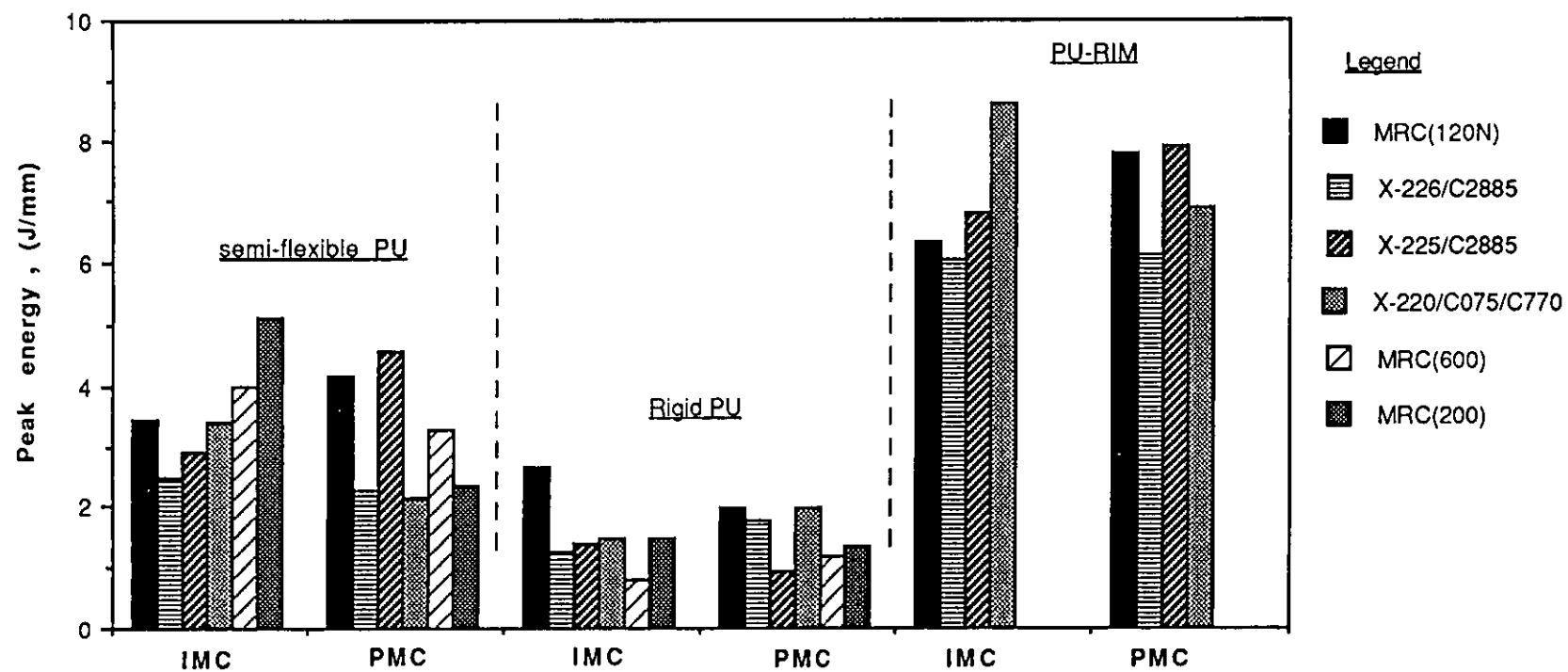


FIGURE 9.16: Average peak energy for IMC and PMC PU substrates (J/mm)

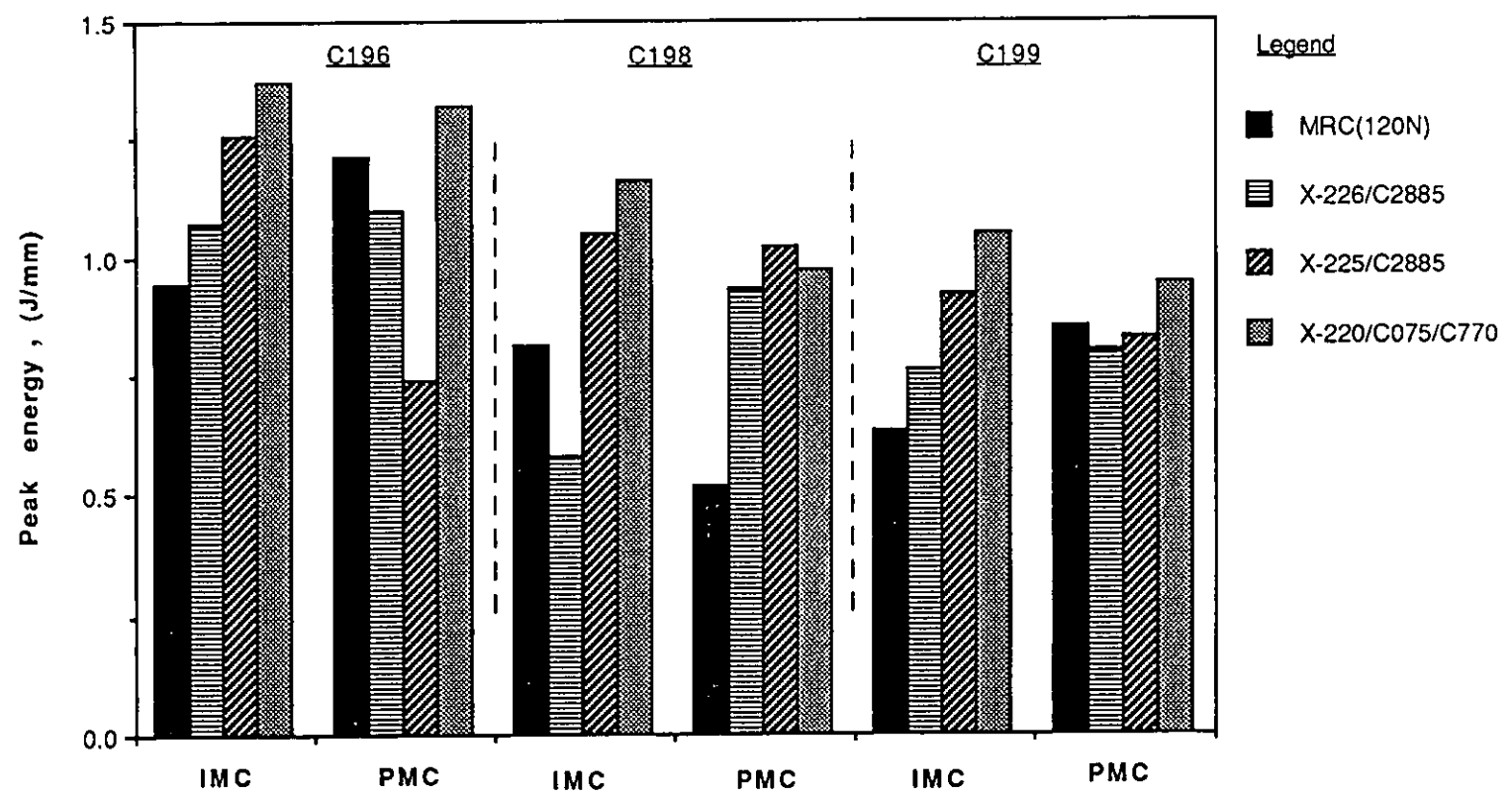


FIGURE 9.17: Average peak energy for IMC and PMC Polyester substrates (J/mm)

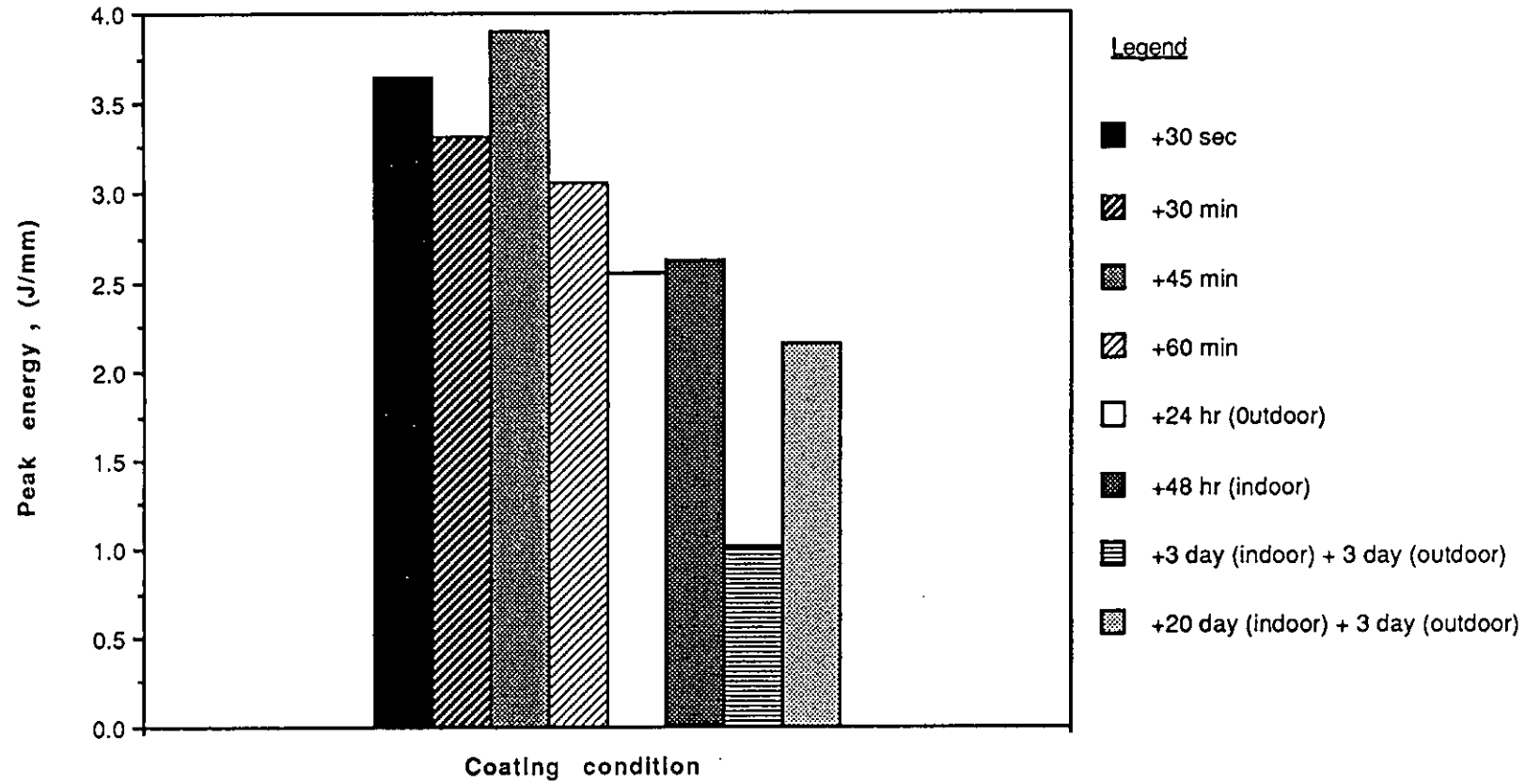


FIGURE 9.18: Average peak energy for coated spray foam substrates (J/mm)

### Effect of substrate materials

#### a) Polyurethane substrates

The IMC and PMC samples of RIM PU showed superior peak energy values to those of semi-flexible and rigid foam substrates. The average peak energies for all semi-flexible foam samples were higher than those of corresponding rigid foams. In a generalised form it can be written that:

$$\begin{array}{c} \text{rigid foam} < \text{semi-flexible foam} < \text{RIM} \\ \hline \text{peak energy increase} \end{array}$$

#### b) Polyester substrates

The peak energies achieved with coated C196 substrates were often higher than those for corresponding C198 and C199 coated surfaces. Generally, the peak energy values of the latter substrates were similar with C198 showing some increase for most of the IMC samples.

### Effect of Coating Materials

#### a) For polyurethane substrates

There was no systematic variation from coating to coating. For semi-flexible foam and RIM substrates the two pack PU coatings MRC (200) and X-220/C075/C770 showed some higher peak energy values for IMC samples than the others. The one pack coating MRC (120N) performed more satisfactorily resulting in higher peak energy for rigid foam.

b) For polyester substrates

The two pack coating X-220/C075/C770 exhibited higher peak energy for both IMC and PMC samples of polyester substrates. The effect of other coatings on impact properties of polyester surfaces could not be systematically distinguished. Nevertheless, it was apparent that one pack coating X-225/C2885 showed some advantage (i.e. higher peak energy) with most of the coated systems and one pack coatings MRC (120N) and X-226/C2885 exhibiting smaller impact energies especially with IMC polyester substrates. As a rough estimate the influence of various coatings on impact properties of IMC and PMC polyesters can be summarised as:

$$\text{MRC (120N)} < \text{X-226/C2885} < \text{X-225/C2885} < \text{X-220/C075/C770}$$

—————→  
peak energy increase

Effect of Coating Processes

a) For polyurethane substrates

Generally, the IMC samples of semi-flexible foam gave greater peak energy than those of PMC. This effect was more evident with samples coated with two pack coatings. The influence of coating processes on IMC and PMC samples of rigid foam and RIM substrates were more complex.

b) For polyester substrates

The IMC samples of three polyester surfaces where two pack coating X-220/C075/C770 and one pack X-225/C2885 were applied showed superiority (i.e. larger peak energy) to their corresponding PMC samples. This effect was reversed for polyester substrates coated with one pack X-226/C2885 coating where PMC specimens exhibited greater peak energies



than IMC's. The influence of coating processes on these surfaces coated with MRC (120N) was not distinguished.

#### Effect of Coating Conditions on Impact Properties of Coated PU Spray Foam

The results shown in Table 9.13 and Figure 9.18 indicated that the coating conditions (i.e. ageing, temperature, humidity) have had some effect on the impact properties of coated specimens. As expected, a simple direct relationship demonstrating the influence of all the factors involved on the impact behaviour could not be proposed. However, it may be stated that, in general, the average peak energy showed some decrease as the time between the substrate foam production and the coating application was increased. The samples whose coatings were applied within the first hour of PU foam production showed similar peak energy values (i.e. standard deviation to be considered). For the other samples in which coatings had been applied from 24 hours to some three weeks after the substrate was produced a reduction of 15 to 45% in peak energy was recorded. The worst specimen was based on a substrate aged for six days; its surface had darkened showing UV attack and that a relatively thick weak boundary layer had been formed.

#### Types of Failure for Various Coated Substrates

Since an assessment based entirely on the peak energy data had its shortcomings, a record of types of failure and the location of fracture of tested samples was therefore necessary in order to gain extra information. The failure analysis of coated PU and polyester samples in the IFWI test where the crack propagation involved a number of variables is shown in Tables 9.11 to 9.13.

It may be argued that the type and extent of failure observed both on the surface and inside the composite systems have been affected by the substrate and coating materials and also by the type of substrate/coating interface due to different coating processes.

For coated PU substrates, both IMC and PMC samples showed typical ductile or ductile/brittle failures upon impact. It was interesting to note that the impacted area with the ductile deformation showed a punch-like fracture surface, mostly associated with IMC samples. For IMC samples of semi-flexible foam, this punched-out area was often found still attached to the test specimen. On the other hand, for PMC specimens the impacted area was normally cracked and broke away from the rest of the test specimen. It may be argued that the ductile deformation observed with many IMC samples, particularly with two pack coatings, indicated a stronger, more coherent interfacial region between substrate and coating. This finding was also observed by some microscopy studies of IMC and PMC samples (see Chapter 11).

Coated polyester substrates exhibited various types of deformation upon impact. Therefore, the appearance of fractured specimens as well as the form of the force-deflection curves and the magnitude of the impact energy were studied in order for various types of failure to be distinguished.

The coated PU spray foam samples showed ductile and ductile/brittle failures upon impact. Ductile/brittle type deformation was generally associated with those samples whose substrates had been subjected to ageing and severe environmental conditions prior to coating. On the other hand, the ductile type failure was often observed with freshly coated substrates (i.e. within the first hour of foam production).

## 9.4 NON-QUANTITATIVE ADHESION TESTS: MEASUREMENTS, RESULTS AND DISCUSSION

### 9.4.1 Introduction

Non-quantitative adhesion tests basically refer to those empirical test procedures used to assess the performance of a coating, by measuring a property (e.g. cross-out and scratch hardness) which depends, among other factors, on the adhesion of the coating to the substrate.

Although the term "hardness" for coating or bulk substrates (not to be confused with IRHD or Shore) has been in use for many years, a true and universal meaning applicable to all cases has proved difficult to find. Similarly a detailed definition for hardness testing would vary with the method of testing and also the hardness value for each test varies with loading weight, loading rate and loading method at the time of observation. Therefore it can be argued that an absolute method of hardness does not exist. Many types of hardness testing are used for polymeric materials [315,331-333]. Cross-cut and scratch methods of hardness testing, although very quick and simple to use have been applied on a number of painted materials and will be reviewed here.

### 9.4.2 Cross-Cut Hardness Test

This is a test method for assessing the adhesion of a coating to a substrate. Bikerman [216] has rejected the validity of the cross-cut method, stating that the knife action will only crush the coating and the crushing force has no relation to the forces acting between the coating and the substrate. Therefore he argues that this type of measurement on a free film clamped at both ends will give very similar

results to the coating/substrate combination. He argues that if the knife is pushed deeper, removing a layer of the substrate, again this does not alter the essential mechanisms but, instead of one, two materials are crushed, and the measured force is the sum of those needed to form coating and substrate separately.

On the other hand, Briggs [334] has argued that the cross-cut and scratch tests give results more closely related to practical paint performance than the more complex quantitative methods.

The test procedure described here is based on a British Standards method of test for paints as BS 3900: Part E6: 1974.

#### 9.4.2.1 Experimental Procedure

Applying a uniform pressure on a multiple cutting tool with six cutting edges 1 mm apart with its face in a plane normal to the specimen surface, a lattice pattern of 25 squares each of 1 mm side was cut into the coating, penetrating through it to the substrate. The sample was then gently cleaned with a soft brush five times backwards and five times forwards along each of the diagonals of the lattice pattern. The pattern was then visually examined for partial or complete detachment of the coating and classified and rated on a numerical, but arbitrary, system according to the extent of detachment. Classification of test results according to BS 3900: Part E6: 1974 is shown in Appendix 3.

Each sample was tested in at least three places. If these three results did not agree, in terms of classification mentioned above, then the test was repeated at three more places and all the results recorded.

#### 9.4.2.2 Results and Discussion

Tables 9.14 and 9.15 show the results of the cross-cut testing of each IMC and PMC substrate/coating combination. These results are also illustrated graphically in Figures 9.19 and 9.20. The effect of different variables on cross-cut hardness results are discussed here.

##### Effect of Substrate Materials

###### a) Polyurethane substrates

The IMC and PMC samples of RIM polyurethane substrate showed better cross-cut hardness performance than semi-flexible and rigid PU substrates. The effect of substrate on hardness is more evident with IMC samples. The overall effect of semi-flexible PU substrates is superior to that of the rigid PU surface.

###### b) Polyester substrates

C<sub>196</sub> polyester substrates gave a more satisfactory cross-cut hardness performance than C<sub>198</sub> and C<sub>199</sub> surfaces. The effect of C<sub>196</sub> substrate is less evident for PMC samples where all types of polyester substrates showed similar hardness values. For IMC specimens, the effect of substrates is more obvious so that it can be written that:

$$\begin{array}{c} C_{199} < C_{198} < C_{196} \\ \xrightarrow{\hspace{1.5cm}} \\ \text{Cross-cut hardness increase} \end{array}$$

##### Effect of coating materials

###### a) For polyurethane substrates

The effect of coating materials on cross-cut hardness of both IMC and PMC samples of RIM-PU substrate can be summarised as:

Substrate/coating Combination	Cross-cut Classification	
	IMC	PMC
PU-RIM/MRC (120N)	2	4
PU-RIM/(X-226/C2885)	1	2
PU-RIM/(X-225/C2885)	2	3
PU-RIM/(X-220/C075/C770)	1	1
Semi-flexible PU/MRC (600)	0	2
Semi-flexible PU/MRC (200)	1	4
Semi-flexible PU/MRC (120N)	3	4
Semi-flexible PU/(X-226/C2885)	4	3
Semi-flexible PU/(X-225/C2885)	3	2
Semi-flexible PU/(X-220/C075/C770)	2	2
Rigid PU/MRC (600)	4	4
Rigid PU/MRC (200)	1	2
Rigid PU/MRC (120N)	2	3
Rigid PU/(X-226/C2885)	5	3
Rigid PU/(X-225/C2885)	4	3
Rigid PU/(X-220/C075/C770)	3	3

TABLE 9.14: Cross-cut hardness results for IMC and PMC polyurethane substrates

Substrate/coating Combination	Cross-cut Classification	
	IMC	PMC
C196/MRC (120N)	2	4
C196/(X-226/C2885)	0	1
C196/(X-225/C2885)	1	2
C196/(X-220/C075/C770)	0	2
C198/MRC (120N)	3	4
C198/(X-226/C2885)	1	1
C198/(X-225/C2885)	2	3
C198/(X-220/C075/C770)	1	2
C199/MRC (120N)	2	4
C199/(X-226/C2885)	2	2
C199/(X-225/C2885)	2	3
C199/(X-220/C075/C770)	2	2

TABLE 9.15: Cross-cut hardness results for IMC and PMC polyester substrates

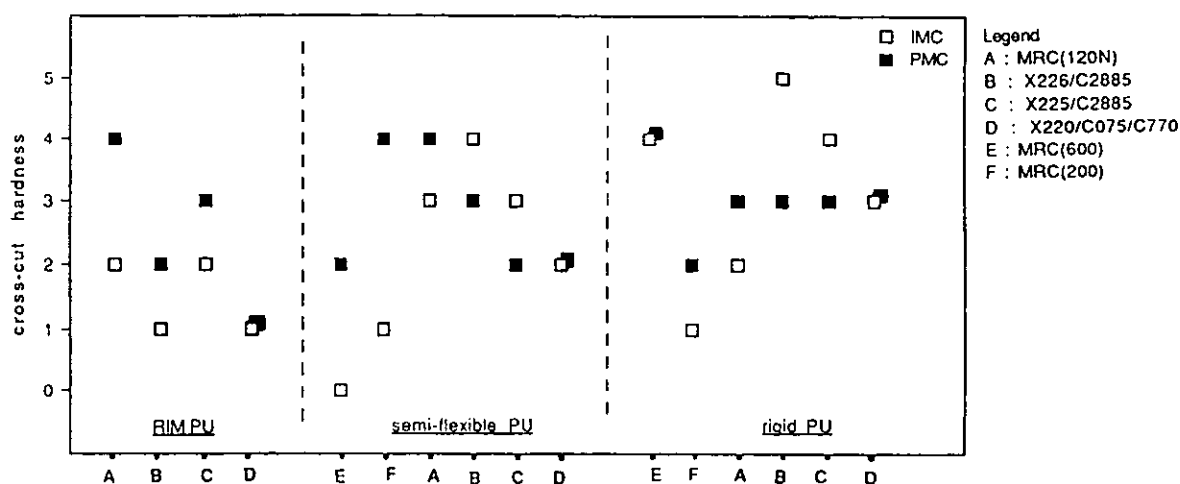


FIGURE 9.19: Cross-cut hardness classification for IMC and PMC PU substrates

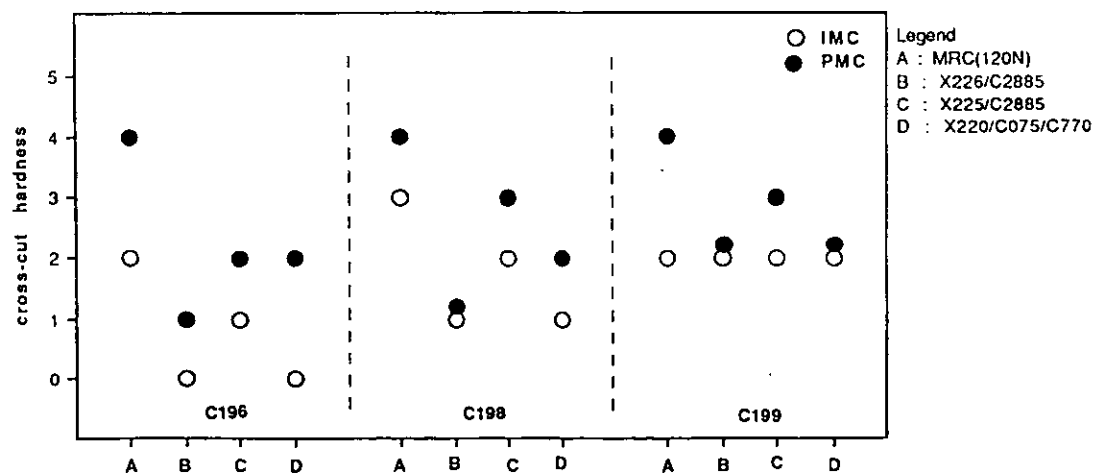


FIGURE 9.20: Cross-cut hardness classification for IMC and PMC polyester substrates





### Effect of Coating Processes

#### a) For polyurethane substrates

In general, the majority of IMC PU substrates showed superiority to their corresponding PMC samples. This distinction was most significant for RIM-PU substrates. For semi-flexible and rigid PU surfaces the hardness values of a number of IMC and PMC samples proved to be very similar. In these cases the difference in the amount of detached coating from corresponding IMC and PMC samples were within 10% to 15%, but because of classification regulations (see Appendix 3), they have been rated differently.

#### b) For polyester substrates

Except for a few cases where the IMC and PMC samples showed similar cross-cut hardness values, for the majority of IMC specimens the hardness values were superior to those of PMC.

It can be concluded that different variables (i.e. substrates, coatings and coating processes) would have different effects on the cross-cut hardness values of coated specimens. This finding is contrary to Bikerman's view stating that the same coating on different substrates would give similar cross-cut hardness values. Bikerman's argument may be generally true for very thick coatings but for thin coating (i.e.  $< 50 \mu\text{m}$ ) and the type of coatings used in these experiments it is not valid.

#### 9.4.3 Scratch Hardness Test

Scratch resistance is the most important method of measuring the hardness of a coating from a practical viewpoint and is widely used in industry [331]. This is usually determined by pencil hardness, a rapid, inexpensive method of measuring the film hardness of a coating

on a substrate in terms of drawing leads or pencil leads of known hardness. The test method followed here is that specified in ASTM D3363-74.

#### 9.4.3.1 Experimental Procedure

A range from 6B to 6H of high quality drawing pencils (Rexel Cumberland: Derwent graphic) were sharpened in such a way that approximately 3 to 6 mm of wood was removed from the point of each pencil, and the exposed pencil leads were abraded using a No 400 carbide abrasive paper. Starting with the hardest lead, the pencil was held firmly against the coated sample (placed on a firm horizontal surface) at a 45° angle and pushed away for a stroke of about 6 mm. Exerting sufficient uniform pressure downward and forward the process is continued down the scale of hardness until a pencil is found that will neither cut through nor scratch the coating. The hardest pencil that does not cut into the coating for a stroke of at least 3 mm will give the gouge hardness, whereas the hardest pencil that will not rupture or scratch the coating will determine the scratch hardness. A minimum of six determinations for gouge hardness and scratch hardness for each pencil were carried out. As may be gathered the technique is likely to be operator sensitive.

#### 9.4.3.2 Results and Discussion

The gouge and scratch hardness results for each IMC and PMC substrate/coating combination are presented in Tables 9.16 and 9.17 and are shown graphically in Figures 9.21 and 9.22. The effect of different variables on hardness values are discussed here.

Substrate/Coating Combination	Gouge Hardness		Scratch Hardness	
	IMC	PMC	IMC	PMC
PU-RIM/MRC(120N)	2H	HB	H	3B
PU-RIM/(X-226/C2885)	3H	F	HB	HB
PU-RIM/(X-225/C2885)	3H	F	F	HB
PU-RIM/(X-220/C075/C770)	4H	B	F	3B
Semi-flexible PU/MRC(600)	6H	2H	HB	2B
Semi-flexible PU/MRC (200)	F	2B	HB	5B
Semi-flexible PU/MRC (120N)	B	B	2B	4B
Semi-flexible PU/ (X-226/C2885)	B	F	3B	5B
Semi-flexible PU/ (X-225/C2885)	F	B	B	3B
Semi-flexible PU/ (X-220/C075/C770)	HB	H	2B	2B
Rigid PU/MRC (600)	HB	2B	B	5B
Rigid PU/MRC (200)	H	H	F	6B
Rigid PU/MRC (120N)	F	B	<6B	<6B
Rigid PU/(X-226/C2885)	B	B	3B	2B
Rigid PU/(X-225/C2885)	HB	B	2B	3B
Rigid PU/(X-220/C075/C770)	H	2B	5B	5B

TABLE 9.16: Scratch hardness results for IMC and PMC polyurethane substrates

Substrate/Coating Combination	Gouge Hardness		Scratch Hardness	
	IMC	PMC	IMC	PMC
C196/MRC (120N)	2H	H	HB	B
C196/(X-226/C2885)	3H	3H	B	H
C196/(X-225/C2885)	3H	4H	2B	2B
C196/(X-220/C075/C770)	6H	2H	F	B
C198/MRC (120N)	H	HB	F	2B
C198/(X-226/C2885)	3H	H	B	B
C198/(X-225/C2885)	6H	3H	2H	2B
C198/(X-220/C075/C770)	3H	3H	3B	B
C199/MRC (120N)	H	2H	3B	3B
C199/(X-226/C2885)	F	H	HB	HB
C199/(X-225/C2885)	2H	B	B	2B
C199/(X-220/C075/C770)	2H	3H	HB	B

TABLE 9.17: Scratch hardness results for IMC and PMC polyester substrates

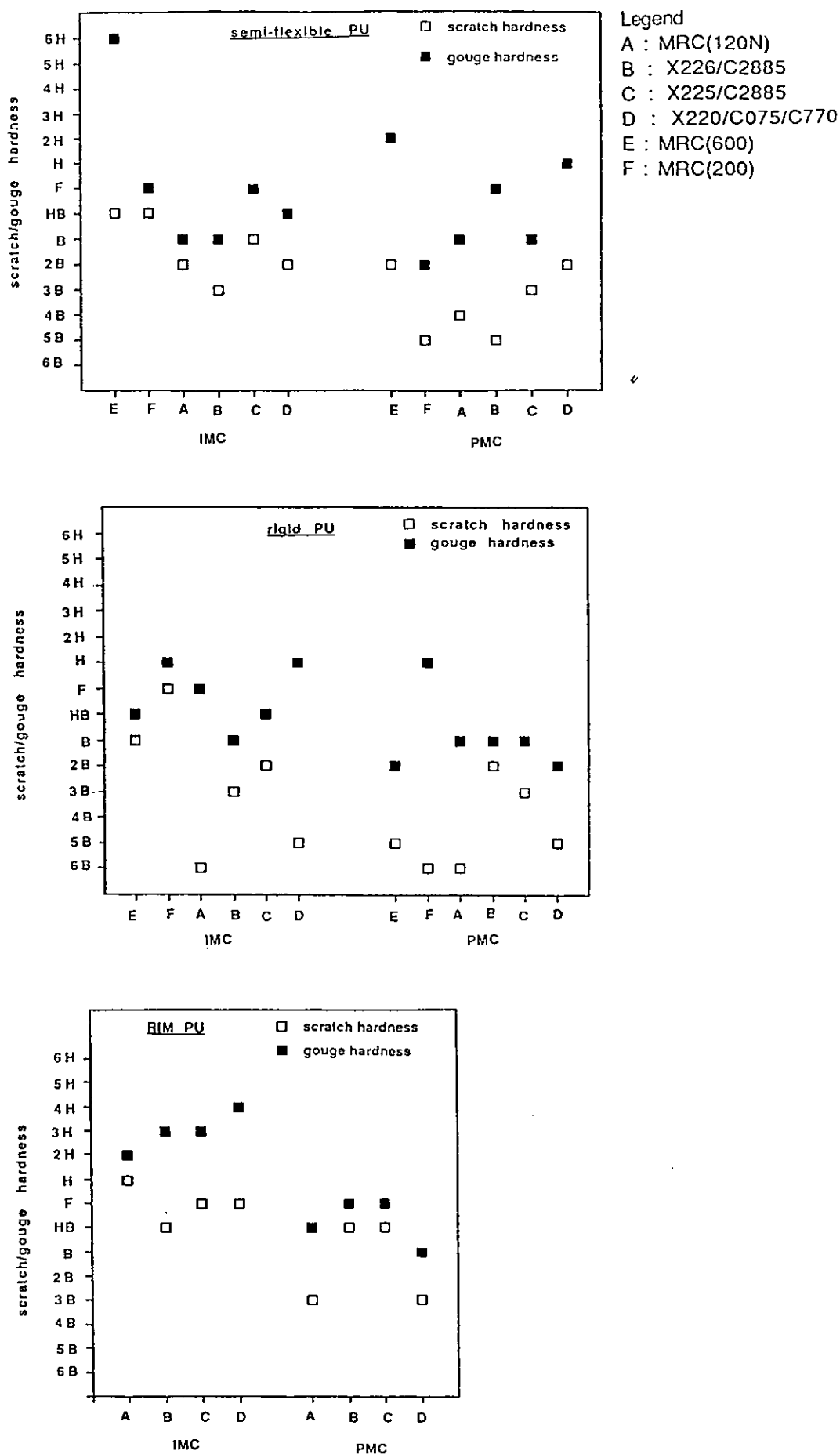


FIGURE 9.21: Scratch hardness classification for IMC and PMC PU substrates

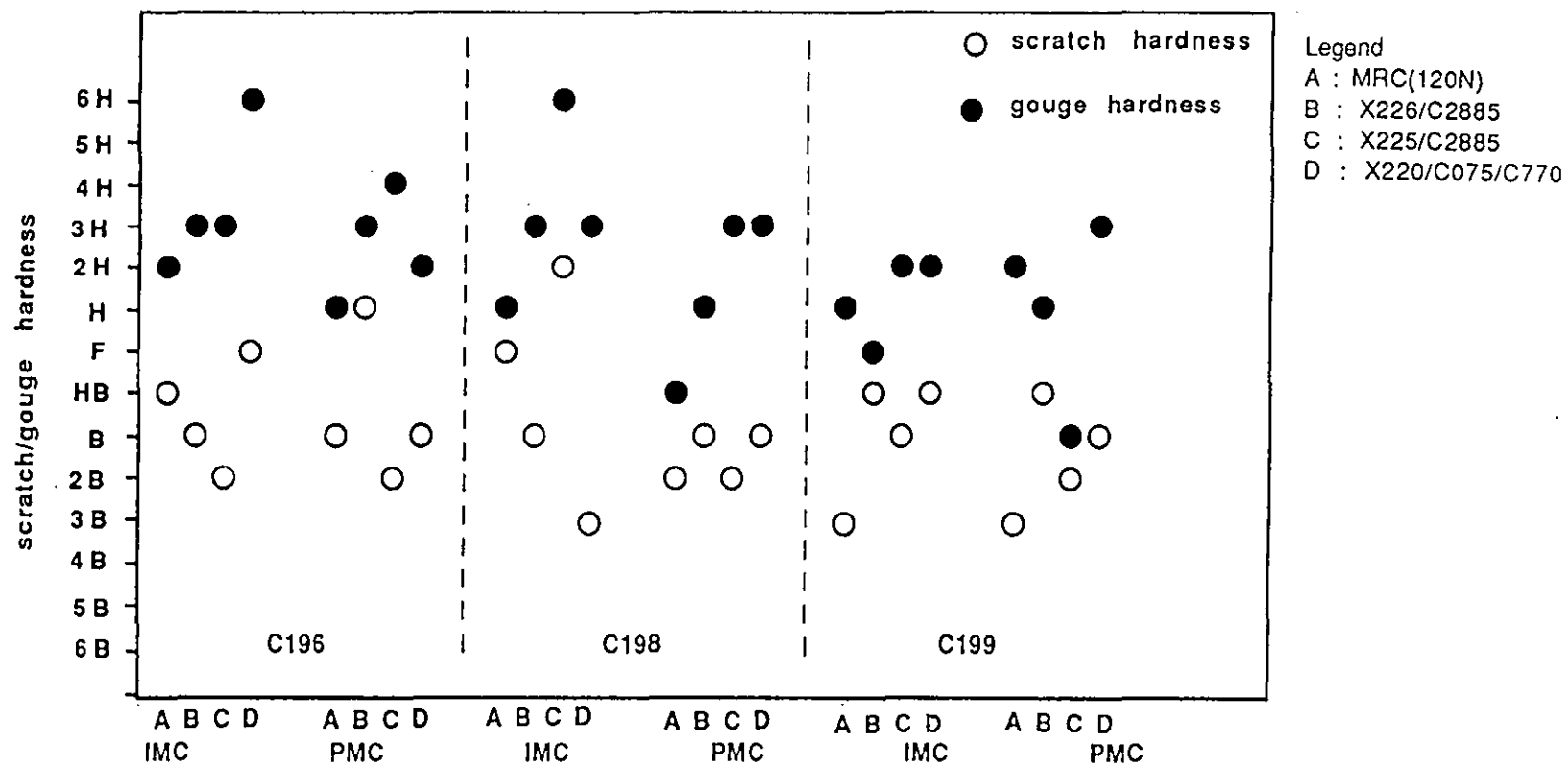


FIGURE 9.22: Scratch hardness classification for IMC and PMC Polyester substrates

### Effect of Substrate Materials

#### a) Polyurethane substrates

RIM polyurethane substrates showed greater scratch and gouge hardness values for both IMC and PMC samples than semi-flexible and rigid PU substrates. With only a few exceptions, all the results obtained on semi-flexible PU substrates were superior to those for rigid PU.

#### b) Polyester substrates

Generally, C<sub>196</sub> polyester substrates gave higher scratch and gouge hardness results than C<sub>198</sub> and C<sub>199</sub> surfaces. This distinction was more pronounced with PMC samples and particularly for gouge hardness values. The overall hardness results for IMC samples of C<sub>198</sub> were higher than those for C<sub>199</sub> but for PMC samples the two substrates showed similar results.

### Effect of Coating Materials

#### a) For polyurethane substrates

There was no systematic variation from coating to coating. For RIM and rigid PU substrates the gouge hardness values for samples coated with 2 pack coatings were generally superior to the other samples.

#### b) For polyester substrates

There was no systematic variation in coating type on hardness. Generally it was recognised that the 2 pack acrylic/PU system (X-220/C075/C770) showed higher gouge hardness than the others.

### Effect of Coating Processes

#### a) For polyurethane substrates

IMC samples of RIM PU gave superior scratch and gouge hardness to PMC specimens. For semi-flexible PU substrates, the scratch hardness for

IMC samples gave either similar or larger hardness than PMC with the exception of gouge hardness for IMC samples coated with (X-226/C2885) which was inferior to its corresponding PMC. For rigid PU substrates, the scratch and gouge hardness for IMC samples were normally higher than PMC values with the exception of the scratch hardness for IMC samples with X-226/C2885 slightly lower than PMC.

b) For polyester substrates

There was no systematic variation between IMC and PMC samples.

It can be concluded that various substrates showed different effects on the scratch hardness of coated samples. Variation from coating to coating could not indicate a very clear effect on the hardness results except with 2 pack PU coatings which generally showed superiority to the other coatings. The coating processes showed some effect on the hardness results mainly for PU substrates and in particular for RIM-PU substrates.

CHAPTER 10  
THERMAL ANALYSIS TECHNIQUES

10.1 INTRODUCTION

Thermal analysis, as used in a wide range of techniques, can be used to determine some changes in physical or mechanical properties of the material when measured as a function of temperature. These techniques include differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), thermogravimetry (TG), and dynamic mechanical thermal analysis (DMTA).

This chapter first reviews the theory of DSC which is the main technique used in this research. This is followed by an examination of its experimental procedure and a report of its results and discussion. To verify the thermal transitions detected by DSC, and to gain more information about the temperature dependence of mechanical properties, this chapter then discusses the theory of DMTA, and reviews its experimental procedure and presents its results and discussions.

10.2 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Since the early 1960s, due to the availability of commercial instrumentation, the DTA with the aid of DSC have been shown to be valuable techniques in the thermal analysis of polymers [335-338].

Thermal properties of polyurethane and polyester polymers have been extensively reviewed in the literature [339-342]. However, there are scarcely any documented reports describing the effect of polymeric coatings on the thermal behaviour of these substrates.



Garn [343] has argued that additional energy due to strain or to mechanical or thermal analysis can affect the thermal decomposition of a material. DSC was applied to investigate and analyse the scans for different coating/substrate systems and hence demonstrate the effect of conditions on the bond formation. As a result he has stated that changing a substituent on the other end of a chemical bond would affect the degradation or decomposition of that bond. Therefore it was assumed that differences in temperatures of degradation of substrate/coating bonds are related to the strengths of these bonds. It has been concluded that differences in thermograms resulting from the degradation of the bond between the coating and the substrate materials may be studied in order for the adhesion energies to be evaluated.

In this research, the DSC scans for IMC and PMC polyurethane and polyester materials are compared with those for substrate or coating only. The change in temperature of the transition peaks or the general trend of the scans or the rate of the decomposition of the bond should yield a measure of the change in bond energy. It has been intended to show that for this type of analysis comparing one sample with another often gives valuable information and this difference found between them is more significant than the absolute values of the transitions.

#### 10.2.1 Theory of DSC

Differential Scanning Calorimetry (DSC) is a technique in which the differences in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and the reference material are subjected to a controlled temperature programme [344]. DSC measurements are normally facilitated by the aid of a Differential Thermal Analyser (DTA). A schematic diagram of a typical

analyser system for DTA/DSC is given in Figure 10.1. The differential heat flow to the sample and the reference material being monitored by thermocouples, is fed to a variable high gain amplifier where the signal is amplified, electronically scaled to read directly in heat flow units and finally recorded on the Y-axis of a recorder. An idealised representation of the three major processes observed by DSC is given in Figure 10.2.

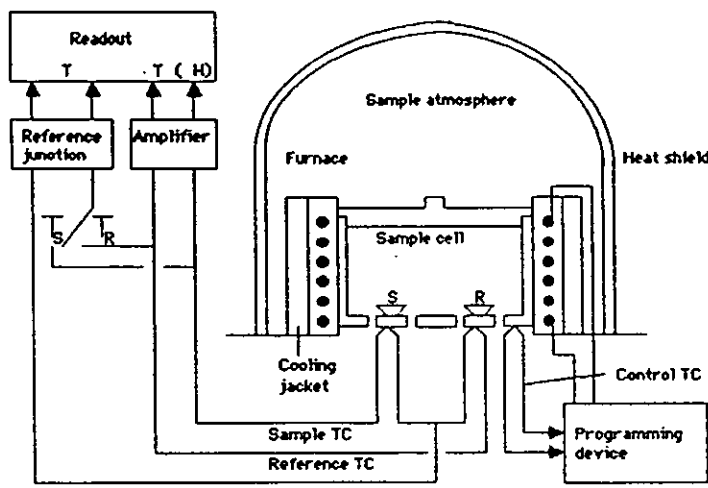


FIGURE 10.1: Schematic diagram of a typical differential thermal analyser system [345]

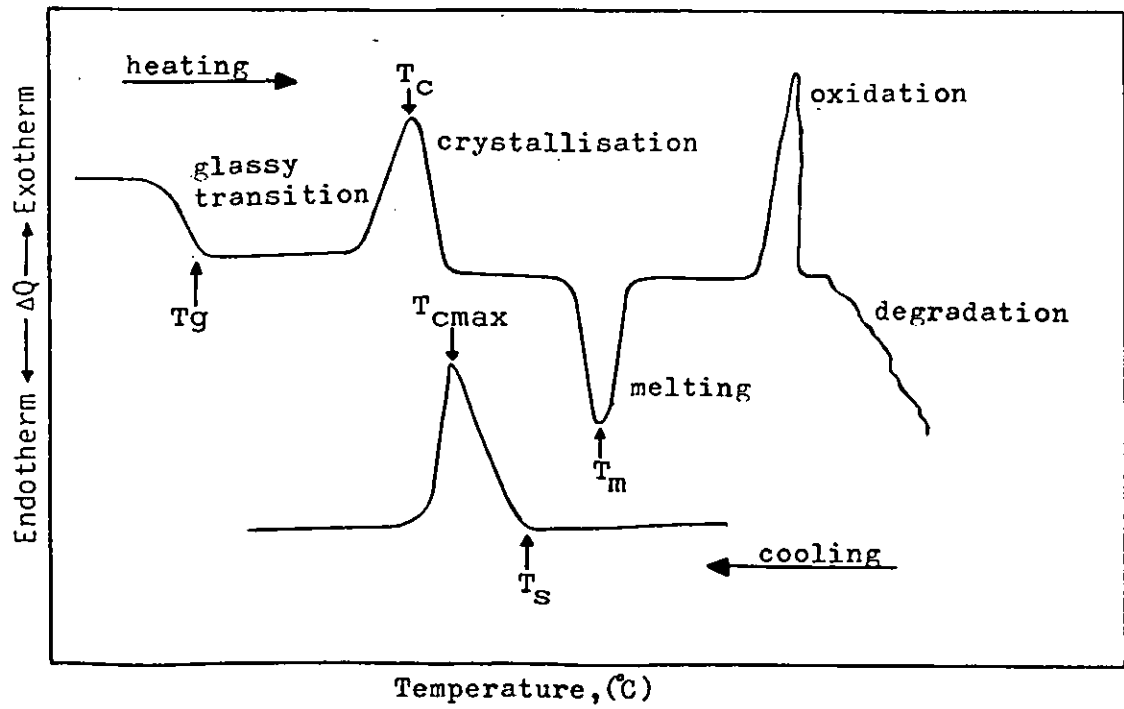


FIGURE 10.2: An ideal representation of major processes observable in DSC

The DSC scans produced may include some or all of the following features [346]:

- a) Glass transition temperature ( $T_g$ ): This is shown as a discontinuous change in slope at the glass/rubber transition temperature, for polymers with a low degree of crystallinity, indicating a transition from a rigid to a flexible structure. It causes a change in heat capacity and hence a shift in base line.
- b) Crystallisation temperature ( $T_c$ ): In addition to the crystallinity already present in semi-crystalline polymer, further crystallisation may be induced in the sample on heating.
- c) Crystalline region melting temperature ( $T_m$ ): The melting of a polymeric material is an endothermic behaviour whose breadth indicates the melting range.
- d) Oxidation and degradation processes: At higher temperatures the polymer may oxidise or degrade depending upon the surrounding atmosphere (experiment run in  $N_2$  atmosphere).
- e) Cooling transitions: Heating is normally continued for some 20 to 30°C above the melting point before cooling is started. This is to ensure that all crystallite nuclei are destroyed in the melt so that subsequent recrystallisation can take place under random environmental conditions. The main transition temperatures associated with the cooling process are  $T_s$ , at which crystallisation starts, and  $T_{cmax}$ , at which the rate of crystallisation is a maximum.

### 10.2.2 DSC: Experimental Procedure

Thermal properties of polyurethane and polyester substrates, various PU based coatings and IMC and PMC samples of different combinations of substrate and coating materials were measured using a Du Pont 990 Differential Thermal Analyser fitted with a Du Pont 910 Differential Scanning Calorimetry (DSC) accessory. A cross-sectional diagram of the DSC cell used in this work is shown in Figure 10.3. Prior to thermal analysis experiments, the instrument was calibrated for temperature using indium (melting point =  $156.5^{\circ}\text{C}$ ) as a standard reference.

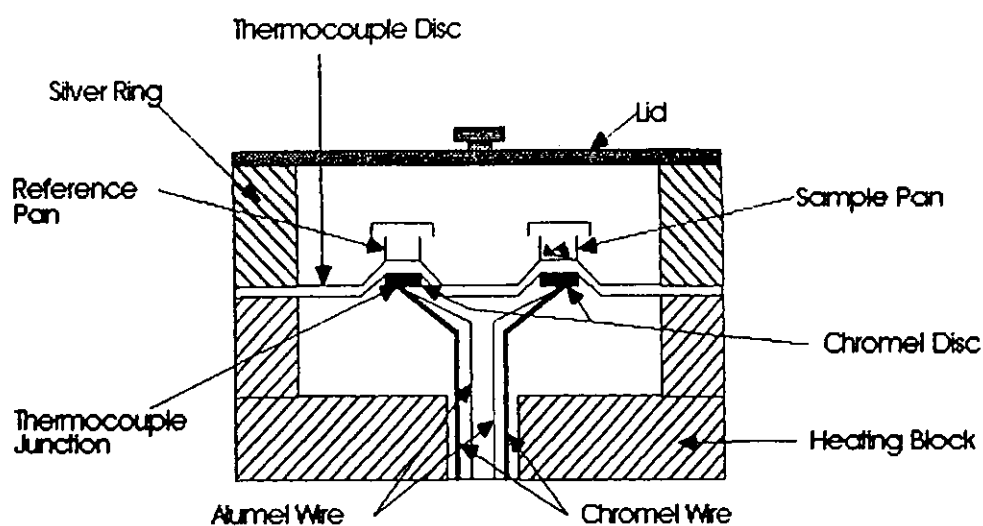


FIGURE 10.3: DSC cell cross section (after Ref 344)

Sample pans were prepared by encapsulating 10 to 12 mg of each substrate or coating material. For coated samples 15 to 20 mg of material proved sufficient but it was recognised that this increase in the sample weight was limited by the size of the standard pans and also by failing to respond to some expansion due to degradation. As a result, larger pans were used for coated specimens. It was found

necessary that substrates of coated materials were microtomed so that a closer ratio between substrate and coating were obtained. The satisfactory substrate/coating ratio (by weight), giving meaningful DSC thermograms, was practised throughout the experiment.

The sample pan and an empty pan, used as a reference, were placed on raised platforms on the thermocouple disc. In the case of all samples the cell was cooled to  $-60^{\circ}\text{C}$  using liquid nitrogen. The cell was then heated at a constant rate of  $20^{\circ}\text{C}/\text{minute}$  with a constant flow rate of 70 mmHg of dry nitrogen gas passing through.

The DSC scans were recorded between  $-50^{\circ}\text{C}$  and  $+300^{\circ}\text{C}$  or room temperature and  $350^{\circ}\text{C}$ . The two pens on the recorder were set at different sensitivities of 5 and 10 mV/cm. All samples were tested at least three times to ensure reliable thermograms were recorded and the irregular effects often associated with settling within the pan for initial scans were discarded.

#### 10.2.3 DSC: Results and Discussion

The DSC results are presented in Figures 10.4 to 10.11. The thermograms for IMC samples are shown as a solid line. Where applicable, superimposed on each IMC thermogram is the DSC trace for the corresponding PMC sample shown as a dashed line.

Figure 10.4 shows the DSC scans of various coatings used in these experiments. Figures 10.5 to 10.7 illustrate the DSC traces for different coated PU substrates where various coatings studied in Figure 10.4 have been applied to these surfaces either using IMC or PMC processes. Figures 10.8 to 10.10 show DSC traces for polyester

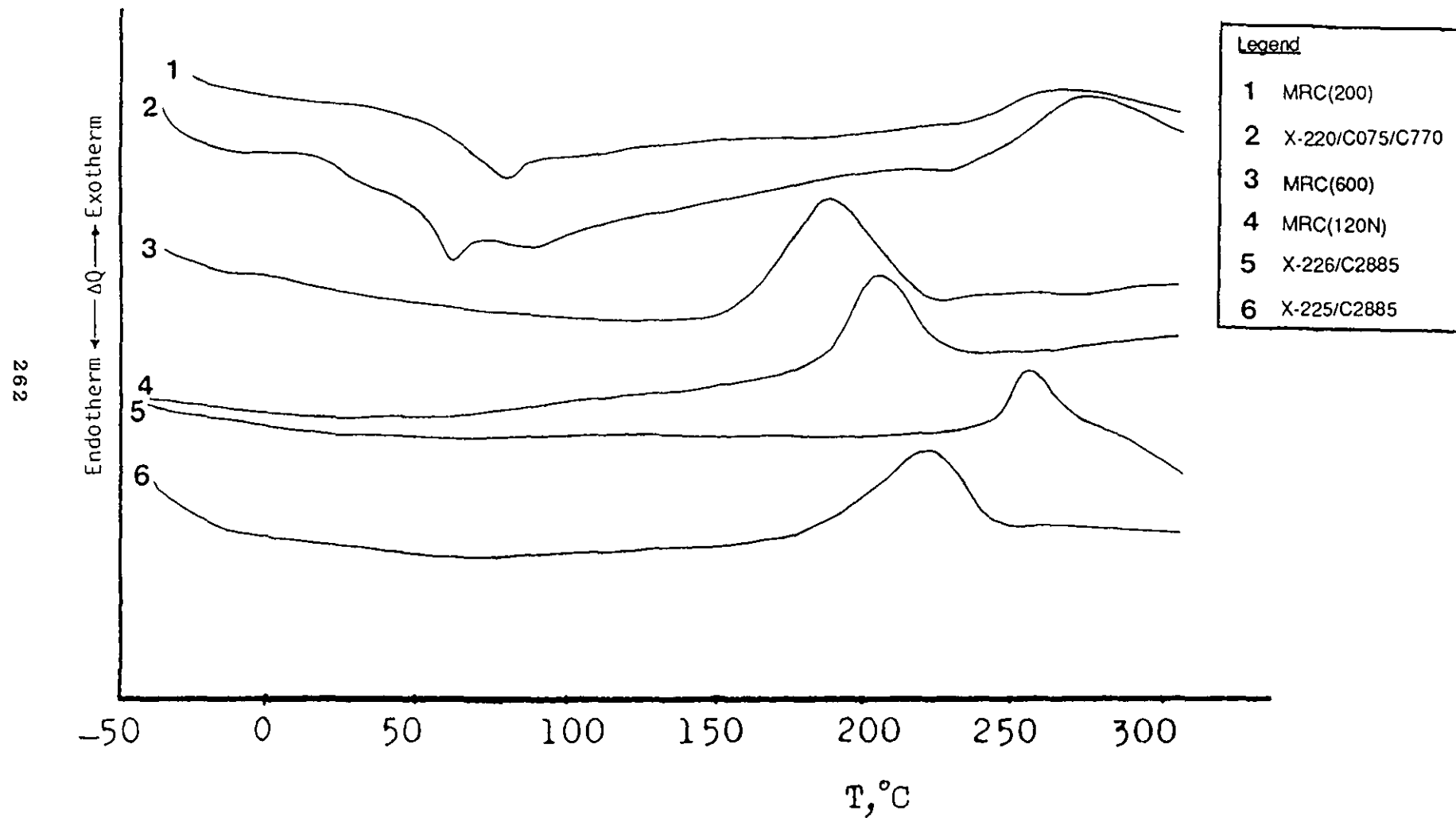


FIGURE 10.4: DSC scans of various one and two pack PU coatings

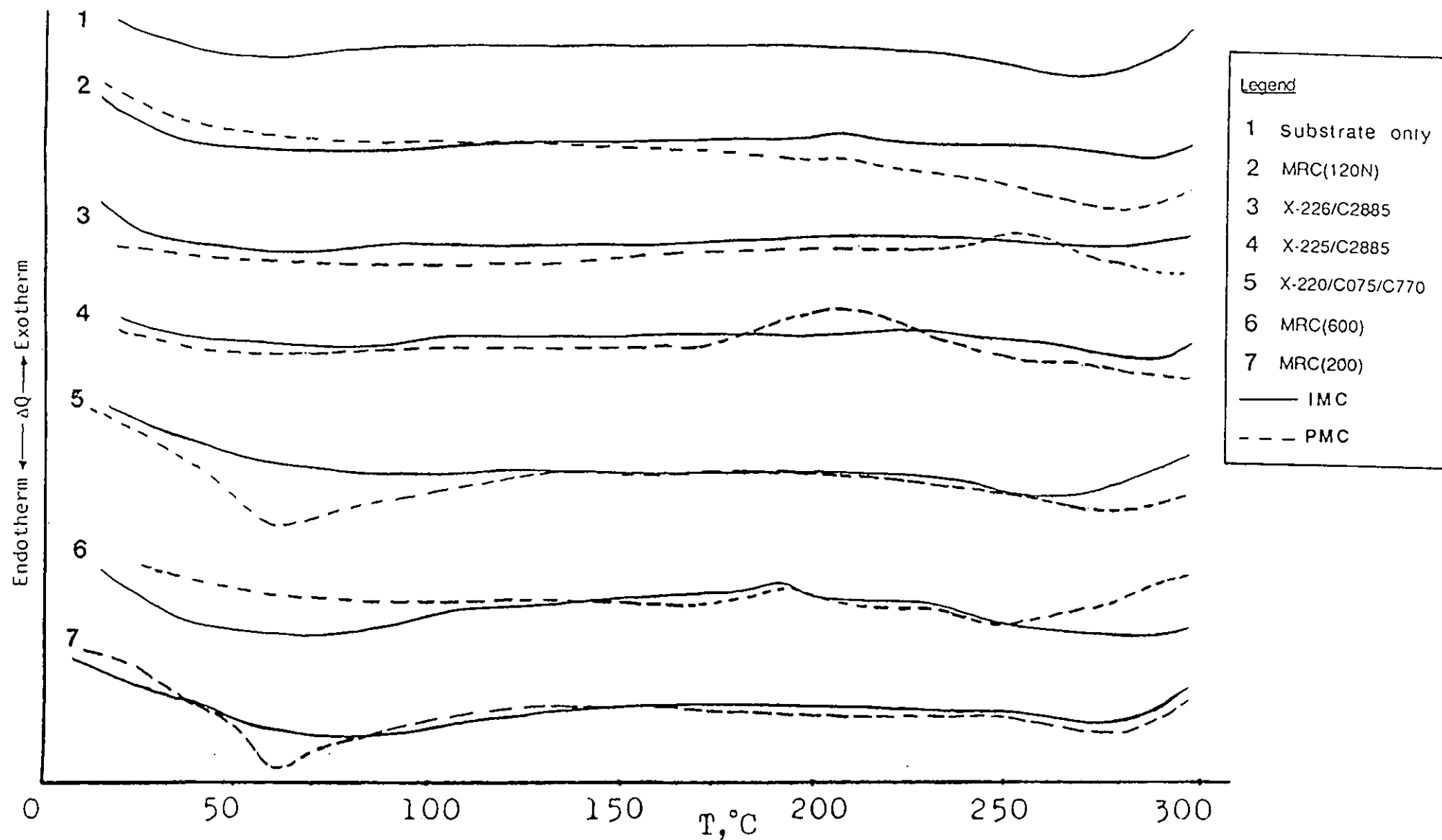


FIGURE 10.5: DSC scans of coated semi-flexible PU foam substrates

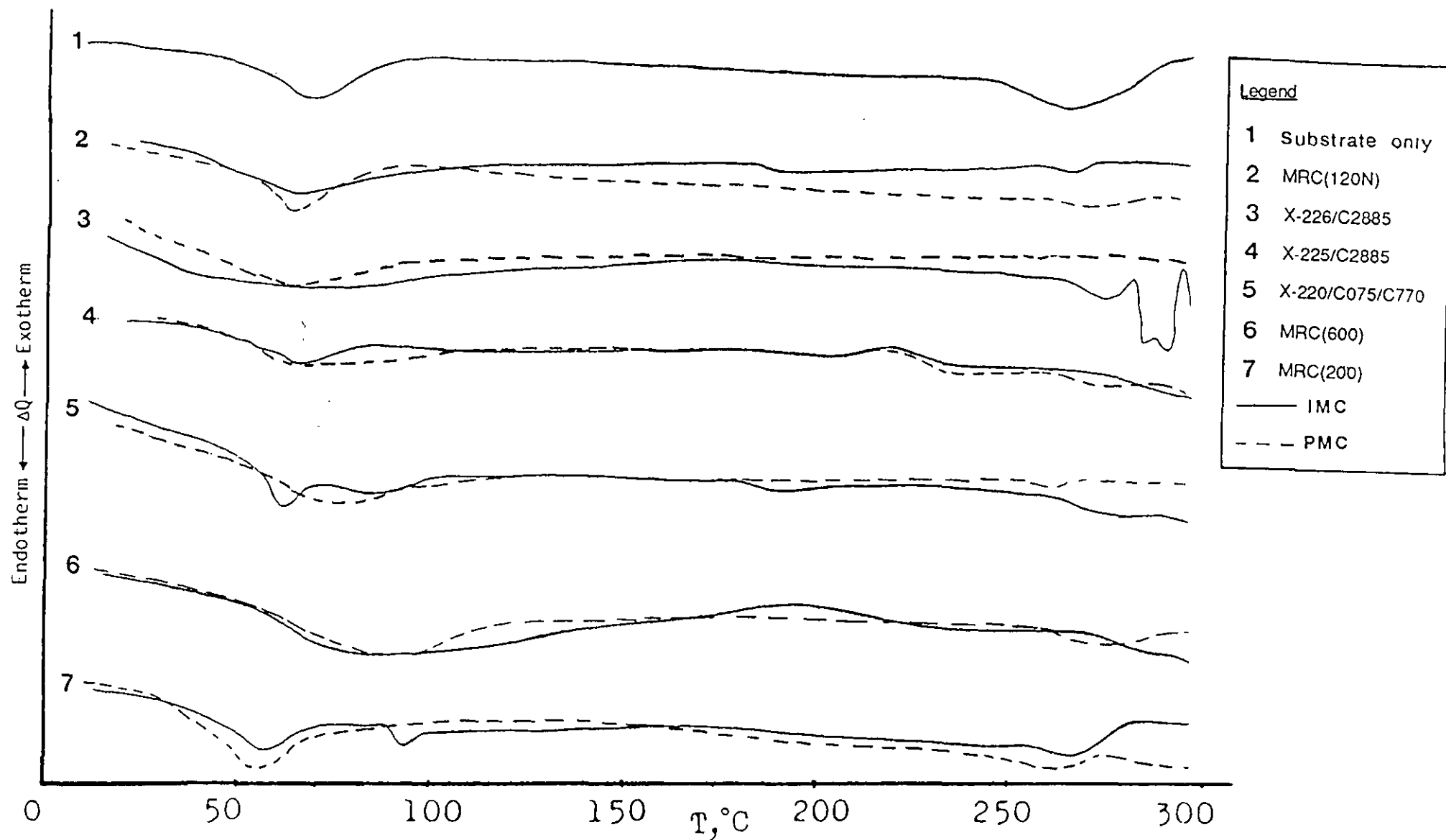


FIGURE 10.6: DSC scans of coated rigid PU foam substrates



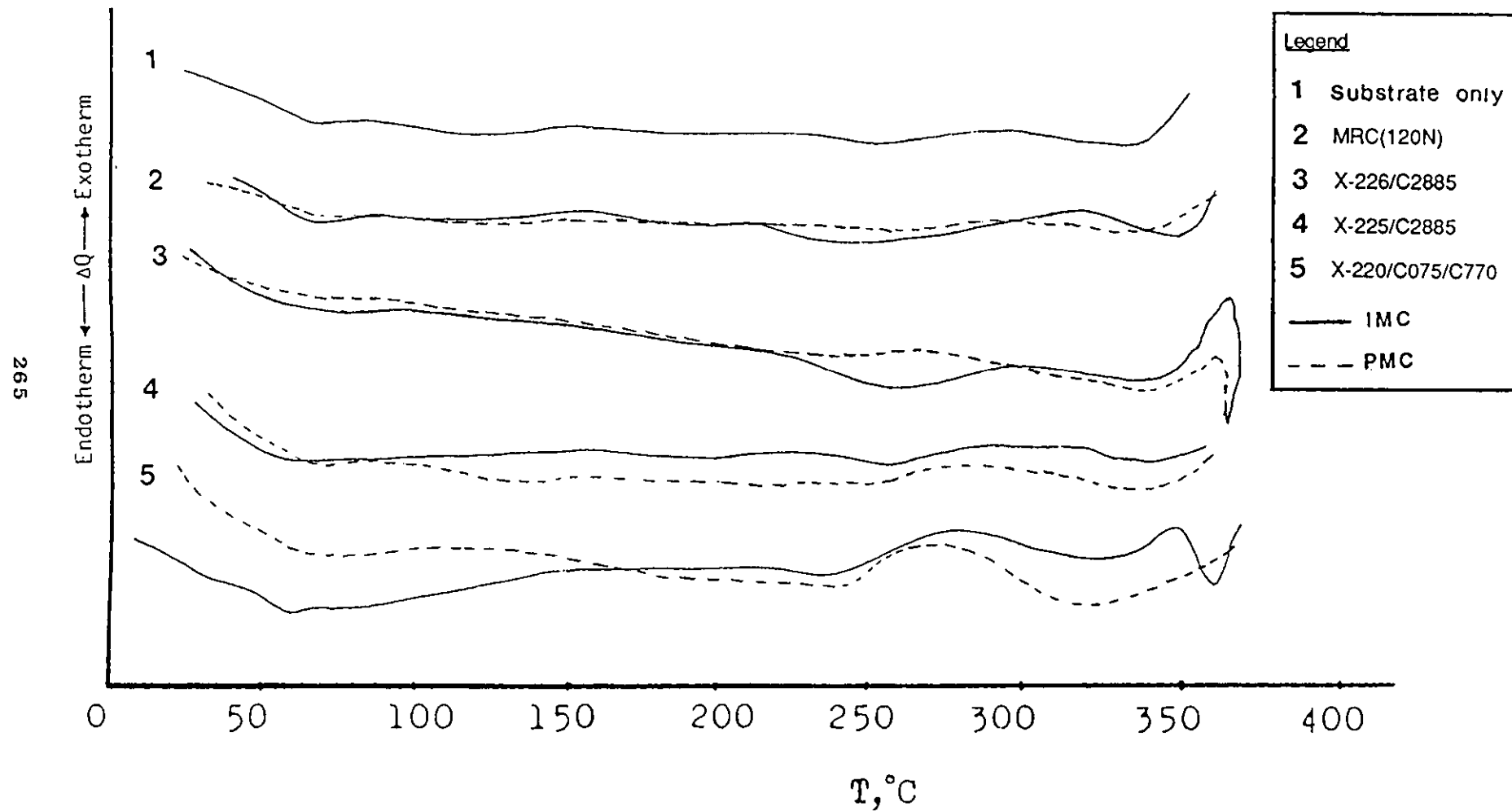


FIGURE 10.7: DSC scans of coated PU-RIM substrates

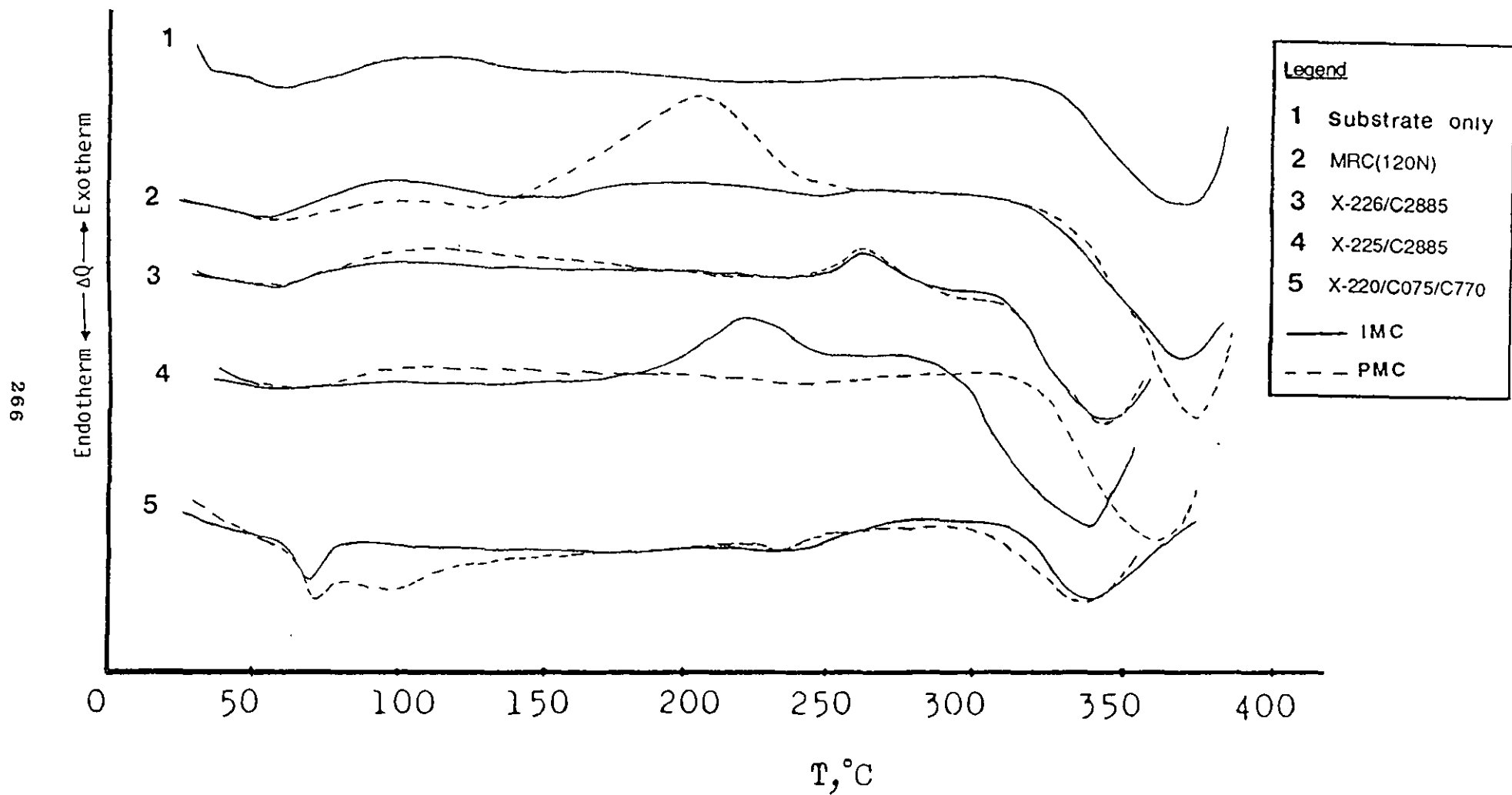


FIGURE 10.8: DSC scans of coated  $C_{196}$  polyester substrates

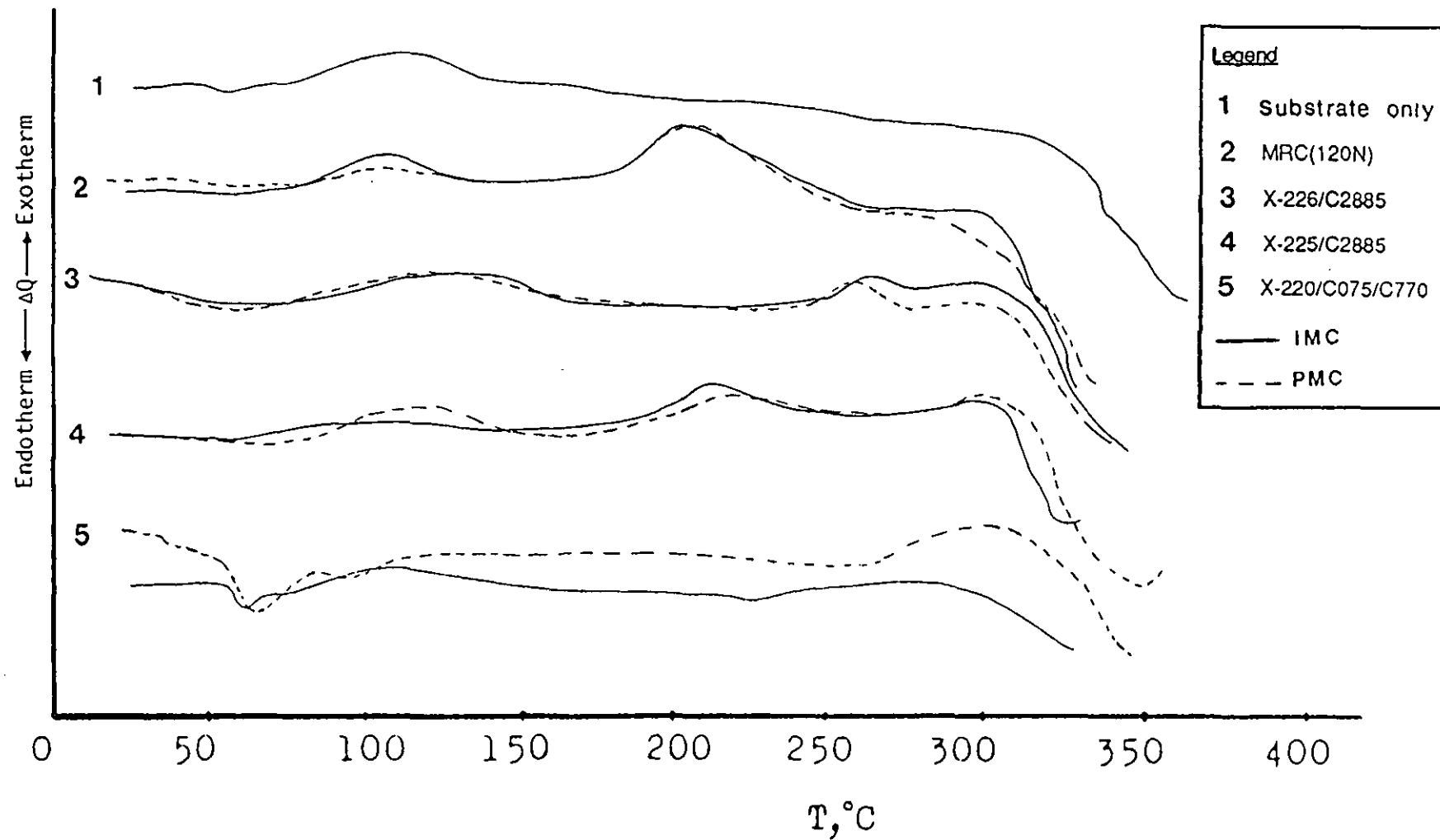


FIGURE 10.9: DSC scans of coated  $C_{198}$  polyester substrates

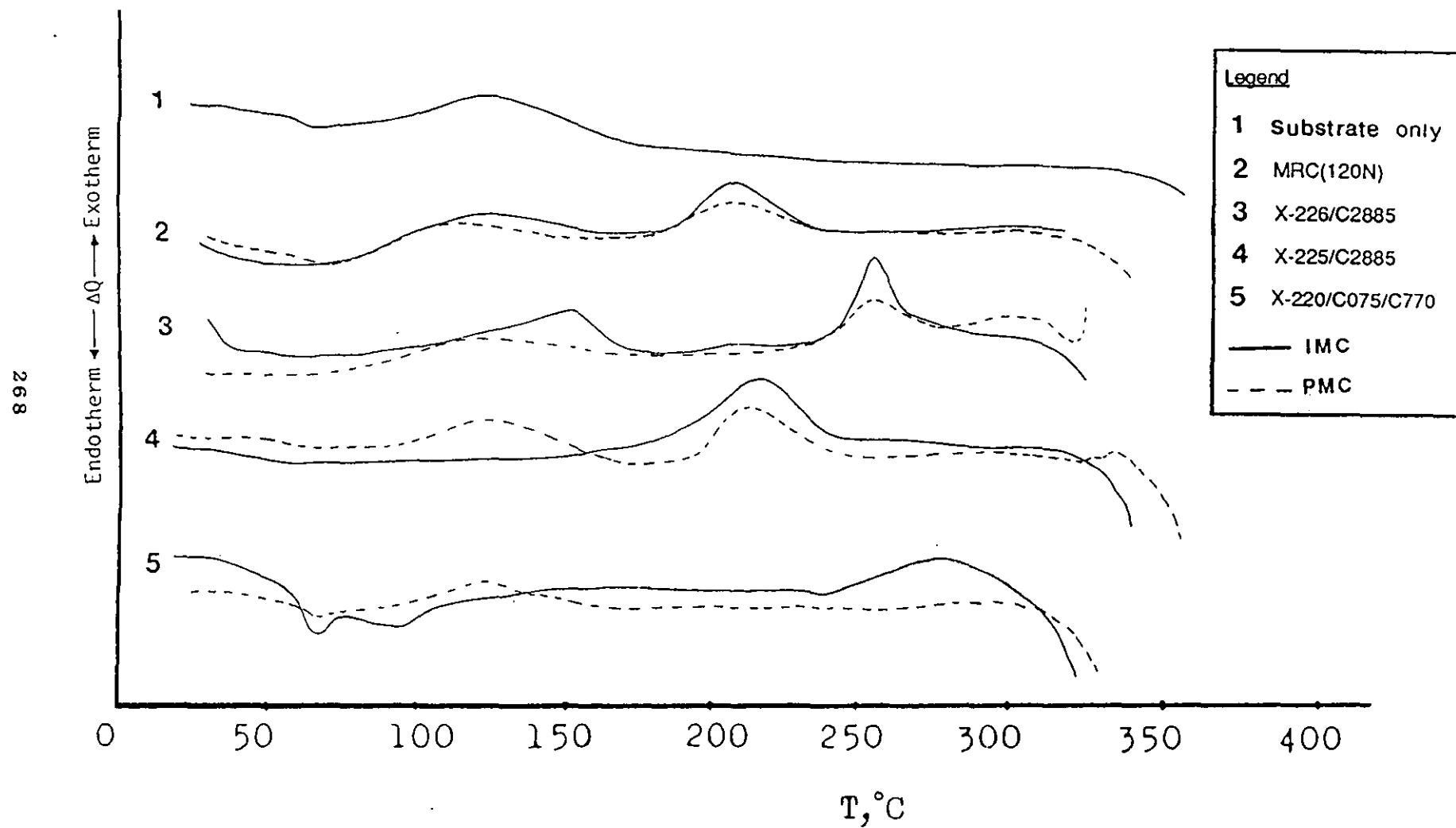


FIGURE 10.10: DSC scans of coated  $C_{199}$  polyester substrates

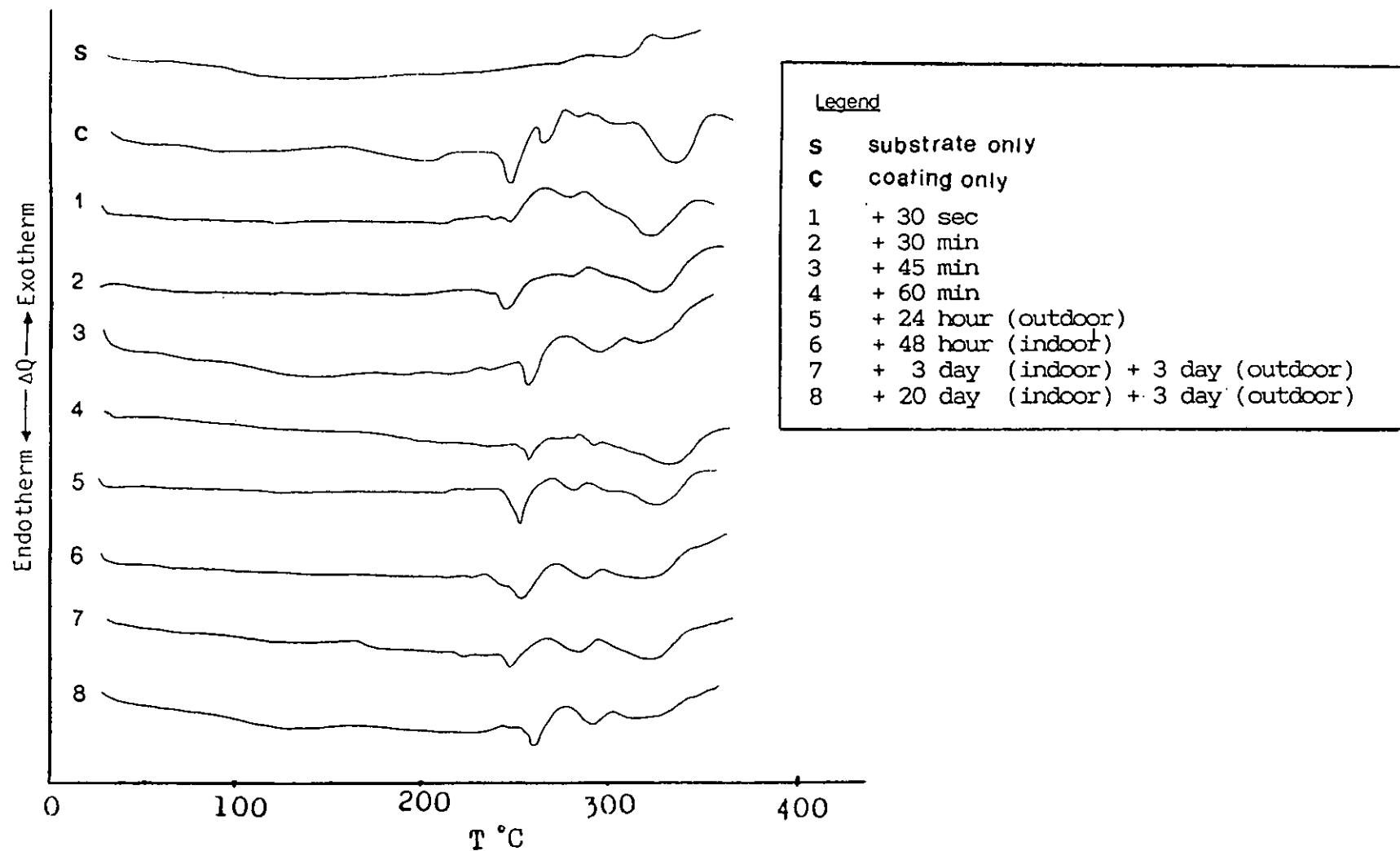


FIGURE 10.11: DSC scans of coated PU spray foam substrates

surfaces coated similarly to the PU substrates mentioned above. Figure 10.11 represents the DSC scans of spray rigid PU foam (Isofoam SS/0658) coated with a PU elastomer coating (Futura-Thane 5000). Here the intention has been to study the effect of various conditions (i.e. ageing, temperature, humidity) on the thermal behaviour of different coated systems. The exact position and values of transition temperatures are only recorded in places where this additional information has been thought necessary. Otherwise, in most cases the differences between DSC traces of similar systems was found to give satisfactory information. The dynamic mechanical thermal analysis (DMTA) has also been applied on many of the systems studied by DSC (see Section 10.3). This was found to be useful since the results obtained by the two techniques are in many ways complementing each other and a number of conclusions derived in one method could be confirmed by the other.

The effect of different variables (i.e. substrate materials, coating types and coating processes) on DSC scans of coated samples are discussed here.

### Effect of Substrate Materials

DSC results of Figures 10.5 to 10.10 provide information concerning the effect of different substrate materials on transition temperatures of coated samples. The results for PU substrates may be summarised as below:

1. The results of DSC traces obtained for coated PU RIM substrates where a minimum of three samples were tested in each case were in good agreement. This was not always true for semi-flexible and rigid foams where in some cases up to six tests had to be carried

out for each sample in order to achieve a statistically meaningful set of results. The discontinuity and variation in results may be due to the difficulties in preparation and microtoming of coated PU foams. Achieving a balanced ratio between substrate and coating also proved a delicate operation. It may also be argued that due to the cellular structure of PU foams a true representation of each system created additional problems.

2. As expected, all the various PU substrates have a significant influence on the thermal behaviour of coated samples. There was no systematic variation between different substrates. However, this effect was found to be more pronounced with semi-flexible foam and RIM PU substrates (especially with IMC samples) than with rigid foam.
3. The effect of PU substrates on thermal behaviour was variably governed by the type of coating and the coating processes involved. The changes in the transition temperatures of the original substrates were often observed at temperatures below 120°C. The amplitude (or depth) of transition regions in DSC traces of coated samples were similar to those of the corresponding uncoated substrates. This observation was not true for the widths of transition regions of coated samples which showed different results to those of the original substrates. This effect was particularly noticeable with rigid foam samples.

The DSC scans of coated polyester substrates are shown in Figures 10.8 to 10.10. The effect of substrates on these thermograms are not readily recognised. This is mostly due to the strong influence shown

by various coatings on DSC scans and hence masking the other factors. Generally, DSC scans of coated C196 and C198 polyester substrates showed close similarities to the corresponding transition temperatures recorded by DSC studies of their uncoated substrates.

#### Effect of Coating Materials

The DSC scans for various types of coating used in this research are shown in Figure 10.4. For two pack coatings (X-220/C075/C770) and MRC (200), two sharp endothermic transitions are observed at 60<sup>o</sup> and 78<sup>o</sup>C respectively. In addition, another two endothermic peaks, less defined, are shown at the 220<sup>o</sup> to 225<sup>o</sup>C region for these two coatings. All one pack coatings showed very distinct exothermic peaks between 180<sup>o</sup> to 250<sup>o</sup>C. Generally, the transition temperatures occurring below room temperature were less pronounced. These will be discussed in the section below detailing DMTA results (see Section 10.3.3).

The effect of various coating materials on DSC scans of coated PU and polyester substrates shown in Figures 10.5 to 10.10 may be summarised as follows:

1. Generally, the DSC scans for PU substrates coated with two pack coatings showed sharp endothermic transitions (below 80<sup>o</sup>C), similar to those for the original coatings. The other endothermic peaks (above 200<sup>o</sup>C) associated with these coatings were not readily observed with the coated samples results. However, the positions of the first transition temperatures observed by both two pack coatings had shifted in the DSC traces of coated polyurethanes. This shift, particularly observed with IMC samples, may be attributed to the internal mould pressure and hence the force involved between substrate and coating in the



processing operation. It is also considered that migration and diffusion (see Section 12.2.1) has made it possible for new structures to be formed at the interfacial regions.

2. The effect of one pack coatings on the DSC scans of coated PU substrates are not immediately obvious. For RIM PU samples (especially with IMC specimens) the exothermic peaks observed by the original one pack coatings are masked by the dominant influence of the substrate transitions. As a result, broad endothermic transition regions with peaks occurring at 235° to 250°C are observed with these systems.

For semi-flexible and rigid foams, the effect of one pack coatings on the transition temperatures of coated samples are clearly evident with subtle transition peaks occurring in the 200 to 250°C region.

3. The DSC scans of coated polyester substrates were strongly influenced by the type of coating used in these systems. This finding was valid for both one and two pack coatings. There were no systematic variations found between the effect of various coatings on transition temperatures.
4. It may be argued that distinct transitions shown by some coatings in DSC scans of coated PU and polyester samples indicate the incompatibility between that surface and a particular coating. In that sense, it is evident that overall performance of two pack coatings resulted in a more favourable (i.e. better compatibility) combination between the two systems.

### Effect of Coating Processes

Considering the coated polymers to be a special form of blends, it can be argued that in theory compatible coated substrates (an idealised situation where complete diffusion of coating into substrate has taken place) would ideally have a single glass transition temperature somewhere between those of the pure coating and substrate components. However, in practice the DSC studies of IMC and PMC PU and polyester substrates proved to be more complex. Nevertheless, there were some interesting observations indicating the influence of the coating processes and the conditions on DSC scans of coated substrates. For polyurethane substrates, the difference between DSC scans of IMC and PMC samples were more pronounced with semi-flexible foams than with the others. The rigid PU foam showed similar transition regions for the majority of IMC and PMC specimens. It is interesting to note that a number of thermograms, especially in the case of PMC samples of semi-flexible foam, showed transition temperatures similar to those of pure coatings. It is assumed that in these cases the independent thermal characteristics of coating and substrate in the composite material is due to a less compatible region. This finding indicates that coating processes as well as the effects of coating and substrates already described in previous sections, have an influence on the thermal properties of coated systems.

At the beginning of an IMC cycle, the PU substrate ingredients are in liquid state reacting over the dried IMC PU film. During the reaction when most of the solvents in the formulations are used then the system becomes too viscous (prior to solidifying) to form separate phases. At the same time, the temperature of the mould as well as the exothermic heat of the reaction are providing additional thermal energy to the system. For IMC specimens, the combination of differing molecular

structures interacting with one another (i.e. the coating and substrate materials) and the different energy inputs because of moulding conditions may be thought to be observable by significant energy variations in their DSC thermograms. The effect of coating processes on the DSC thermograms of coated polyester substrates was not easily distinguished. Although an exactly identical performance within similar coating processes was not apparent, there were a number of cases where some common features could be recognised.

The DSC scans of the majority of the IMC and PMC polyester samples shown in Figures 10.8 to 10.10 illustrate the transition temperatures markedly resembling those of the original (pure) substrate and coating materials. This view was especially apparent with C198 and C199 coated systems. The lack of any influence exercised by the coating processing/conditions on thermal behaviour of coated systems on the one hand and the strong effect shown by energy levels within a single material (substrate or coating) on the other hand are factors indicating a very poor compatibility between the two phases.

#### Effect of Coating Conditions on DSC Scans of Coated PU Spray Foam

The DSC thermograms of rigid PU foam (Isofoam SS/0658) substrate, and a PU elastomer (Futura-Thane 5000) as coating, with a series of substrate/coating combinations produced at various conditions are shown in Figure 10.11. The influence of starting materials (substrate and coating) were observed with all coated samples. The endothermic peak observed at about 250°C with the original coating is the dominant transition occurring in all the scans.

Although transition temperatures of coated samples showed some discrepancy, there was not a systematically uniform change in order to

draw a direct relationship between the coating conditions and the thermal behaviour. It must be emphasised that the effect of a number of variances (i.e. ageing, temperature, humidity) often acting simultaneously upon these systems inevitably has made it a more complex task to analyse by thermal techniques. However, changes in the DSC scans due to the thermal histories of the samples is evidently showing that the conditions applied to the PU foam prior to coating has had some effect on the thermal properties of the final composite.

### 10.3 DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA)

Dynamic Mechanical Thermal Analysis is a technique for studying the effect of molecular structure and phase morphology on the physical properties of polymeric materials [347-349]. DMTA techniques give quantitative measurements of modulus changes for first order thermodynamic transitions ( $\alpha$ ) such as melting and crystallisation. The resolution of the glass transition temperature ( $T_g$ ) observed by DSC/DTA is rather poor and in the case of minor components, the detection of secondary transition ( $\beta, \gamma$ ) is impossible. However, DMTA detects ( $T_g$ ) and ( $\alpha$ ) transitions with a sensitivity of about 1000 times higher than DSC/DTA and measures  $\beta$  and  $\gamma$  transitions quantitatively [349]

Dynamic mechanical properties of rigid and flexible PU foams, representing a special form of composites in which the modulus is reduced by air or blowing agent, have been studied by others [350,351]. The long relaxation time of the flexible PU observed at room temperature in recovery from large deformation has been attributed to the proximity of its  $T_g$  at 25°C to room temperature.

Wedgewood et al [352] studied the dynamic mechanical properties of some PU based coatings in the temperature range of -160 to 120°C. Three transition (relaxation) regions  $\alpha$ ,  $\beta$  and  $\gamma$  were observed for most systems. The  $\alpha$  transition was assigned to the coating's T<sub>g</sub>, whereas  $\beta$  and  $\gamma$  transitions were mainly associated with interactions and molecular motions in the soft segments (usually a polyester or polyether diol). The  $\beta$  transitions were particularly associated with the effects of absorbed water in the urethanes, and the differences in the  $\gamma$  transitions showed a strong indication that local motions of the CH<sub>2</sub> chain sequences in the soft segments were different.

Bratton et al [353] investigated the cure characteristics and mechanical properties of a number of polymeric coatings either as free films or coatings attached to metal substrates. Their DMTA results showed that different values of T<sub>g</sub> are obtained depending on the coating conditions. This difference was too large to be attributable to either a poor clamping, or to the differences in analysis frequencies (see 10.3.1). They argued that there may be a correlation between the direction of shift in measured T<sub>g</sub> and adhesion of the coating to the substrate. Coatings which adhered well to substrates gave higher glass transition temperatures when on the substrate than when studied as free films, whereas coatings which adhered poorly gave a higher value of T<sub>g</sub> when analysed as free films. Another interesting finding was that the thickness of the substrate had a significant effect upon the temperature at which the measured T<sub>g</sub> occurred. It was also demonstrated that the type of metal substrate would affect the measured T<sub>g</sub>.

The DMTA technique has been used successfully for coated and laminated polymeric materials [349,351]. The DMTA results for a laminated

polymer such as an adhesive tape showed a low transition temperature due to the rubbery adhesive layer and a high transition temperature due to the polyethylene terephthalate (PET) backing. An interesting observation was made on dynamic mechanical properties of coated PET films [351]: the coating had a very pronounced effect on the mechanical loss behaviour. The uncoated sample showed the relation behaviour characteristic of PET with the glass transition ( $T_g$ ) at  $120^{\circ}\text{C}$  and a secondary transition at  $-60^{\circ}\text{C}$ . The sample with a good quality coating showed a third transition at  $50^{\circ}\text{C}$ , while the intensity of the transition was reduced substantially with the poor quality coating. The poor coating appeared to be related to the uneven wetting of the substrate.

#### 10.3.1 Theory of DMTA

The dynamic mechanical thermal analyser (DMTA) test method measures the stiffness and energy absorption properties of a material by applying a small sinusoidal stress to the sample and measuring the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) [20,348,349,354]. The quantity ( $E'$ ) is called the storage modulus because it defines the energy stored and recovered per cycle in a material and ( $E''$ ), loss modulus measures the energy dissipated or lost per cycle. The ratio of these moduli,  $\tan\delta = E''/E'$ , often referred to as the mechanical loss tangent varies with temperature and reaches a maximum at the glass transition temperature of the sample  $T_g$ . The relationships between  $E'$ ,  $E''$ ,  $\tan\delta$  and the dynamic Young's modulus ( $E^*$ ) is shown in Figure 10.12.

A sample can be measured over a range of temperatures and at various frequencies. The effect of temperature on storage modulus ( $E'$ ) and  $\tan\delta$  is shown in Figure 10.13. Relaxation processes may be studied in more

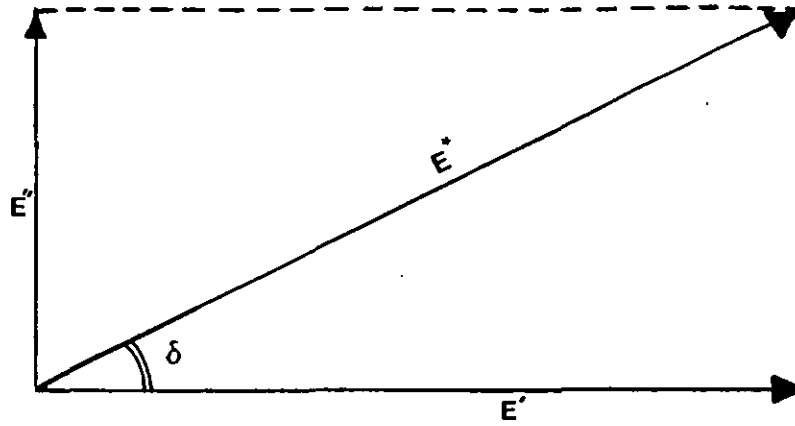


FIGURE 10.12: Argand diagram showing dynamic storage  $E'$  and loss  $E''$  moduli and  $\tan\delta$  under sinusoidal loading (after Ref 349)

detail by obtaining data over a range of frequencies, in addition to temperature. Frequency multiplexing is a common method of achieving frequency coverage. The effect of the frequency multiplexing technique in shifting the storage modulus and  $\tan\delta$  curves is shown in Figure 10.14.

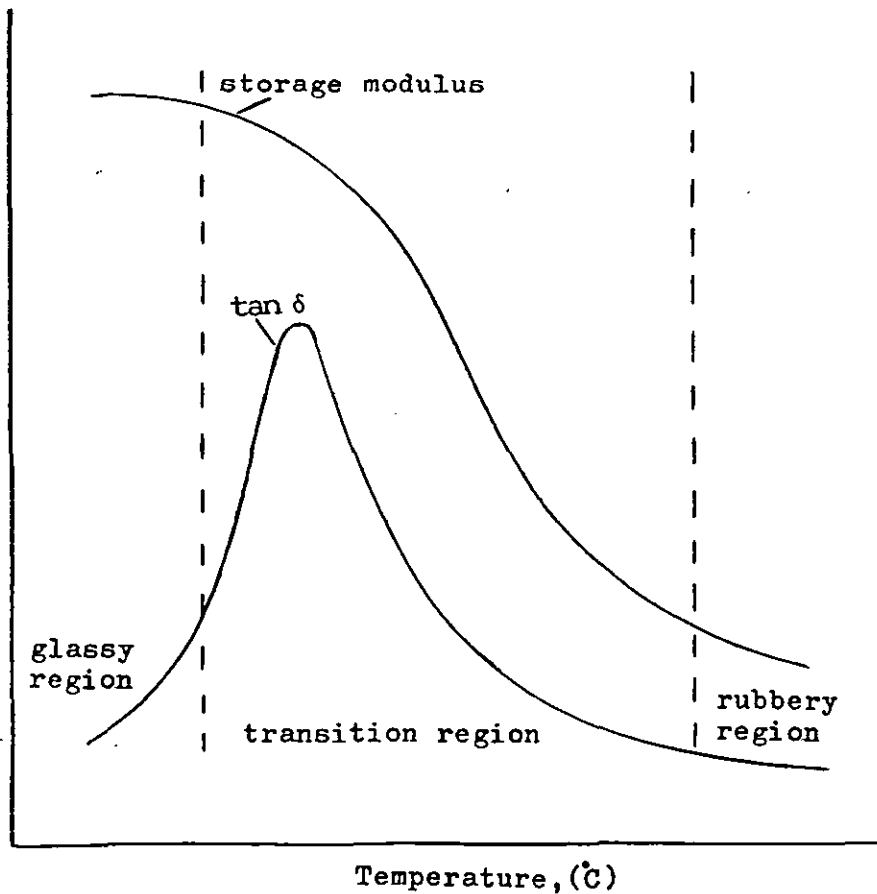


FIGURE 10.13: A schematic representation of temperature on storage modulus and  $\tan\delta$  (after Ref 20)

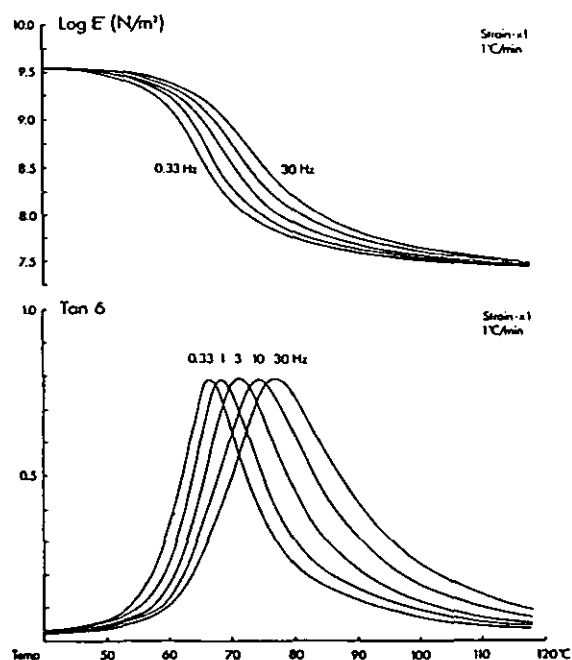


FIGURE 10.14: The effect of frequency multiplexing on storage modulus and  $\tan \delta$  (after ref 348)

### 10.3.2 DMTA: Experimental Procedure

All measurements were made using a Polymer Laboratories Dynamic Mechanical Thermal Analyser (PL-DMTA), shown schematically in Figure 10.15(a). The sample arrangement in the form of a rectangular bar of material was firmly clamped at both ends and also held by a central clamp. The central point of the bar was constantly vibrated sinusoidally by a drive shaft connected to an oscillator. A dual cantilever clamp frame used in this work is shown in Figure 10.15(b).

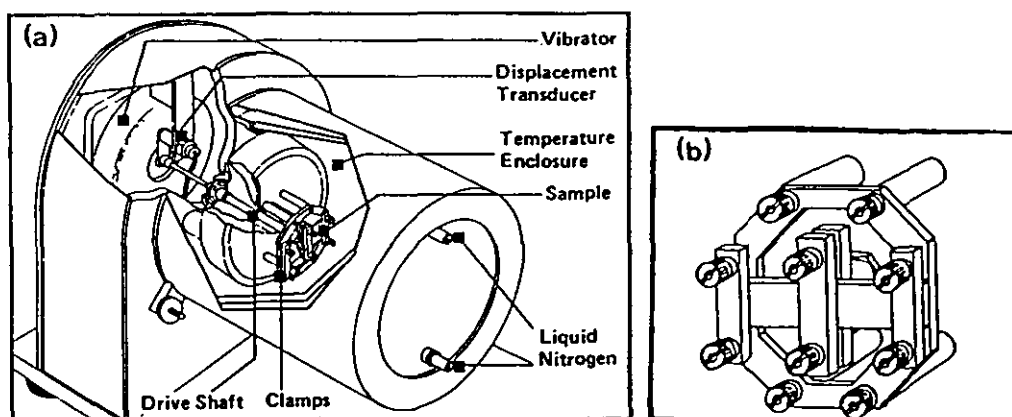


FIGURE 10.15: (a) A schematic diagram of the mechanical head of PL-DMTA  
(b) A typical dual cantilever clamping device used in the bending mode (after Ref 349)



For substrates and IMC and PMC samples, the rectangular strip test specimen of dimensions (40 x 10 x 4 mm) was used. For coatings, the formulations were coated on to one side of a rectangular steel bar substrate of dimensions (40 x 9.5 x 3 mm) with the exception of "Futura-Thane 5000", an elastomeric urethane coating, whose 0.95 mm average thickness was sufficiently thick to be tested as a free film. The clamped samples were then cooled using liquid nitrogen being introduced into the sample chamber by the aid of a glass funnel. Most measurements were carried out at 1 Hz frequency with strain setting of X1 for substrates and coated materials and X4 for free coating film samples. The heating rate was set at 4°C/minute and most specimens were tested over the temperature range of -80°C to 250°C. The sensitivity values for different functions of an X-Y recorder were set and the  $\log E'$  and  $\tan \delta$  were plotted.

### 10.3.3 DMTA: Results and Discussion

The DMTA results are presented in Figures 10.16 to 10.19. The results for various coatings applied to the steel bar showed large differences. These discrepancies indicated that the adhesion of polymeric coatings to the metal substrate bars brought about other factors influencing the dynamic mechanical results. It may be argued that as various coatings would adhere differently to different substrates, then the DMTA results obtained by coated steel bars are not true representatives of these coatings observed in IMC and PMC samples. Therefore a comparison based on the data obtained by coated steel bars and used for polymeric substrates proved misleading and was therefore discarded.

The DMTA scans for a number of in-mould and post-mould coated PU-RIM substrates are shown in Figure 10.16. The intensity and location of transition peaks for corresponding IMC and PMC samples show distinctive differences. A number of secondary transitions not observed with IMCs are particularly shown with PMCs. This effect seems

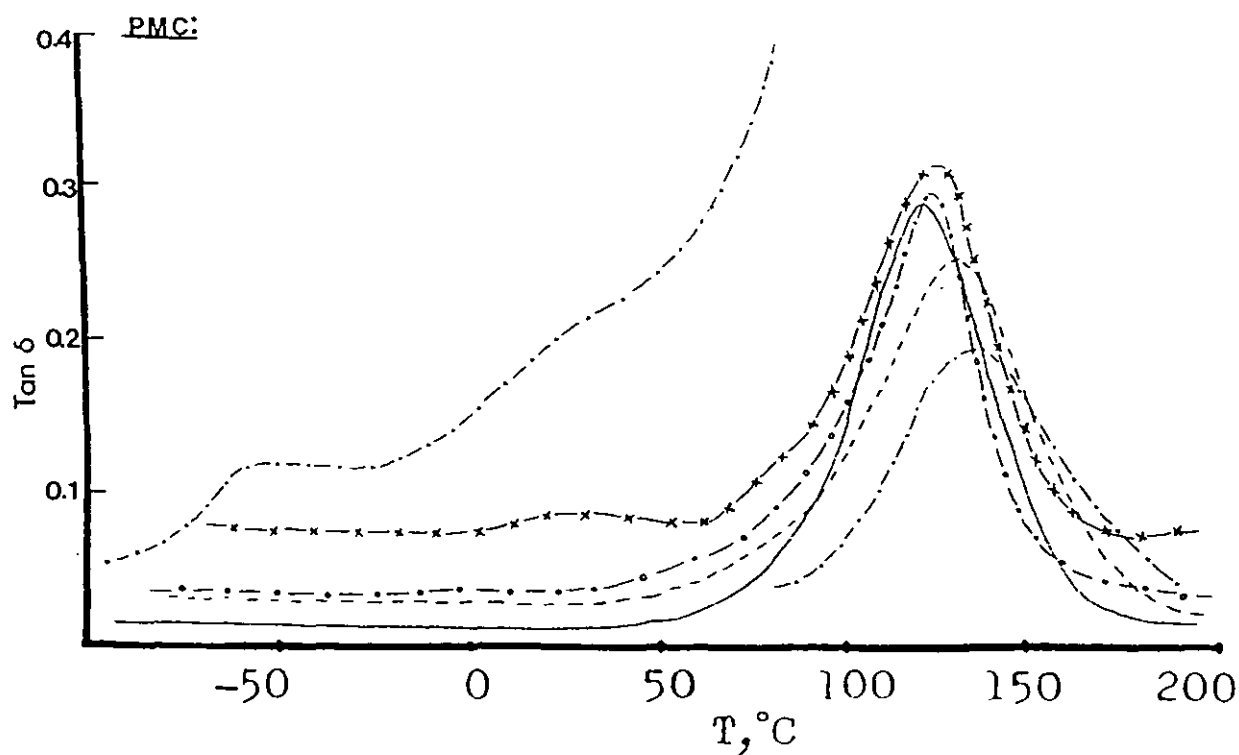
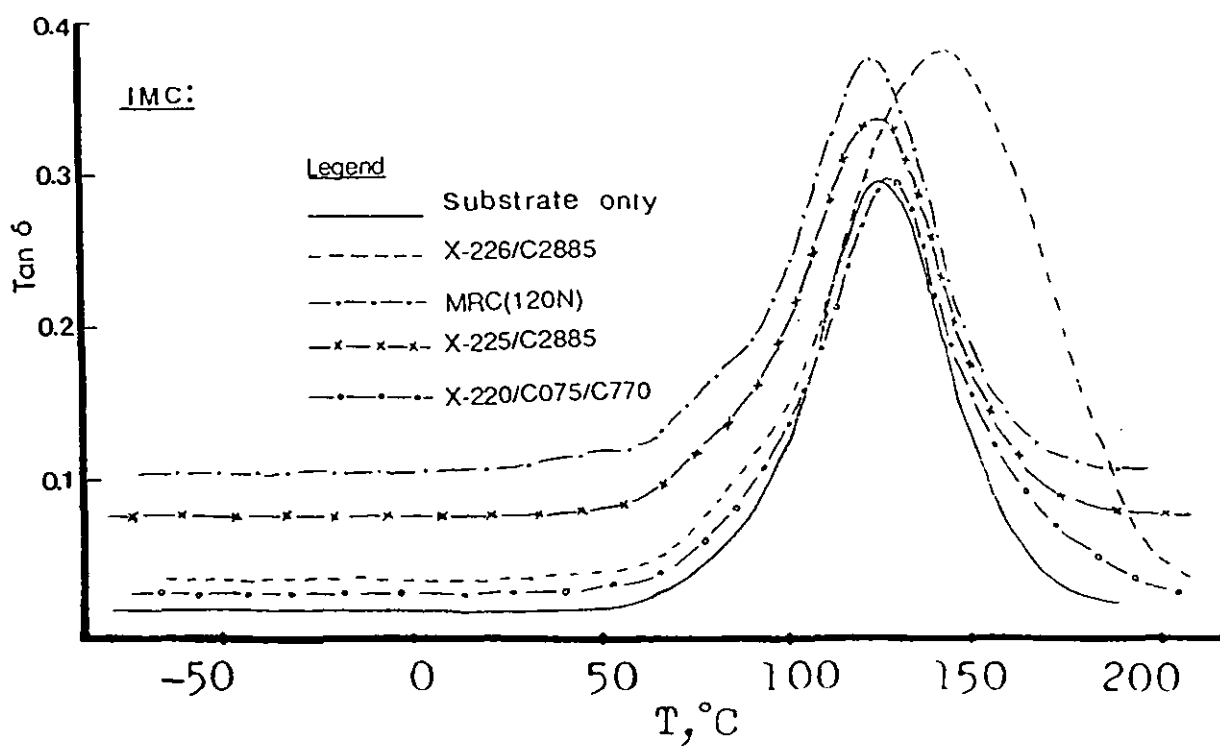


FIGURE 10.16: DMTA scans of IMC and PMC PU-RIM substrates

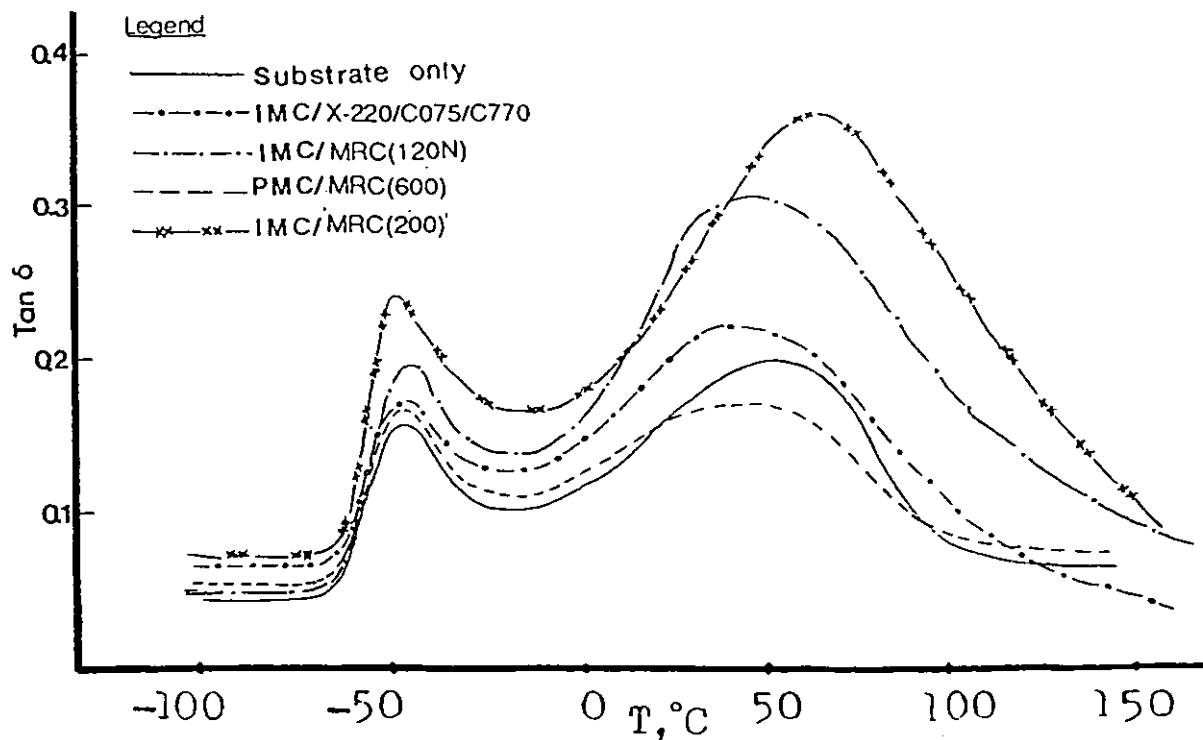


FIGURE 10.17: DMTA scans of coated semi-flexible PU foam substrates

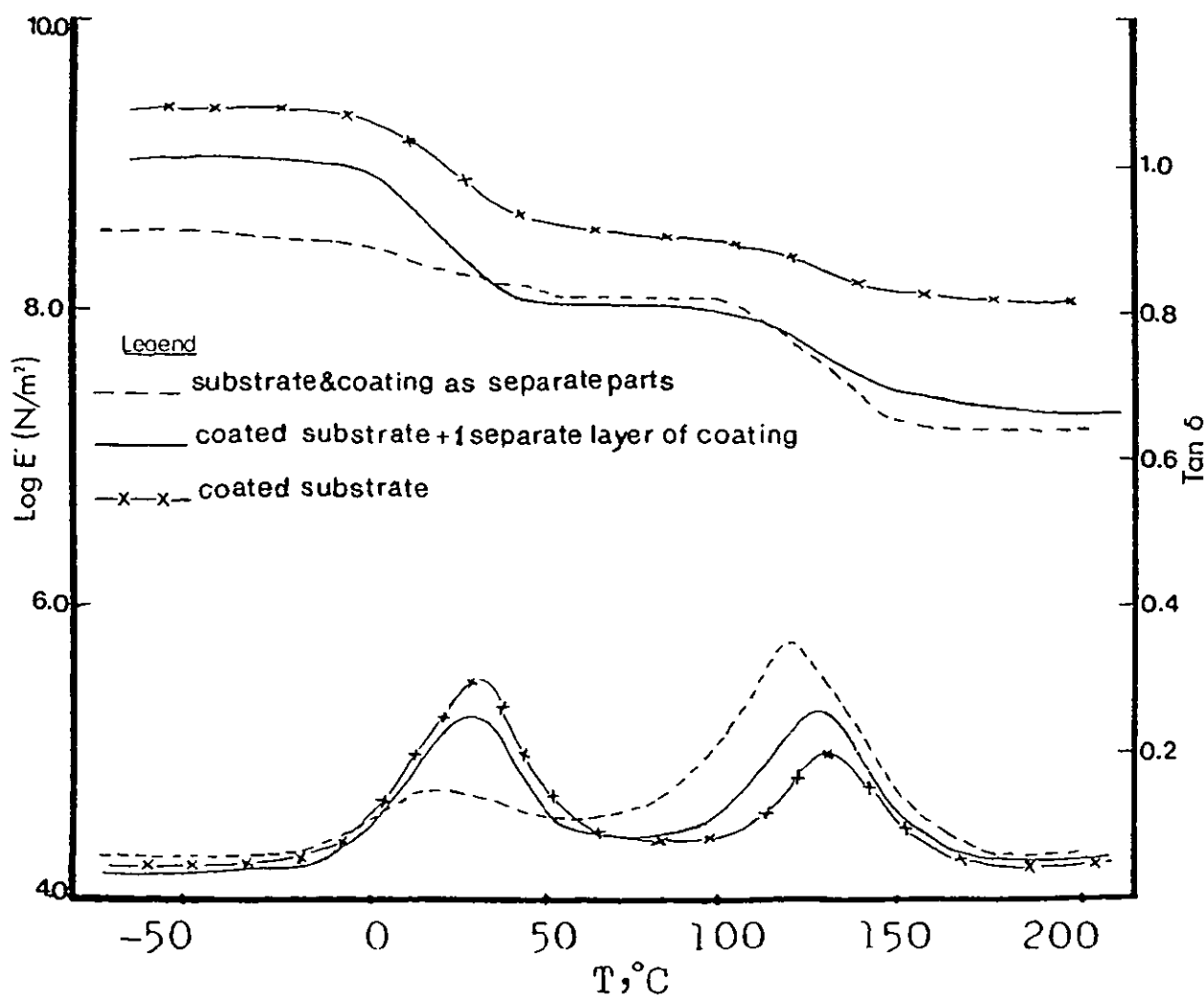


FIGURE 10.18: DMTA scans of coated PU spray foam substrate

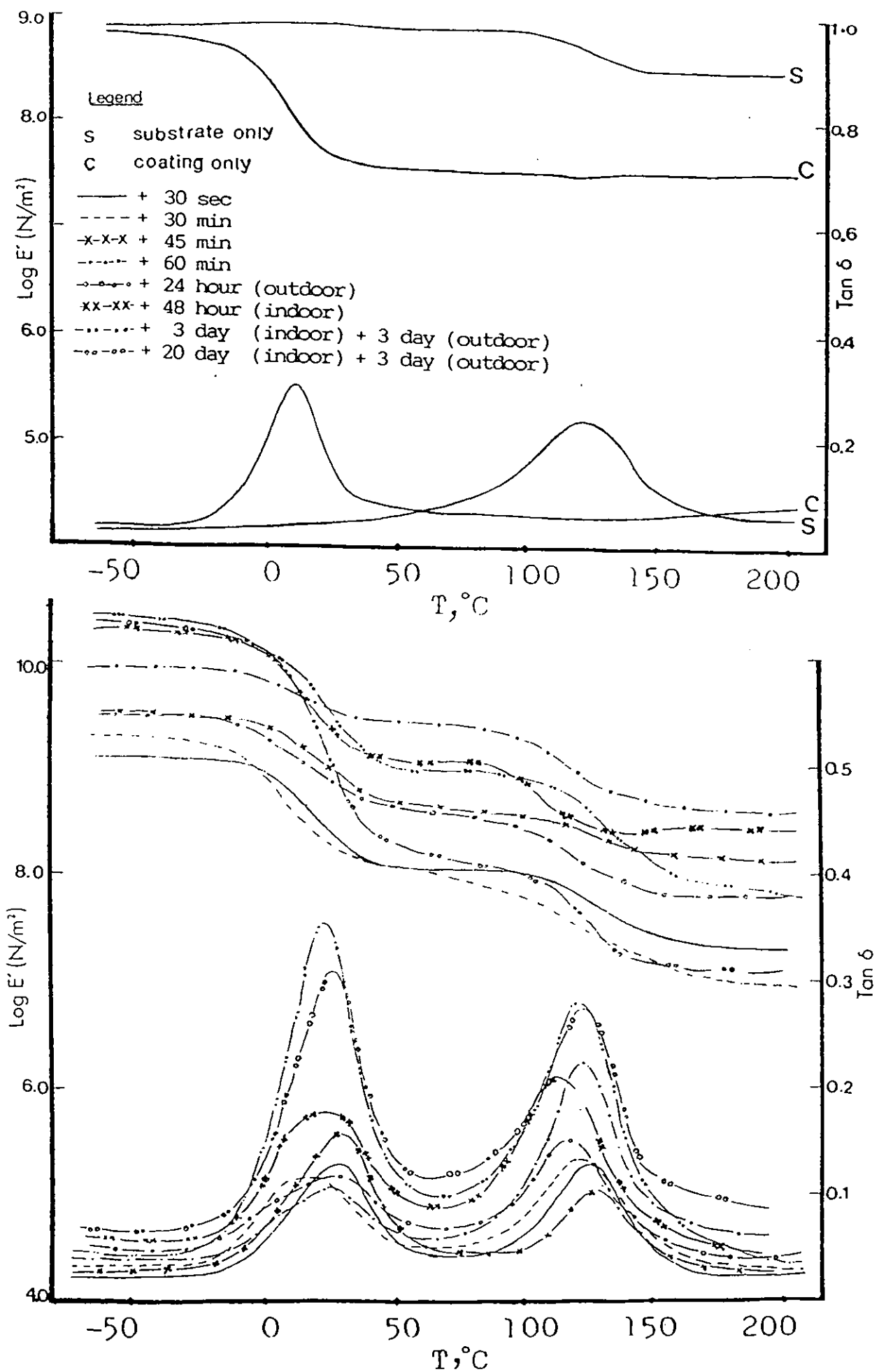


FIGURE 10.19: DMTA scans of coating, substrate and coated PU spray foam substrates

to be more pronounced with one pack than two pack coated systems. It is further observed that the  $\alpha$ -transition is normally broader in IMC and PMC samples of PU-RIM and also coated semi-flexible PU foam (Figure 10.17) than it is for the corresponding uncoated substrates. It may be argued that these differences in the local mode of transition is due to some degree of heterogeneity for the less compatible combination. This may be explained in terms of different coating processes producing physically and chemically different interfacial regions. For PMCs the molecular attraction forces between substrate and coating are weak and scattered whereas for IMCs, as a result of a number of beneficial parameters (i.e. mould temperature and pressure, exothermic heat of reaction, and the possibility of free radicals on freshly made surfaces), the chances of developing larger and more intimate attraction forces are greater.

Similarly it may be argued that for a number of IMC samples, the thermal diffusion of molecular segments across the interface (see Section 12.2.2) has resulted in different adhesion strength properties. The differences observed in DMTA scans of these materials are therefore reflecting these changes in energy required to dissociate various bond energies. It can be concluded that the method of processing (e.g. IMC and PMC) can have a significant effect on the extent of phase separation and on the morphology of the interfacial region. A similar view has also been observed by Wang and Cooper [354] in a study on the morphology and properties of PVC-PU blends. Although the appearance of a single glass transition temperature suggesting phase mixing in polymer blends does not hold wholly true in this research, it is anticipated that coated PUs showing relaxation transitions similar to those of corresponding uncoated substrates indicate better mixing and compatibility and a more homogeneously formed interfacial region.

It is clear that based on the above argument, it may be presumed that for IMC and PMC systems having different adhesion properties the stiffness measured by storage modulus and loss modulus of each system are different. For an asymmetrically coated composite (i.e. a single sided coating on a substrate) measured in a single cantilever bending mode, the following expressions have been suggested by Wetton [349]:

$$(KE') \text{ Composite} = E'_s b \left(\frac{t_s}{\ell}\right)^3 + \frac{1}{2} E'_c b \left[\left(\frac{t_s + 2t_c}{\ell}\right)^3 - \left(\frac{t_s}{\ell}\right)^3\right] f$$

$$(KE'') \text{ Composite} = E''_s b \left(\frac{t_s}{\ell}\right)^3 + \frac{1}{2} E''_c b \left[\left(\frac{t_s + 2t_c}{\ell}\right)^3 - \left(\frac{t_s}{\ell}\right)^3\right] f$$

where  $b$ ,  $t$  and  $\ell$  are the breadth, thickness and length respectively of the sample and the subscripts  $s$  and  $c$  refer to substrate and coating respectively, and  $f$  is a semi-empirical factor depending on the stiffness of coated systems. It has been argued that as the coating stiffness increases, so the neutral plane for the composite will move and the neutral plane approximation will no longer be valid.

The DMTA scans for a number of rigid PU spray foams coated at various coating conditions are shown in Figures 10.18 and 10.19. These scans show two distinctive transition temperatures corresponding to those of the original substrate and coating materials. These transitions show different amplitudes indicating that the coating processes and environmental conditions have had some effect on the interfacial formation shown by changes in mechanical loss behaviour.

CHAPTER 11  
SCANNING ELECTRON MICROSCOPY (SEM) AND  
X-RAY MICROANALYSIS

**11.1 INTRODUCTION**

The electron microscopes were first developed and demonstrated in Germany in the 1930s. The scanning electron microscope (SEM) was proposed and described by Knoll in 1935 and Von Ardenne in 1938. However it was in 1956 that Stewart and Snelling introduced the first commercial SEM [355-357].

The majority of modern commercial SEMs working in the same magnification range will normally display a larger depth of focus than the light microscope (i.e. up to X1000 greater). They can also cover a wide magnification range (i.e. from below X10 to X200,000 with a best resolution of 10 nm) with the ability of first observing an area at a low magnification and progressively increasing magnification and resolution [355,358]. Much of the early experiments with SEM have been used to examine the metal/polymer surfaces [359,360]. Johari et al [361] using SEM, studied the adhesion between a PU paint coating bonded to a titanium alloy. The SEM micrographs of fractured samples revealed some traces of an epoxy primer undercoat belonging to the PU coating on the titanium surface and also showed that the gaps formed were due to failure within the coating region itself and not in the interfacial region. Hence, a strong bond between the coating and the metal surface was indicated.

The development of SEM created a demand for analytical techniques to determine the chemical composition of the features revealed by the microscopes. Fitzgerald et al [362] published a significant paper in 1968 in which they were first to describe the use of an X-ray detector on an electron beam microanalyser. Today, several types of X-ray detectors with various applications can be used in conjunction with a SEM to provide chemical analysis of the sample along with surface topography measurements [363,364].

Although SEM has been used in studying the structure of PU and other polymers and has also been employed in various coatings research [365,366], there are very few examples in which SEM of polymeric substrates coated with polymeric materials and their interface region have been investigated. In this research, SEM studies of IMC and PMC samples of polyurethane and polyester substrates coated with various coatings are reported. Also, the elemental analysis of interfacial regions carried out with an energy dispersive X-ray microanalyser (EDX), a solid state detector, are reviewed.

### 11.2 SEM AND EDX TECHNIQUES

The SEM provides surface information about bulk specimens by scanning a medium energy (5 to 30 KV) electron beam across the surface and detecting the returning electron signal. The emission of electrons from the irradiated specimen will cover the whole energy range [355,367]. Generally speaking, it is the secondary electrons which are amplified and sent to a cathode ray tube (CRT) to form the image. Since electrons do not travel very far due to air molecules collision under normal atmospheric pressures, the operating section of the electron microscope, including the specimen, must be maintained under



high vacuum. The electrons accelerated by an anode at a voltage range of 1 to 200 KV, are then directed towards an electrostatic or electromagnetic field onto the specimen. Having passed through more electrostatic or electromagnetic lenses, the secondary electrons reflected from the specimen surface are finally recorded on a fluorescent screen or photographic plate. While high magnifications are easy to obtain with the SEM, very low magnifications are difficult to achieve as they require large deflection angles. The principles of SEM are shown schematically in Figure 11.1.

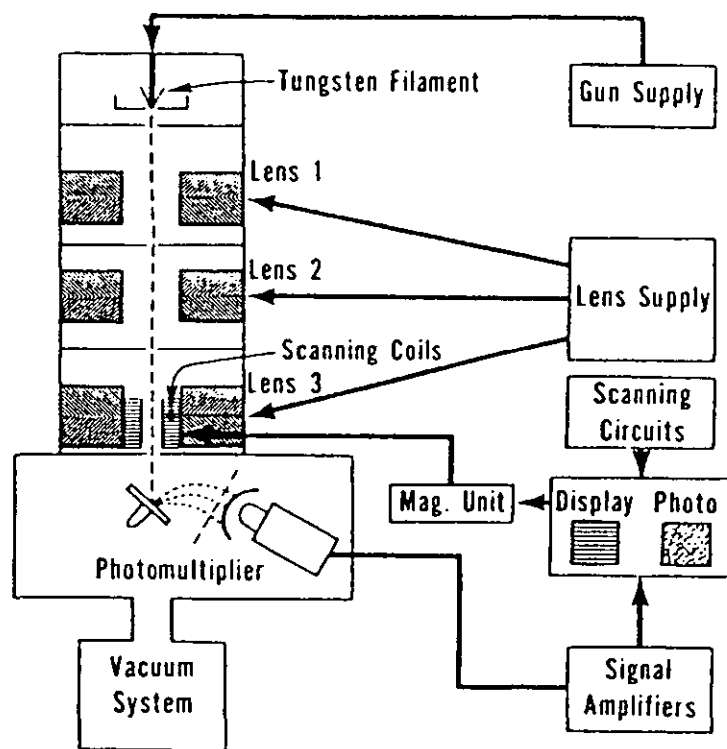


FIGURE 11.1: Schematic of a scanning electron microscope (SEM) equipped with energy dispersive X-ray analysis (EDX) (after Ref 355)

When X-ray analysis is carried out in the SEM, the fine scanning probe is made stationary on a region of interest from which the X-rays emitted under the effect of the electron beam provide information

about the nature and amount of elements present in that excited area [357,367]. EDX can give elemental composition information for layer thickness to 1 to 2  $\mu\text{m}$ . Although ED analysers may be used to detect elements of atomic number down to that of oxygen, best results given are for elements above fluorine ( $Z=9$ ) [368]. To avoid any problems a more vigilant detection for elements co-existing in a sample whose X-ray energies are too close is needed.

### 11.3 COATING PROCESS

Nearly all non-contacting specimens examined in the SEM or analysed by an X-ray detector need to be coated with a thin film of conducting material. This coating is necessary to eliminate or reduce the electric charge which builds up in a non-conducting specimen when scanned by a beam of high-energy electrons. In the absence of a coating layer, non-conductive specimens examined at optimal instrumental parameters invariably exhibit charging phenomena which result in image distortion and thermal radiation damage which can lead to a significant loss of material from the specimen [355,357].

The conducting coatings include carbon or heavy metals such as silver, gold or gold-palladium alloy if a smaller metal grain size is required. Metal coating can be produced in a variety of ways, but of these methods only thermal evaporation and sputtering are useful for coating specimens for SEM and X-ray microanalysis. The cold diode sputtering technique was employed in this research.

#### 11.4 EXPERIMENTAL PROCEDURE

Samples for SEM and EDX analysis were microtomed having been cooled using liquid nitrogen. Visual examination of all specimens was carried out using a Cambridge Stereoscan model 2A microscope. The microanalyser fitted to the SEM was a LINK type 860 series. Specimens for SEM examination were 10 to 15 mm maximum dimensions because of the limited size of the vacuum chamber. These were attached to Al specimen holders (stubs) and a thin layer of silver was applied upon the samples by a sputtering process under high vacuum conditions. The prepared samples were then placed in the SEM column with the chamber being automatically vacuum cycled and the microscope in operation mode.

The interfacial regions between the substrate and coating in different systems were then thoroughly examined by the image being projected onto a fluorescent screen. A diversion mechanism enabled the screen to be replaced by a photographic medium and a number of areas of interest were recorded by a 35 mm camera.

For each sample, the energy of emitted photons by an X-ray source were measured to determine what elements were present (qualitative analysis) and from their intensity the quantities of each element present in the specimens were determined. This procedure was carried out at a point 40  $\mu\text{m}$  inside each substrate and was repeated at 20, 10, 5, 2 and 1  $\mu\text{m}$  distance from the coating depending on the nature/shape of the interface. Then the above procedure was repeated with a starting point inside the coating. A minimum of 10 positions inside each system were chosen and the data collected was averaged.

## 11.5 RESULTS AND DISCUSSION

The SEM results are given in Figures 11.2 to 11.13. In order to make a comparison between different systems, these micrographs have been grouped according to their types of substrate. Polyurethane substrates (semi-flexible, rigid, and RIM) and polyesters (C<sub>196</sub>, C<sub>198</sub>, and C<sub>199</sub>) are dealt with first followed by an SEM review of coated rigid PU spray foam. The results of elemental analysis of these systems by EDX are documented in the last section.

### SEM Results of Polyurethane Substrates

Figures 11.2 to 11.7 show the SEM micrographs for coated samples of semi-flexible, rigid and RIM PU substrates.

#### a) For semi-flexible PU foam

Figures 11.2(a) and 11.2(b) show typical IMC and PMC systems of semi-flexible PU foams. At 50 to 200 magnifications it is not possible to discern any differences between the two systems. Nevertheless it is recognised that with 2 pack coatings particularly, and also with 1 pack MRC (600) PU coating, the damage produced by microtoming is less evident. An interesting observation was made at higher magnifications (e.g. at 500 to 1200) which revealed some differences at the boundary between the mating surfaces of IMC and PMC samples. This is shown in Figures 11.2(c) and 11.2(d) where typical IMC systems showed a diffuse interface possibly due to a better compatibility of the two systems. In contrast the PMC samples revealed a more distinct, sharper interfacial region.

Figures 11.3(a) to 11.3(d) show typical micrographs of coated semi-flexible foams at 2000 to 10,000 magnifications. Most of the IMC

systems revealed a diffuse type of interface. Any particular variation between these systems was not observed. Therefore the degree of diffusion and a classification of the systems was not easily discerned. It could only be stated confidently that with the two pack MRC (200) PU coating shown in Figures 11.3(b) and 11.3(c) a more diffuse interfacial region was observed.

Generally PMC samples showed more distinct boundaries between coating and substrate than their corresponding IMC systems. This effect could not be directly related to the coating type. Nevertheless, it was established that with some coatings such as MRC (120N) shown in Figure 11.3(d) and also with MRC (600) the interface was more diffuse and no obvious boundaries were observed.

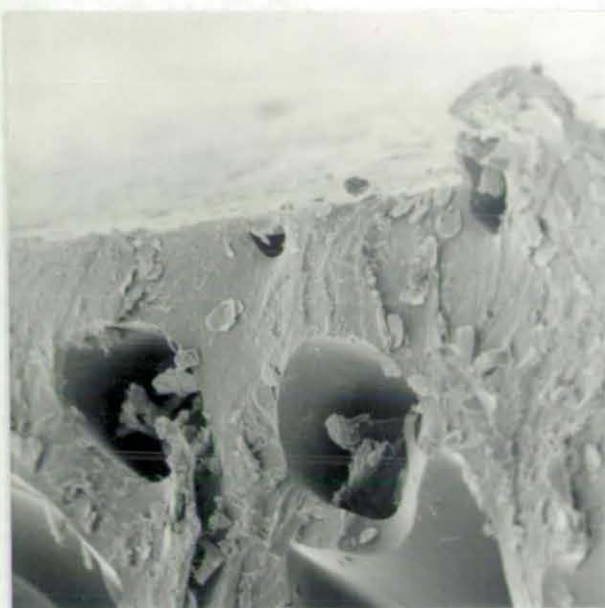
**b) For rigid PU foam substrate**

Figures 11.4 and 11.5 show typical SEM micrographs of coated rigid PU foams. At low magnification (e.g. at 100X) the photomicrographs shown in Figures 11.4(a) and 11.4(b) are very similar to those of semi-flexible substrate. However, the SEM results at higher magnifications shown in Figures 11.4(c) and 11.4(d) revealed a distinct boundary between coating and substrate. This effect was more pronounced with the one pack coatings.

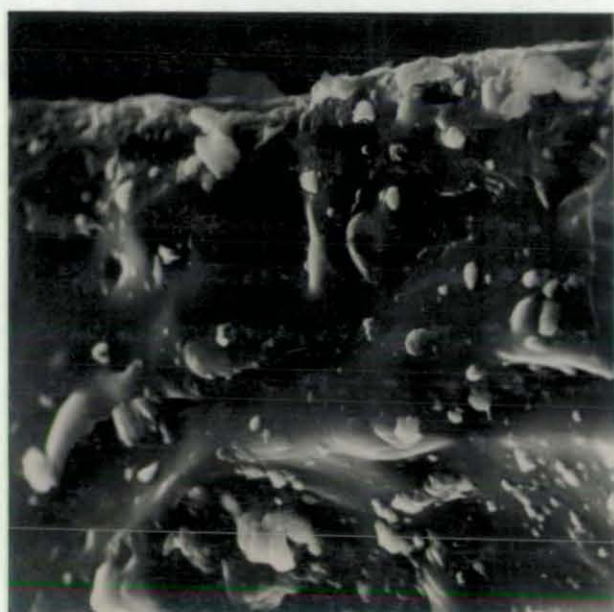
Figures 11.5(a) to 11.5(d) demonstrate typical examples of IMC and PMC systems on rigid foam substrates at magnifications up to 10,000. It is interesting to note that some pigment particles are visible particularly at high magnifications. The interfacial region observed with the two pack (i.e. MRC (200) and X-220/C075/C770) and one pack MRC (120N) coatings were particularly diffuse. This effect may be explained due to similar solubility parameters between the two phases



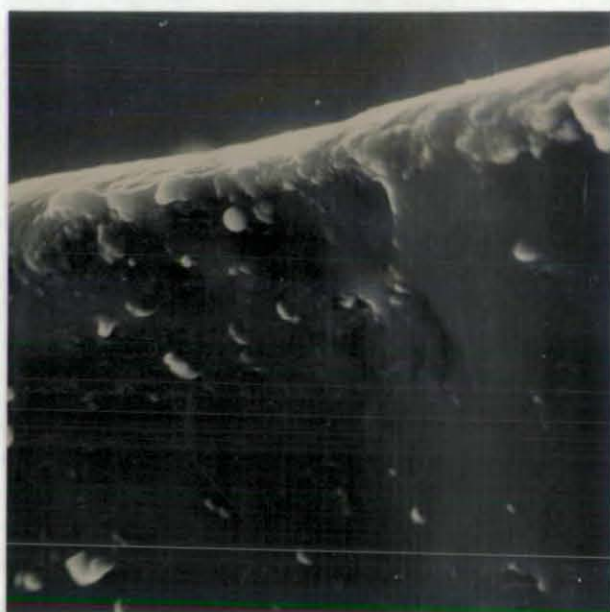
(a) | 200 μm |



(b) | 200 μm |



(c) | 16 μm |



(d) | 20 μm |

FIGURE 11.2: SEM micrographs of coated semi-flexible PU foam substrate:

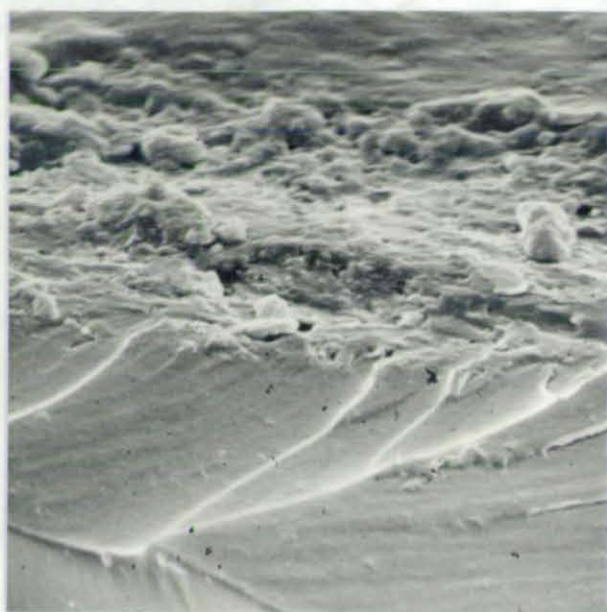
- |                           |         |
|---------------------------|---------|
| (a) IMC/MRC (600)         | (x100)  |
| (b) PMC/(X-225/C2885)     | (x100)  |
| (c) IMC/(X-220/0075/C770) | (x1250) |
| (d) PMC/MRC (600)         | (x1000) |





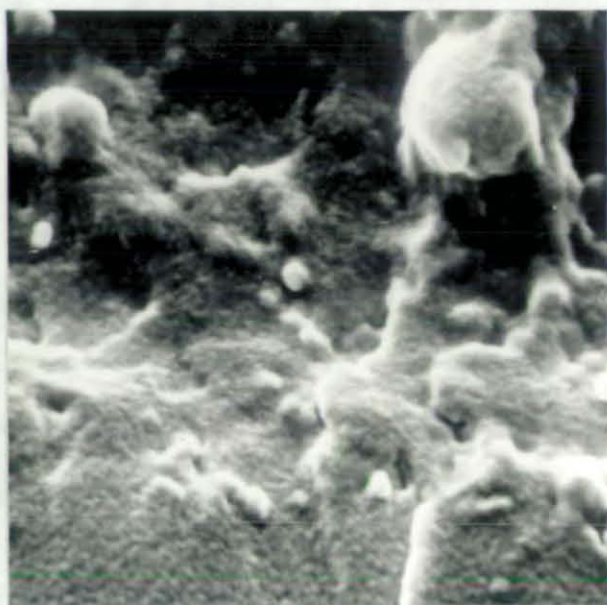
(a)

10 μm



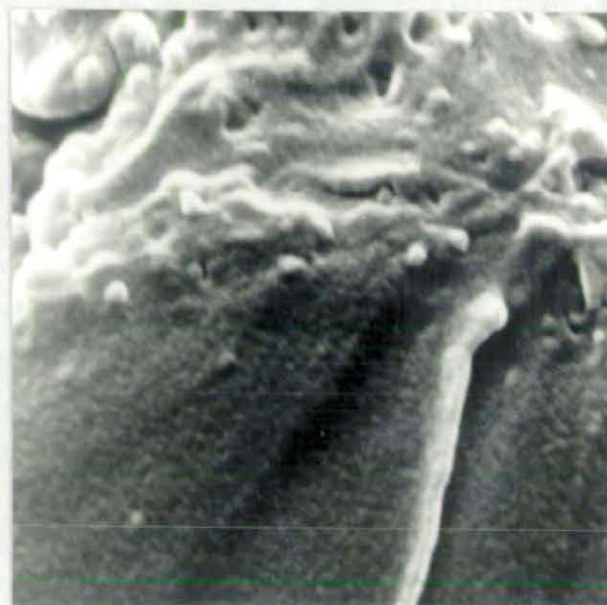
(b)

10 μm



(c)

2 μm



(d)

2 μm

FIGURE 11.3: SEM micrographs of coated semi-flexible PU foam substrate:

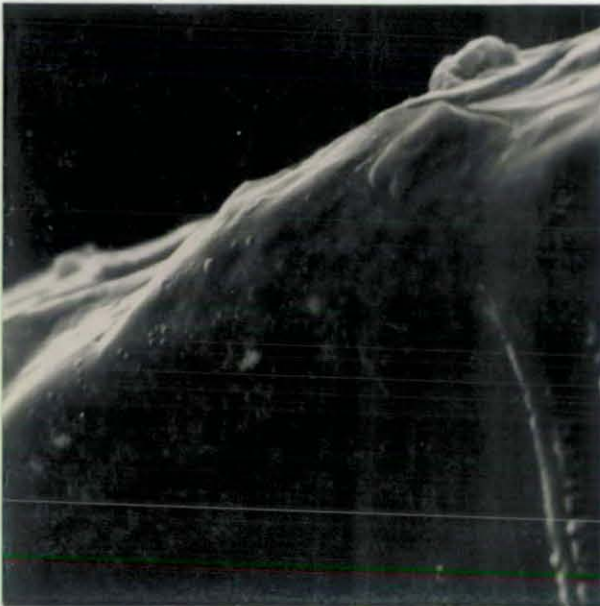
- |                    |           |
|--------------------|-----------|
| (a) IMC/MRC (120N) | (x2000)   |
| (b) IMC/MRC (200)  | (x2000)   |
| (c) IMC/MRC (200)  | (x10,000) |
| (d) PMC/MRC (120N) | (x10,000) |



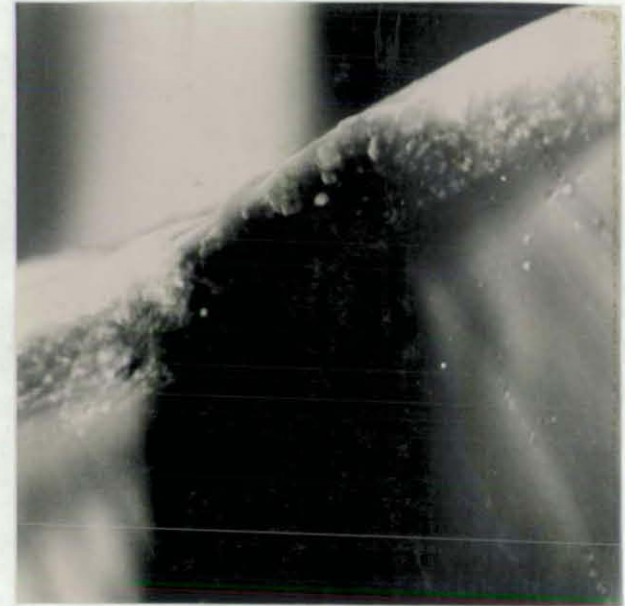
(a) 200 μm



(b) 200 μm



(c) 20 μm



(d) 16 μm

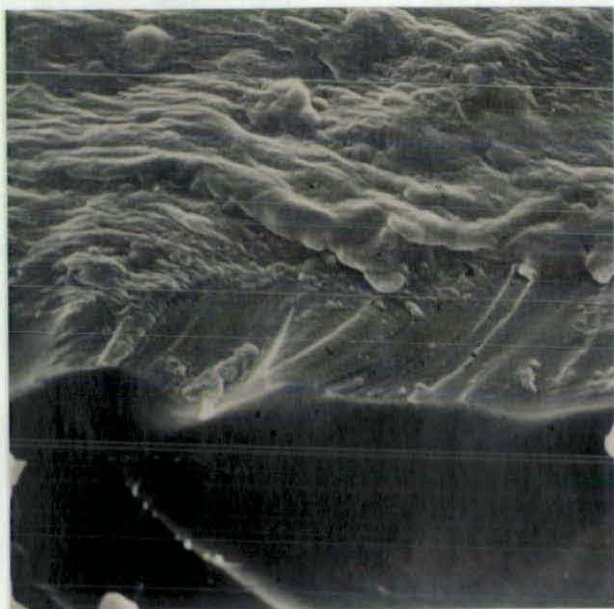
FIGURE 11.4: SEM micrographs of coated rigid PU foam substrate:  
 (a) IMC/MRC (120N) (x100)  
 (b) PMC/MRC (200) (x100)  
 (c) IMC/(X-225/C2885) (x1000)  
 (d) PMC/MRC (600) (x1250)





(a)

10  $\mu\text{m}$



(b)

10  $\mu\text{m}$



(c)

2  $\mu\text{m}$



(d)

2  $\mu\text{m}$

FIGURE 11.5: SEM micrographs of coated rigid PU foam substrate:

- |                           |           |
|---------------------------|-----------|
| (a) PMC/MRC (120N)        | (x2000)   |
| (b) IMC/MRC (200)         | (x2000)   |
| (c) IMC/MRC (120N)        | (x10,000) |
| (d) IMC/(X-220/0075/C770) | (x10,000) |

(especially with MRC (120N) being formulated mainly for application to rigid substrates). This view has also been noted by Princen [369] in blended polymers of close solubility parameters forming uniform, mutually dissolved films, whereas polymers with larger differences in the parameters produced a more separated, less diffuse film. The effect of solubility parameters on the pull-off adhesion test results of IMC and PMC systems (see Sections 12.2.1 and 12.2.3) also complements these findings.

c) For RIM PU substrates

Figures 11.6 and 11.7 show the micrographs for IMC and PMC samples of RIM PU substrates. Various magnifications were employed and it was decided that the range of 100 to 1000 magnification would best suit these systems. At low magnifications (e.g. at 100X) the typical micrographs shown in Figures 11.6(a) and 11.6(b) revealed very diffuse interfaces and this effect was common for both 1 and 2 pack coatings of both IMC and PMC samples.

Some interesting observations shown in Figures 11.6(c) and 11.6(d) were made on the samples that had already been subjected to some stress in a tensile adhesion pull-off test. With one pack coatings some failure, particularly at or near the interfacial region between substrate and coating were clearly observed. This effect was shown for both IMC and PMC samples. Although in most cases the failure was a mixed type between substrate and the coating, the cohesive failure within coating and mixed failure between coating and adhesive were also observed. A typical example is shown in Figure 11.7(a).

The micrographs for two pack PU coating at higher magnifications (e.g. 500 to 1200X) shown in Figures 11.7(b) and 11.7(c) demonstrated some





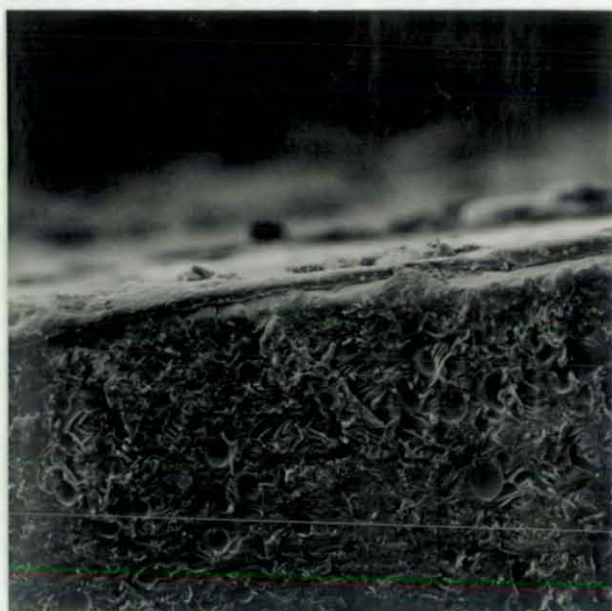
(a)

200  $\mu\text{m}$



(b)

200  $\mu\text{m}$



(c)

100  $\mu\text{m}$



(d)

100  $\mu\text{m}$

FIGURE 11.6: SEM micrographs of coated PU-RIM substrate:

- |     |                       |        |
|-----|-----------------------|--------|
| (a) | IMC/(X-226/C2885)     | (x100) |
| (b) | PMC/(X-220/0075/C770) | (x100) |
| (c) | IMC/(X-226/C2885)     | (x200) |
| (d) | PMC/(X-225/C2885)     | (x200) |

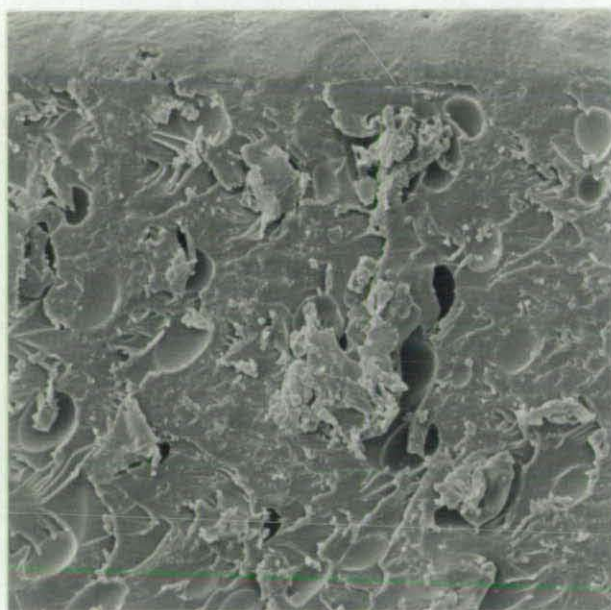




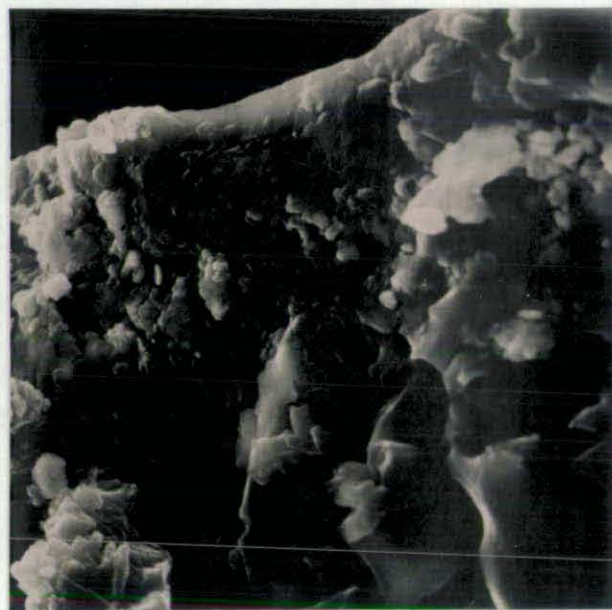
(a) 100 μm



(b) 40 μm



(c) 40 μm



(d) 16 μm

FIGURE 11.7: SEM micrographs of coated PU-RIM substrate:

- |     |                       |         |
|-----|-----------------------|---------|
| (a) | IMC/MRC (120N)        | (x200)  |
| (b) | PMC/(X-220/C075/C770) | (x500)  |
| (c) | IMC/(X-220/C075/C770) | (x500)  |
| (d) | IMC/(X-220/C075/C770) | (x1250) |

differences to those of one pack systems. Both IMC and PMC samples revealed a more diffuse (especially with IMC samples) interfacial region. This diffuse boundary of the interface also shown in Figure 11.7(d) may suggest diffusion of the mating surfaces (see EDX results and discussion).

#### SEM Results of Polyester Substrates

Figures 11.8 to 11.11 show typical SEM micrographs of coated polyester substrates.

Some typical results of coated C<sub>196</sub> substrate shown in Figures 11.8(a) to 11.8(d) of the interfacial region revealed both diffuse and sharp boundaries between coating and the substrate. The effect of coating type and coating process was not easily distinguished. The exception to this was with IMC samples of C<sub>196</sub> substrate being coated with the two pack PU coating shown in Figure 11.8(a), where all SEM micrographs revealed a very diffuse interface.

Figures 11.9(a) to 11.9(d) show typical SEM micrographs of coated C<sub>198</sub> substrate. A systematic variation between different systems was not recognised. Although a number of diffuse interfaces were observed with many IMC samples, in most cases it was not a continuous effect.

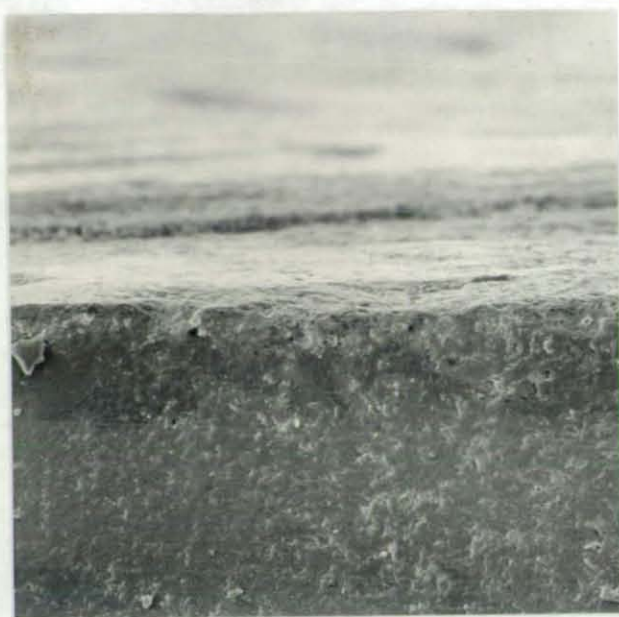
Figure 11.9(d) showed a particular problem with PMC samples of C<sub>198</sub> polyester coated with one pack PU coating MRC (120N). It illustrated a few distinct boundaries with several breaks in the interface. In explanation, the discontinuous layers of coating are showing a repeated painting application due to difficulties in properly wetting the substrate.

Figures 11.10(a) to 11.10(d) show typical SEM results of coated C<sub>199</sub> substrate. Both diffuse and sharp interfaces were observed. A systematic variation between different types of coatings was not observed. The damage produced by microtoming was seen in many samples, for example 11.10(a) and 11.10(b), showing ductile failure in the paint film.

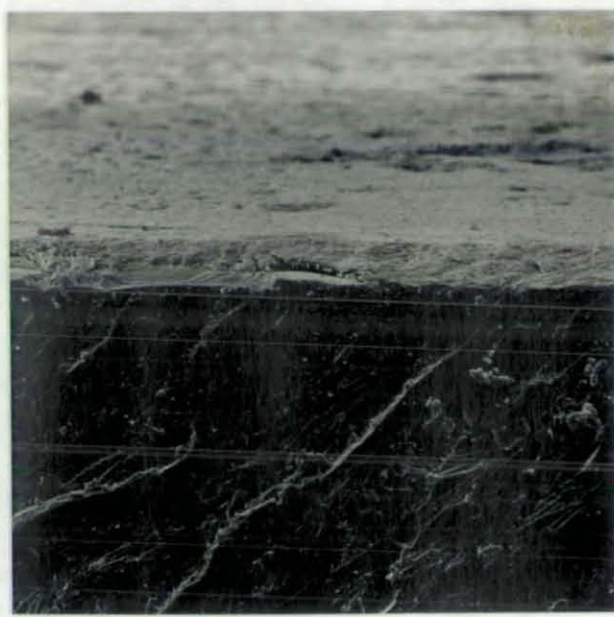
Figure 11.11 shows some examples of IMC and PMC samples of polyester substrates after being subjected to the tensile pull-off adhesion test. Micrographs 11.11(a) and 11.11(b) demonstrate typical failures within many IMC systems. Figure 11.11(a) shows the micrograph of C<sub>199</sub> coated with X-226/C2885, a one pack coating. This type of failure was also observed with C<sub>196</sub> and C<sub>198</sub> substrates coated with the same and other one and two pack coatings. It shows a clear failure in the coating region and also a few areas where the substrate is beginning to fail under the stress. Figure 11.11(b) illustrates the SEM micrograph of C<sub>196</sub> coated with two pack PU, X-220/C075/C770 coating. The coating shows typical cohesive failure whereas the substrate and the interfacial region are quite intact.

The micrographs in Figures 11.11(c) and 11.11(d) are showing failures of PMC samples of C<sub>199</sub> and C<sub>196</sub> substrates coated with MRC (120N) and X-225/C2885 coating respectively. These two types of failure were also observed with some of the C<sub>198</sub> coated surfaces. Although it may be argued that some minor mixed failure between substrate and coating is evident, the majority of cases showed a very pronounced clear cut failure between the two phases. Hence, these are regarded as typical interfacial failures for coated polyester substrates. It must be emphasised that generally IMC and PMC samples showed very similar visual appearances (i.e. with the naked eye) and it was only with the





(a) 100 μm



(b) 100 μm



(c) 100 μm



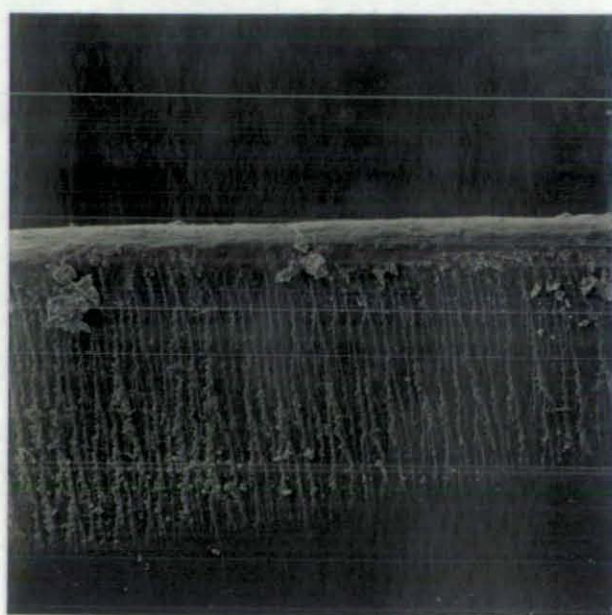
(d) 100 μm

FIGURE 11.8: SEM micrographs of coated C<sub>196</sub> polyester substrate:  
 (a) IMC/(X-220/C075/C770) (x200)  
 (b) FMC/(X-226/C2885) (x200)  
 (c) IMC/MRC (120N) (x200)  
 (d) FMC/(X-225/C2885) (x200)



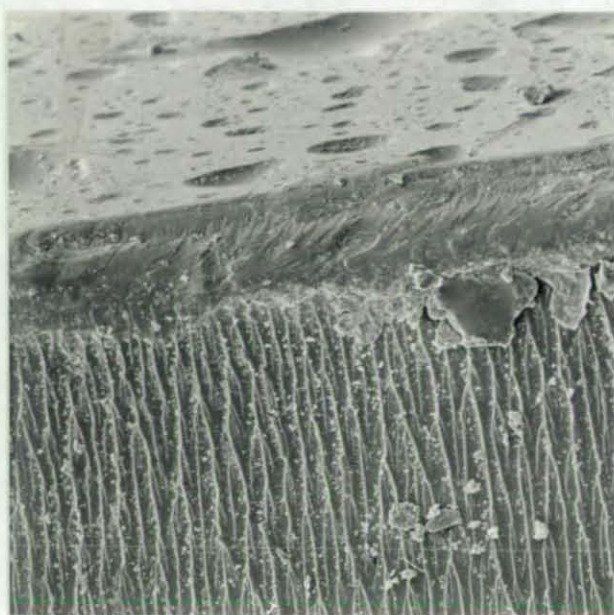
(a)

100 μm



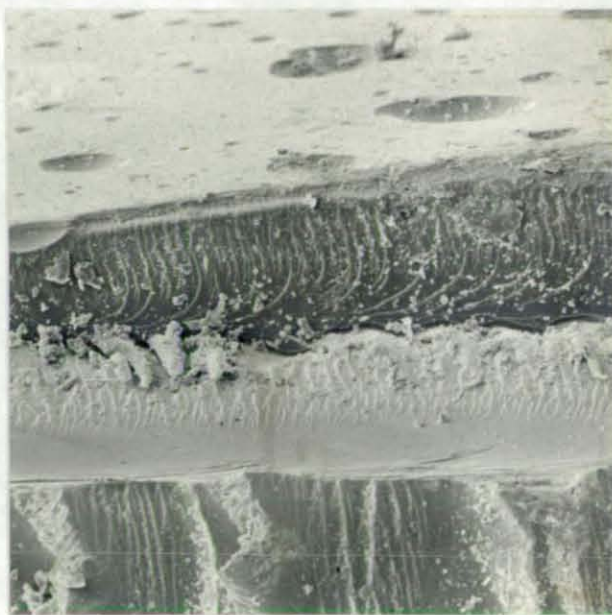
(b)

100 μm



(c)

40 μm



(d)

40 μm

FIGURE 11.9: SEM micrographs of coated C<sub>198</sub> polyester substrate:

- |     |                       |        |
|-----|-----------------------|--------|
| (a) | IMC/(X-225/C2885)     | (x200) |
| (b) | IMC/(X-220/0075/C770) | (x200) |
| (c) | PMC/(X-226/C2885)     | (x500) |
| (d) | PMC/MRC (120N)        | (x500) |

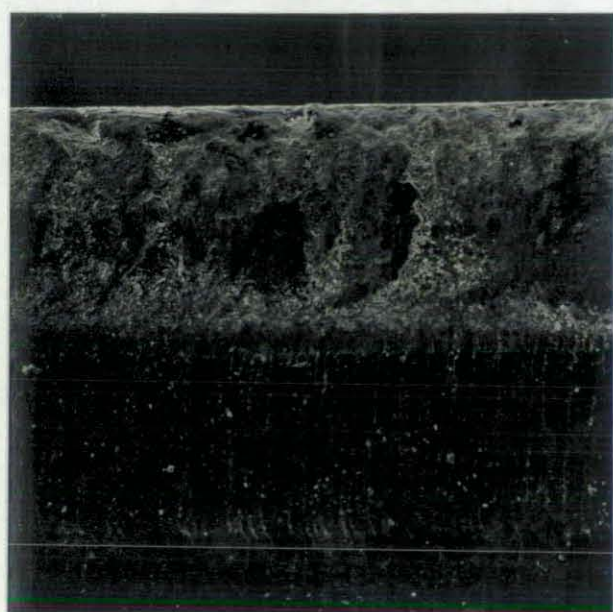




(a) 40 μm



(b) 40 μm



(c) 40 μm



(d) 40 μm

FIGURE 11.10: SEM micrographs of coated C<sub>199</sub> polyester substrate:  
 (a) IMC/(X-220/C075/C770) (x500)  
 (b) IMC/(X-225/C2885) (x500)  
 (c) PMC/(X-226/C2885) (x500)  
 (d) PMC/(X-225/C2885) (x500)





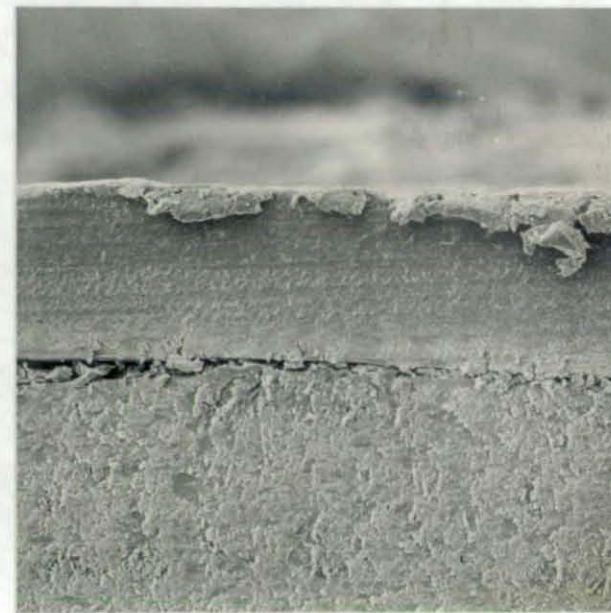
(a) 16 μm



(b) 16 μm



(c) 16 μm



(d) 16 μm

FIGURE 11.11: SEM micrographs of coated polyester substrates after adhesion pull-off test:

- |     |   |         |
|-----|---|---------|
| (a) | IMC C <sub>199</sub> /(X-226/C2885)     | (x1250) |
| (b) | IMC C <sub>196</sub> /(X-220/C075/C770) | (x1250) |
| (c) | PMC C <sub>199</sub> /MRC (120N)        | (x1250) |
| (d) | PMC C <sub>196</sub> /(X-225/C2885)     | (x1250) |

aid of SEM micrographs that more detailed information on interfacial bonding (i.e. adhesion and compatibility) was revealed.

#### SEM Results of Coated PU Spray Foam

Figures 11.12 and 11.13 show the SEM micrographs for one pack coating (Futura-Thane 5000) designed for "heavy build" (i.e. thick coating resulting from a single spray pass) on spray grade PU rigid foam (Isofoam SS-0658).

The SEM results of rigid foam coated within the first hour of production are shown in Figures 11.12(a) to 11.12(d). The micrographs shown in Figures 11.13(a) to 11.13(d) are representing those systems for which the substrate has been subjected to some deliberate conditions and treatment (i.e. ageing, temperature and humidity) before the coating is applied. Different magnifications were tried. However, even at 50X magnification the aeration in the coating and at the interface for most of the systems is clearly visible on top of the closed cell foam. The air traps at or near the coating/substrate interface suggest potential weakness in the structure. Air-trapping may be attributed to the relatively high viscosity, high solids coating used to give 0.5 to 1.5 mm dry thickness in a single pass (c.f. low viscosity IMC and PMC coatings at 5 to 40  $\mu\text{m}$ ) [314]. There is no systematic variation found between different systems. However, the samples coated in early stages of foam production shown in Figure 11.12 revealed a more diffuse interface than those coated at a much later stage as shown in Figure 11.13. This may be due to a change in substrate topography as well as the possibility of some free isocyanate being present in the early stages. Discontinuity and air traps at the interface particularly visible in Figures 11.13(b) to 11.13(d) are likely to make initiation of delamination easier. This





(a)

400 μm



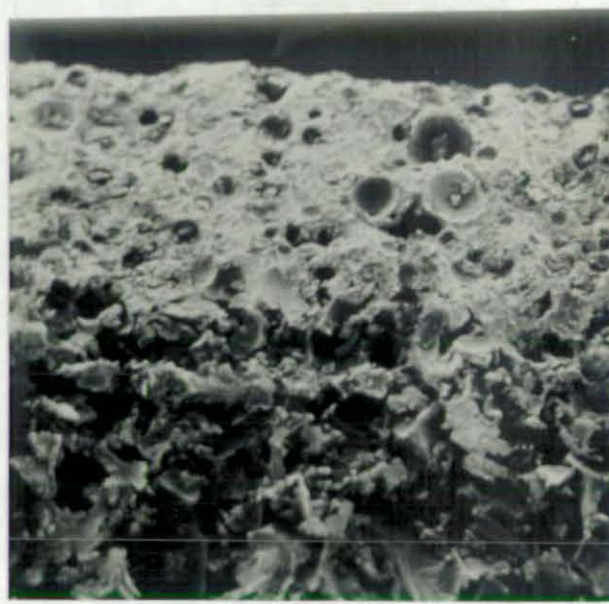
(b)

400 μm



(c)

400 μm



(d)

400 μm

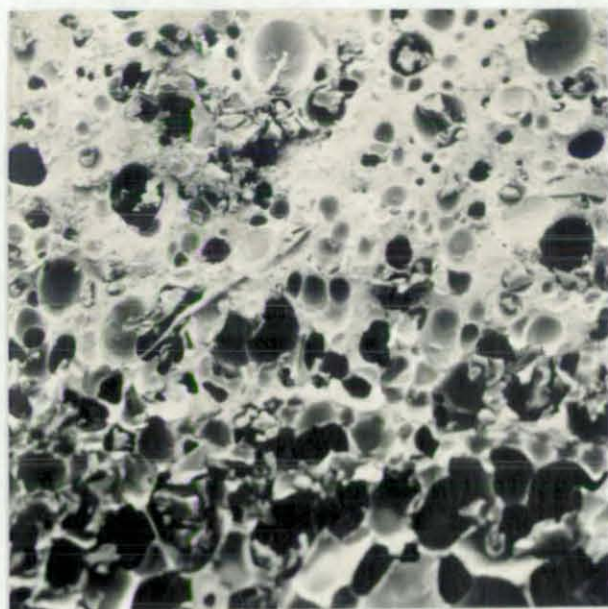
FIGURE 11.12: SEM micrographs of coated PU spray foam substrate at various coating conditions (x50):

- (a) + 30 sec
- (b) + 30 min
- (c) + 45 min
- (d) + 60 min

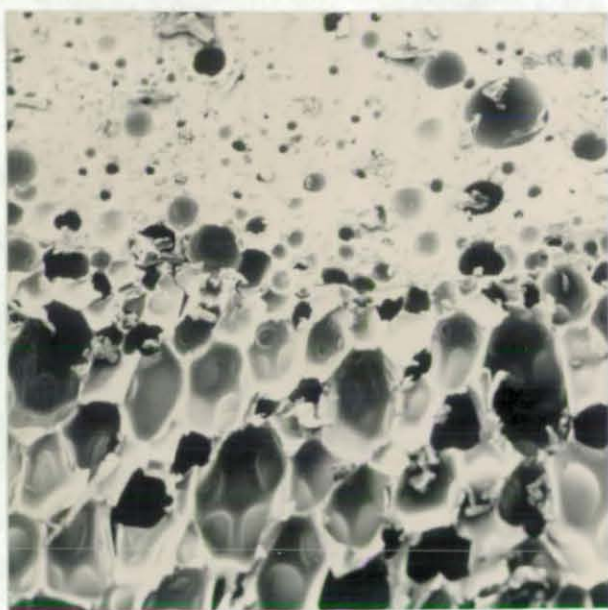




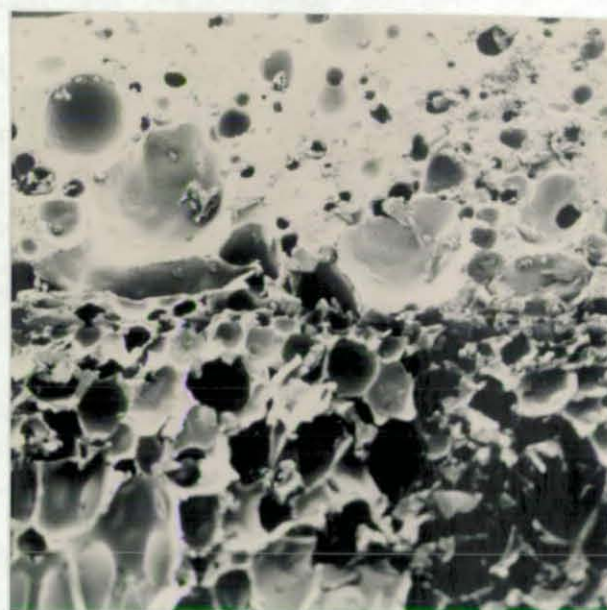
(a) 400 μm



(b) 400 μm



(c) 400 μm



(d) 400 μm

FIGURE 11.13: SEM micrographs of coated PU spray foam substrate at various coating conditions (x50):

- (a) + 24 hr (outdoor)
- (b) + 48 hr (indoor)
- (c) + 3 day (indoor) + 3 day (outdoor)
- (d) + 20 day (indoor) + 3 day (outdoor)

observation further explains some differences in mechanical properties already mentioned in tensile pull-off adhesion (see Section 9.2.5) and impact (see Section 9.3.4) of the coated samples.

#### EDX Results and Discussion

The EDX technique was basically applied in connection with SEM studies of coated systems and was meant only as a complementary tool to provide more information about the nature of interfacial regions. The EDX results are shown in Figures 11.14 to 11.16. For the majority of the PMC systems the elemental analysis of the substrate, coating and interface by EDX did not reveal any significant systematic variation between different regions (i.e. each layer was showing its own elemental characteristic unaffected by those of neighbouring regions). This in part may be due to the close similarities in chemical structure/formulation of the substrate and coating (i.e. for PU/PU systems). It may also be argued that the nature and the shape of the interface in many cases made it difficult for a reliable investigation to be carried out. Consequently, the results reported are reflecting only those systems where a number of analyses at different regions showed good agreement. This proved to be only applicable to some IMC systems.

Figures 11.14 and 11.15 show the elemental analysis of IMC samples of semi-flexible PU foam with two pack MRC (200) and one pack MRC (600) coatings respectively. Both interfacial regions revealed the presence of elements belonging to substrate and coating materials. Figure 11.16 shows the EDX results of IMC samples of RIM PU coated with a two pack acrylic/urethane coating (X-220/C075/C770). Again, the interface is acting as a transitional layer between the adjacent regions.

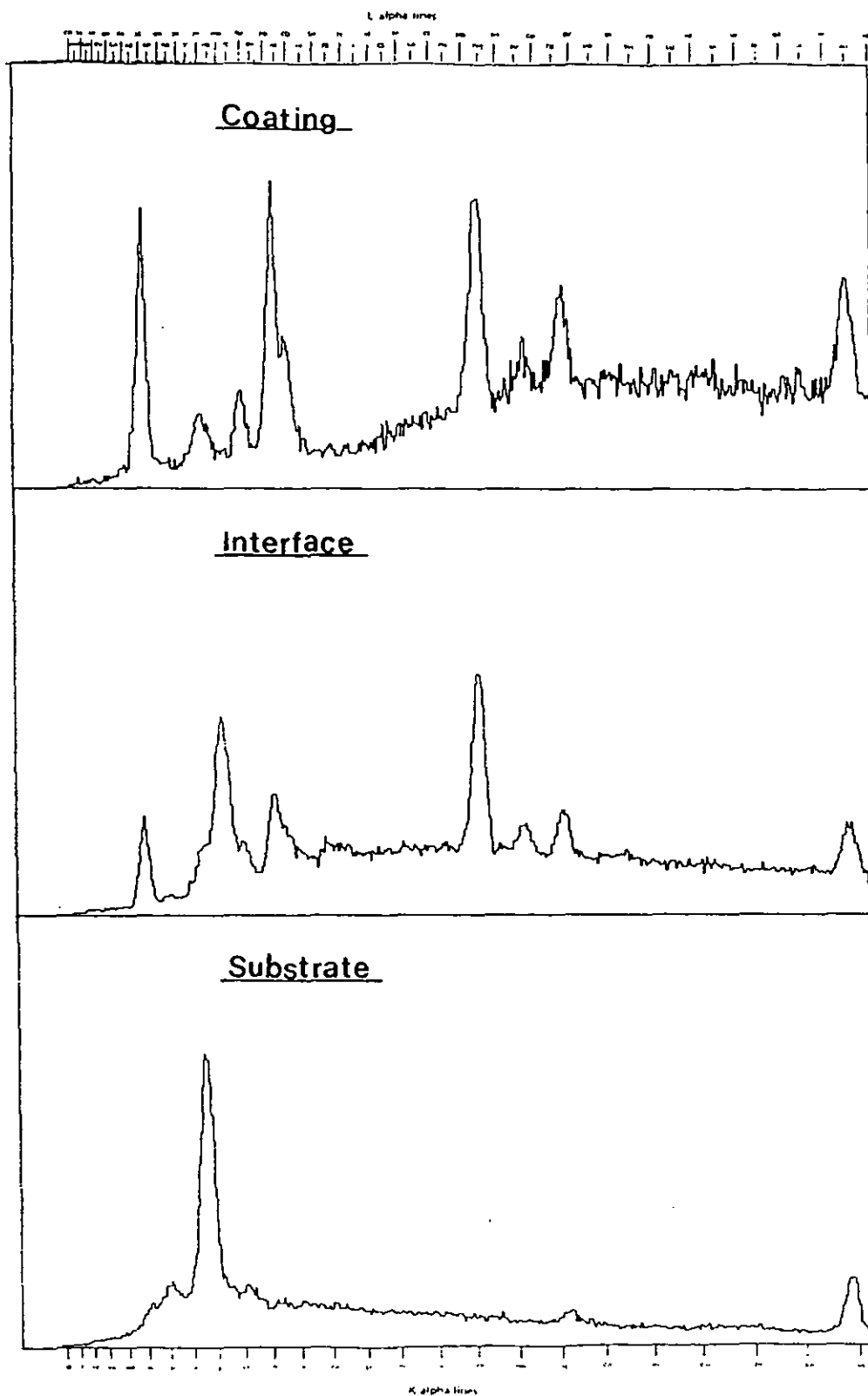


FIGURE 11.14: EDX elemental analysis of in-mould coated semi-flexible PU foam substrate with 2 pack MRC (200) coating

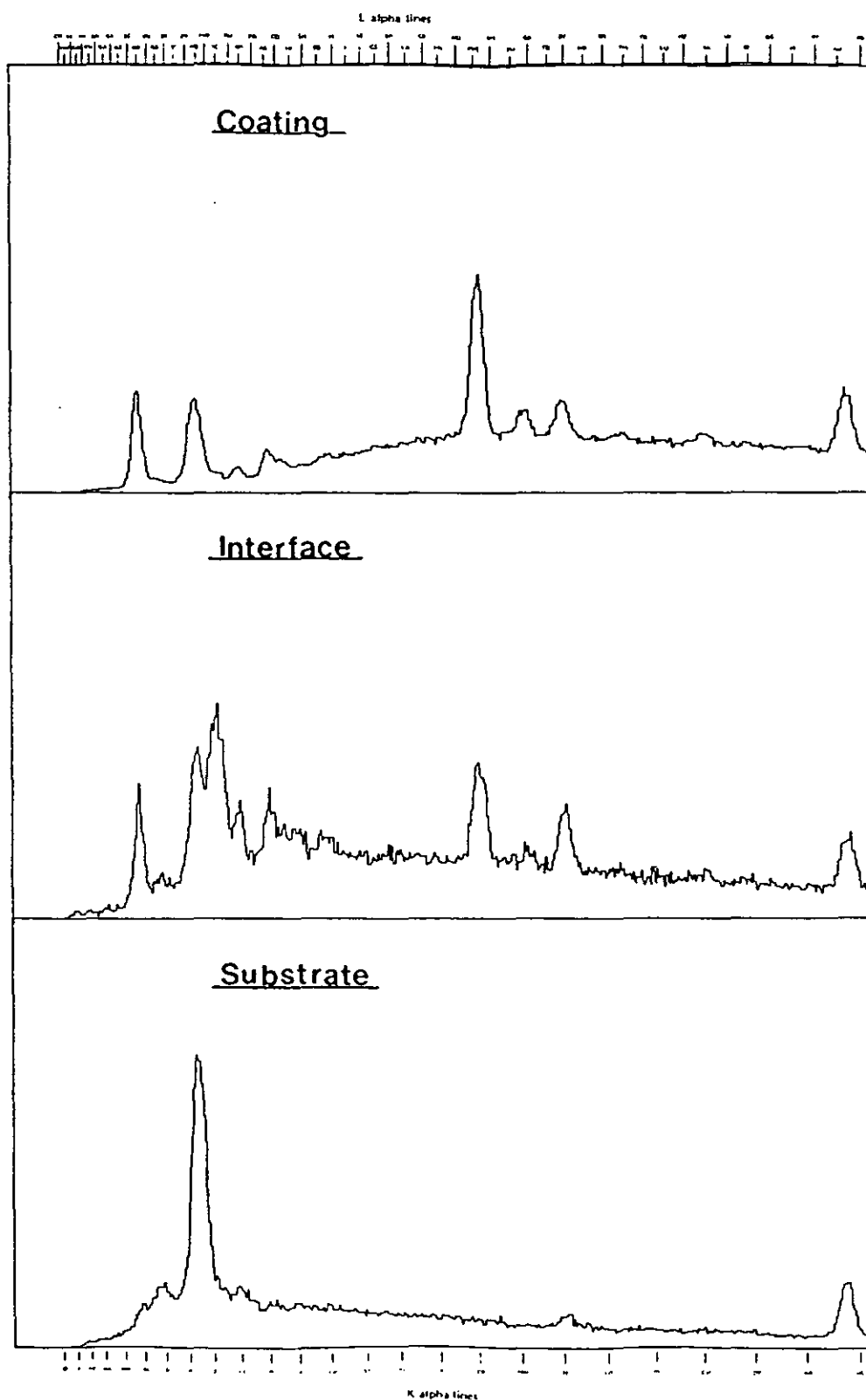


FIGURE 11.15: EDX elemental analysis of in-mould coated semi-flexible PU foam substrate with 1 pack MRC (600) coating



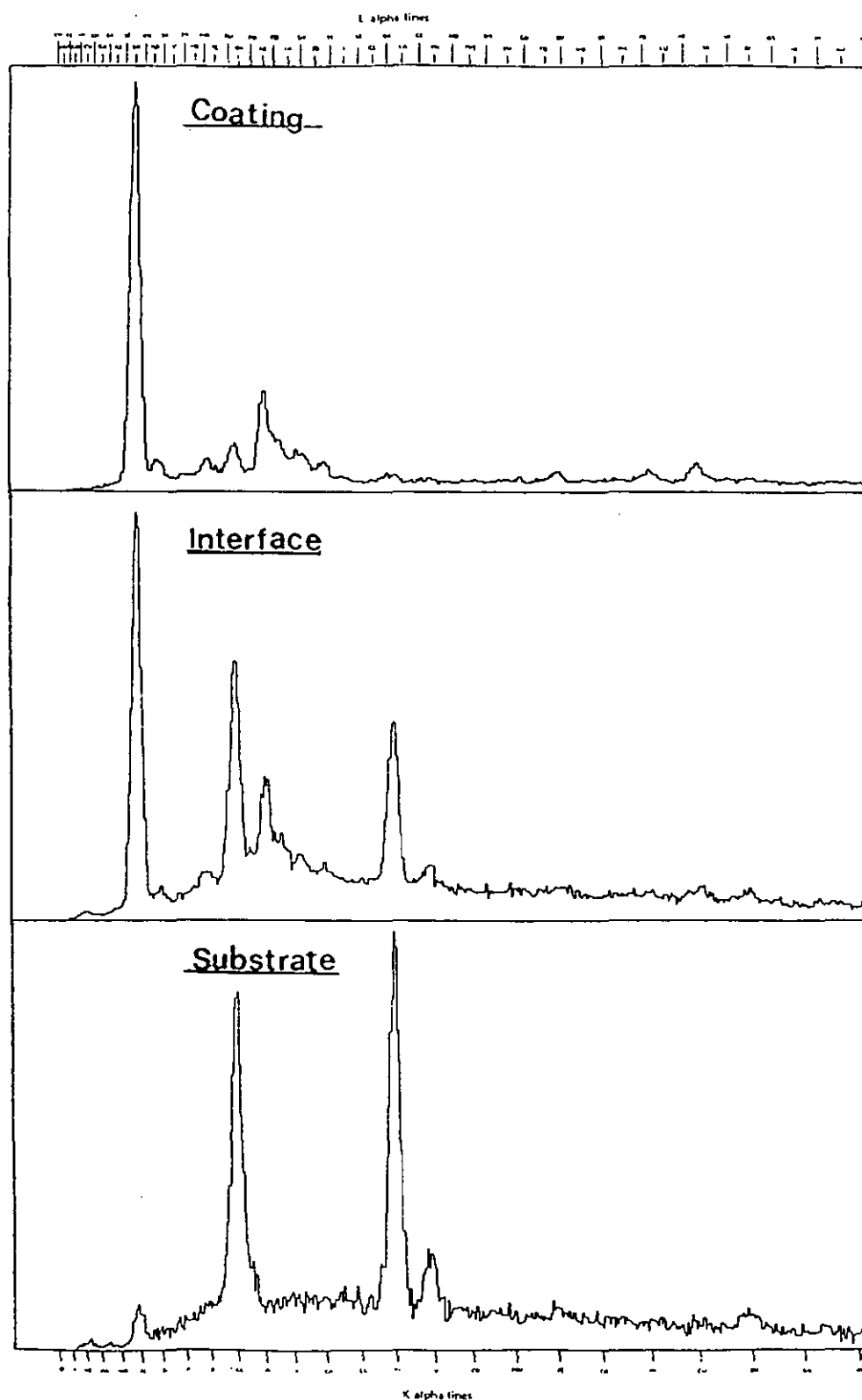


FIGURE 11.16: EDX elemental analysis of in-mould coated RIM-PU substrate with 2 pack (X-220/C075/C770) coating

The EDX analysis results enforce the view already established by SEM micrographs of IMC samples of semi-flexible and RIM PU substrates (see 11.5(a) and 11.5(c) micrographs) that the very diffuse interfaces observed with these systems is the result of diffusion between the mating surfaces.

## CHAPTER 12

### DISCUSSION

#### 12.1 INTRODUCTION

The results obtained from a number of tests on IMC and PMC samples of polyurethane and polyester substrates have been presented and briefly discussed in Chapters 8 to 11 inclusive. Within this chapter it is hoped to draw together various results, examine their interrelationships and develop an overall thesis of the adhesion phenomena related to PU surface coating on PU substrate.

The structure of this Chapter is as follows: the first section discusses the results in more detail and examines the possible interrelations between the different parameters involved. The second section proposes a number of scenarios for the interfacial interaction of a coating on a polymer substrate.

#### 12.2 DISCUSSION

##### 12.2.1 General Discussion on IMC and PMC Performances

The influence of a number of parameters on the performance of IMC and PMC samples has been mentioned throughout this thesis. A more detailed discussion is given in this section.

1. The Gibb's free energy equation stated as [370,371]:

$$\Delta G = \Delta H - T\Delta S$$

where  $\Delta G$  is the free energy of mixing,  $\Delta H$  is the enthalpy of mixing and  $T\Delta S$  is the product of temperature and entropy of mixing, may be applied to the IMC and PMC systems studied in this research. As a result, it may be argued that in substrate/coating interactions, as temperature increases, so does the value of  $\Delta G$ , provided  $\Delta H$  is small. Therefore if any mixing is to take place, the enthalpy of mixing must be small. Furthermore,  $\Delta H$  has been shown to relate the properties of the components by the thermodynamic equation [372]:

$$\Delta H = V_m (\delta_A - \delta_B)^2 \phi_A \phi_B$$

where  $V_m$  is total molar volume of mixing and  $\phi$  is volume fraction of each component (all difficult to establish). As already discussed in Section 9.2.5, when the solubility parameters of substrate and coating (i.e.  $\delta_A$  and  $\delta_B$ ) are similar (a more favourable condition for the IMC process) then  $\Delta H$  is small and the chances of mixing and compatibility are increased. It can further be concluded that due to the above reasoning, for PU and polyester substrates in-mould coated with chemically similar coating materials, the higher temperature of the IMC process results in a more negative  $\Delta G$  value, creating conditions for better mixing.

The above view emphasising the importance of temperature on establishing a stronger interfacial region is a fundamental argument in favour of the theory of diffusion, where some mobility of phases is assumed (see Section 4.2.4). In practice, the superior mechanical and thermal results obtained by a number of IMC specimens (see Chapters 9 and 10) and the SEM micrographs

shown in Chapter 11, where a diffuse interfacial layer is indicating more penetration and better mixing, are believed to be partly due to an increase in the temperature of the processing compared to those of corresponding PMC samples. It can be said that the temperature rise in the IMC process has in effect increased the thermal motion of molecules in substrate formulation. This in turn accelerates the rate of diffusive penetration. It can further be argued that the temperature rise in IMC may be associated with increased desorption of physically adsorbed species. A temperature increase will decrease packing of such adsorbed films, raising the critical surface tension of the system and thus causing  $\theta$  to decrease. This is contrary to the PMC process where traces of mould release and other adsorbed materials have made the wetting and spreading conditions more difficult.

It can also be said that in general an increase in adhesion properties of IMC samples is partly related to the effect of temperature on the equilibrium contact angle. This can be shown by the linear relationship between the surface tension,  $\gamma_{LV}$ , of organic liquids (i.e. solvents in the paint formulation) and the temperature,  $T$  [373]. An increase in temperature decreases  $\gamma_{LV}$ , therefore:

$$\gamma_{LV} = a - bT \quad (1)$$

The contact angle measurements (see Chapters 5 and 8) indicates a relationship between  $\cos\theta$  (or  $\cos^2 \theta/2$ ) and  $\gamma_{LV}$ :

$$\cos\theta = c - d \gamma_{LV} \quad (2)$$

Combining equations (1) and (2):

$$\cos \theta = (c-ad) + bdT \quad (3)$$

When the surface composition of the solid is constant,  $a$ ,  $b$ ,  $c$  and  $d$  are all positive. Equation (3) shows that  $\cos \theta$  increases (or  $\theta$  decreases) with increasing temperature which is borne out in practice. The effect of temperature on improving the wettability (smaller  $\theta$ ) in IMC is another factor emphasising the importance of diffusion theory in this research.

2. It has already been discussed in Chapter 9 that the solubility parameters of substrate and coating (i.e.  $\delta_A$  and  $\delta_B$ ) can influence the interaction parameter,  $X_{AB}$ , of IMC and PMC processes. Further to this view, it may be added that a more favourable situation for solubility is achieved when the similarities in the structural/chemical formulations of the two systems are increased. It has been established [374] that, with  $X_{AB}$  and  $X_{BA}$  as the interaction parameters of a system, a relationship such as:

$$X_{AB} = \left( \frac{V_A}{V_B} \right) X_{BA}$$

exist, where  $V_A$  and  $V_B$  are the molar volumes of substrates and coating respectively.

From the above argument and the effect of temperature already discussed in the previous section, it may be concluded that  $V_A$  and  $V_B$  are closer for IMC than the corresponding PMC. Therefore

the interaction parameters for IMC are more similar and in effect the compatibility is maximised. Furthermore, it may be argued that interfacial region formation for the IMC and PMC systems are different since solubility values for substrate ingredients in an IMC process and those for coatings applied in the PMC process are different.

Similar means have been shown by a number of reports [375] investigating the effect of physical and chemical factors upon the solubility parameter of many polymeric systems. It is clear from this data that interfacial tension and the solubility parameters of such systems are related. For this research it may be argued that matching the solubility parameters of substrate and coating materials (a more pronounced factor with IMC PU systems) has minimised the interfacial tension which in effect has increased the driving force for wetting and has resulted in stronger adhesive strength.

3. Furthermore, it can be shown that the relative molecular structure and viscosity of substrate and coating are different in IMC and PMC processes. In an IMC cycle, substrate formulation in a liquid state is in contact with a freshly prepared coating (i.e. having a chemically and physically active surface) whereas for PMC, liquid paint resin in solvent is sprayed on a less active solid substrate. It has been shown [376,377] that the viscosity of polymeric materials is strongly dependent on temperature, polymer concentration, solvent viscosity and molecular weight of polymers. Voyutskii et al [149,152] have presented some data and suggested that adhesion increases with the decrease in molecular weight. Wu [378] has shown that the

diffusion coefficient decreases with increasing molecular weight. Both observations logically suggest small molecules are more mobile than large ones respectively leading to better diffusion. Diffusion coefficient of oligomers and polymers have been measured and found to be of the order of  $10^{-13}$  to  $10^{-17}$  cm<sup>2</sup>/sec, therefore indicating that small but significant interdiffusion across the interfacial thickness of 10 to 1000 Å can occur within minutes to hours.

It can also be added that shape/configuration of substrate and coating molecules has possibly affected the adhesive strength. We can say that reduced adhesion properties of IMC samples of PU and polyester substrates coated with (X-226/C2885) is partly due to the bulky side groups (i.e. vinyls) reducing the diffusibility. Similar views have been shown by others [152,379] indicating that the presence of short bulky side chains in a macromolecule has an adverse effect on polymer adhesion whereas sufficiently long side groups may play the role of individual chains and diffuse into the substrate.

From the above argument, it is clear that viscosity and molecular differences in IMC and PMC systems in this research and their effect on adhesion properties of coated samples is best explained by the diffusion theory: the lower viscosity, the absence of bulky side groups, and the decrease of the dimensions of the molecules promote an increase in the flexibility, mobility, and diffusibility of molecular chains and a consequent increase in adhesion.



4. The ageing of PU, polyester and spray PU foam substrates affected by WB layers and the adverse environmental conditions clearly showed inferior adhesion properties with a number of PMC samples compared to those of freshly made PMC and IMC specimens. In order to further develop this observation, the ageing of IMC paint surfaces was examined by Fourier transform infra-red spectrometry (FT-IR), using a reflectance technique. The technique for following rapid loss or gain of certain constituent groups by FT-IR is novel, but has considerable advantage over normal IR spectrometry e.g. for isolating  $-N=C=O$  from urethane or urea groups [314]. The results with a flexible fully reacted polyether PU coating shown in Figure 8.18 (see Section 8.3.2), was found to contain free  $-N=C=O$  at low levels in the wet film and was present up to five minutes after the film had become touch-dry at 20°C. Since this was also associated with carbon dioxide detectable to the same time, isocyanate loss in ageing was thought due to atmospheric moisture attack although other hypotheses suggest themselves. It is presumed the isocyanate group is associated with chain ends, particularly of oligomeric material, disappearing after five minutes by internal adsorption (i.e. as cohesive strength develops in the film). This indicates two important points. First, the IMC surface is chemically as well as physically active, further promoting wetting and spreading. Second, there is potential for chemisorptive as well as adsorptive bonding, if the two mating surfaces can be brought together. This may help to explain the excellent adhesive bonding in some one pack IMCs for PUs (e.g. X-225/C2885 coating and PU RIM substrate). However the best adhesion properties are observed with two pack coatings (e.g. X-220/0075/C770). Ganster and Knipp [380] have used IR spectrometry to study the relative

reduction in residual isocyanate groups at the PU surfaces as a function of time and hence establish the conditions necessary for demoulding without release agent. They have shown that due to denser chemical crosslinking of rigid mouldings, these surfaces can soon attain a molecular weight high enough to allow easy demoulding. In the case of linearly structured flexible PUs (i.e. having a lower degree of crosslinking) however, a measurable proportion of  $-N=C=O$  groups at the surface have not undergone complete reaction (i.e. some low molecular polymer constituents still present at the surface) and therefore demoulding without release agent is not possible. The adhesive bonding results are presented in Chapter 9 and a detailed discussion is presented in Section 12.2.3.

5. The above view has also been stated by Wu [381] and others [382], expressing the increase in adhesive strength with respect to the functional groups present in the system as:

$$f = f_0 + KC^n$$

where  $f$  is the adhesive strength when the concentration of functional groups is  $C$ ,  $f_0$  is the adhesive strength when the functional group is absent, and  $K$  and  $n$  are positive constants.

The above relationship may serve as a guideline but it cannot be generalised because of its shortcomings. First, the parameter  $K$  does not take into account all the external and internal factors influencing the adhesion properties of IMC and PMC samples. Second, the relationship cannot be true for all cases since it does not take into account the limit of excessive amounts of

functional groups which can safely be introduced into the system without decreasing the adhesive strength. It may be argued that although some isocyanate groups on the coating surface will promote adhesion to polar substrates (i.e. PU and polyester), the introduction of excess free  $-N=C=O$  can drastically change the bulk properties of the coating and subsequent decrease in interfacial strength.

6. As already pointed out in Chapter 4, in order for substrate and coating materials to make a strong interfacial region, their real areas of contact need to be increased (i.e. the two surfaces approach each other and are ultimately held apart by contact of their surface irregularities). This means that substrate or coating or both of them must be made to conform better to the surface roughness of the other. This implies in a practical sense, that one of the materials should be fluid when placed in contact with the other. Although these outlined requirements are met in both the IMC and PMC processes, their results presented in preceding chapters showed variations normally with IMCs showing superiority. This can be explained due to the processing conditions involved. For PMCs the coating material sprayed on PU or polyester solid surfaces are making a number of microbridges on these substrates and trapping air bubbles (see Section 12.2.5). As a result, little penetration into the surface roughness of the substrate (more pronounced with aged substrates) is possible and hence stress concentrations due to contact angles larger than zero are produced (see Section 12.2.2). In contrast, the conditions for IMCs are different since the spontaneous spread of substrate ingredients in a fluid mobile state over a layer of freshly made paint in a heated mould increases the

interfacial area of contact. The reason is that a more complete flow into the micro irregularities of the coating surface displaces the air traps and also any contamination more satisfactorily. It can be presumed that the zero or very low contact angle due to complete spreading reduces and minimises the areas of stress concentrations.

It can be concluded that in the IMC process, the effect of spontaneous spreading is two fold: the real area of contact is increased and the areas of stress concentration is minimised.

7. Following the previous discussion, it seems appropriate to study the effect of friction on the adhesion properties of IMC and PMC samples. By definition, friction is the resistance to motion which exists when an object is moved tangentially with respect to the surface of another which it touches. The frictional force  $F$  is proportional to the normal force  $L$ , that is:  $F = fL$ , where  $f$  is defined as the coefficient of friction. It has been shown that a number of factors such as surface quality, traces of contamination, pressure, temperature and others will affect the coefficient of friction [383,384].

The friction and adhesion may be connected by considering that friction is the shear strength of boundaries formed at the regions of real contact, whereas adhesion is the tensile strength. Generally, materials that give a low coefficient of friction give poor adhesion and subsequently high friction materials give, in principle, a strong adhesion.

The parameters affecting friction mentioned above are basically those which are influencing the adhesion properties of coated PU and polyester substrates. With smooth surfaces (e.g. idealised IMC surfaces), the friction tends to be low because the real area of contact grows excessively, whereas with very rough surfaces (e.g. spray PU foam substrate affected by adverse environmental conditions), the friction is high because of the need to lift one surface over the irregularities on the other. This means that for IMC systems a lower friction (i.e. a high coefficient of friction) results in an increase in wettability (i.e. improved  $\gamma_C$ ) whereas for PMCs a higher friction (i.e. a low coefficient of friction) results in a decrease in wettability (i.e. reduced  $\gamma_C$ ). A similar view has been shown by Bikales [385] in demonstrating a direct relationship between coefficient of friction and the critical surface tension of polymers.

#### 12.2.2 Discussion on Thermodynamic Properties of Coated Samples

Contact angle and wettability results for PU and polyester substrates were presented and briefly discussed in Chapter 8. This section attempts to discuss the effect of a number of thermodynamic parameters on the adhesion properties of these surfaces. A number of relationships found between thermodynamic surface properties and other physical and chemical factors studied in this research will also be discussed.

1. The wettability results of PE and PTFE surfaces (see Section 8.1) and their comparison with the results obtained by others showed that the contact angle measurements are valid and can be applied to other polymeric surfaces. It was also shown that surface tension test fluids (inks) gave acceptable and trustworthy results.

The linear equations for  $\cos\theta$  and  $\cos^2 \theta/2$  plots against  $\gamma_{LV}$  gave acceptable values for the critical surface tension. However in many cases a rectilinear band providing a range of  $\gamma_C$  values is more beneficial resulting in more meaningful values. This is first due to the different wetting characteristics of various liquids e.g. polar and non-polar on PU and polyester substrates giving scattered results but all of them satisfying the general conditions:  $\gamma_{LV} < \gamma_C$  for spreading. Second, Young's equation (see Section 5.7.1.1) may be presented as:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

Therefore the wettability of a surface and the type of relationship shown by a plot of  $\cos\theta$  against  $\gamma_{LV}$  is affected by the  $(\gamma_{SV} - \gamma_{SL})$  value. Applying this argument to our IMC and PMC systems, it is clear that in corresponding cases,  $\gamma_{SV}$  is larger for IMC than for PMC (i.e. free or less contamination). It was also established in preceding discussions that in general the IMC process provided a better affinity between coating and substrate materials. This in effect results in lower interfacial tension, i.e. smaller  $\gamma_{SL}$ . Hence for similar substrate/coating combinations it is argued that  $\cos\theta$  will be larger and  $\theta$  smaller in IMC than corresponding PMC. It may be concluded that as a result better wetting and spreading conditions are expected for IMCs which in effect is demonstrated by their overall superior adhesion properties.

From the above discussion it may be argued that the poor wetting of some coatings associated with a number of PMC samples tends to produce greater stress concentration at the free surface of the substrates where failure is mainly observed. As the contact angles become larger, the maximum stress concentration increases and moves towards the linear boundary where the coating and atmosphere make contact with the substrate.

2. The relationships between  $W_A$ ,  $S_C$  and  $\gamma_{LV}$  were discussed in the preceding chapter (see Section 8.2.5). It was shown in Figures 8.8 and 8.9 that for PU and polyester substrates  $W_A$  and  $S_C$  varied as a function of  $\gamma_{LV}$  resulting in a parabolic curve with a maximum point. Closer and more approximate values for Max  $W_A$  and Max  $S_C$  and the corresponding  $\gamma_{LV}$  may be found by using the quadratic equations for  $W_A$  and  $S_C$ . However, it is clear that in most cases especially with polar polyurethane surfaces, the change in the magnitude of  $W_A$  near and after reaching the maximum value is greatly moderated by the effect of the hydrogen-bonding action of the high surface tension liquids such as water, glycerol, and formamide each of which is an effective hydrogen donating compound. A similar view has been observed by Zisman [386] studying a number of fluorinated polymer surfaces where some unexpectedly larger values of  $W_A$  have been attributed to greater effectiveness in hydrogen bonding manifested by the fluorocarbon polymers.

The above argument is further demonstrated by the relationships found between Max  $W_A$ ,  $\gamma_S$ ,  $\gamma_S^p$ , and  $\gamma_S^d$  shown in Figure 12.1. It may be stated that surface tension of PU and polyester substrates calculated by harmonic mean and equation of state methods (see

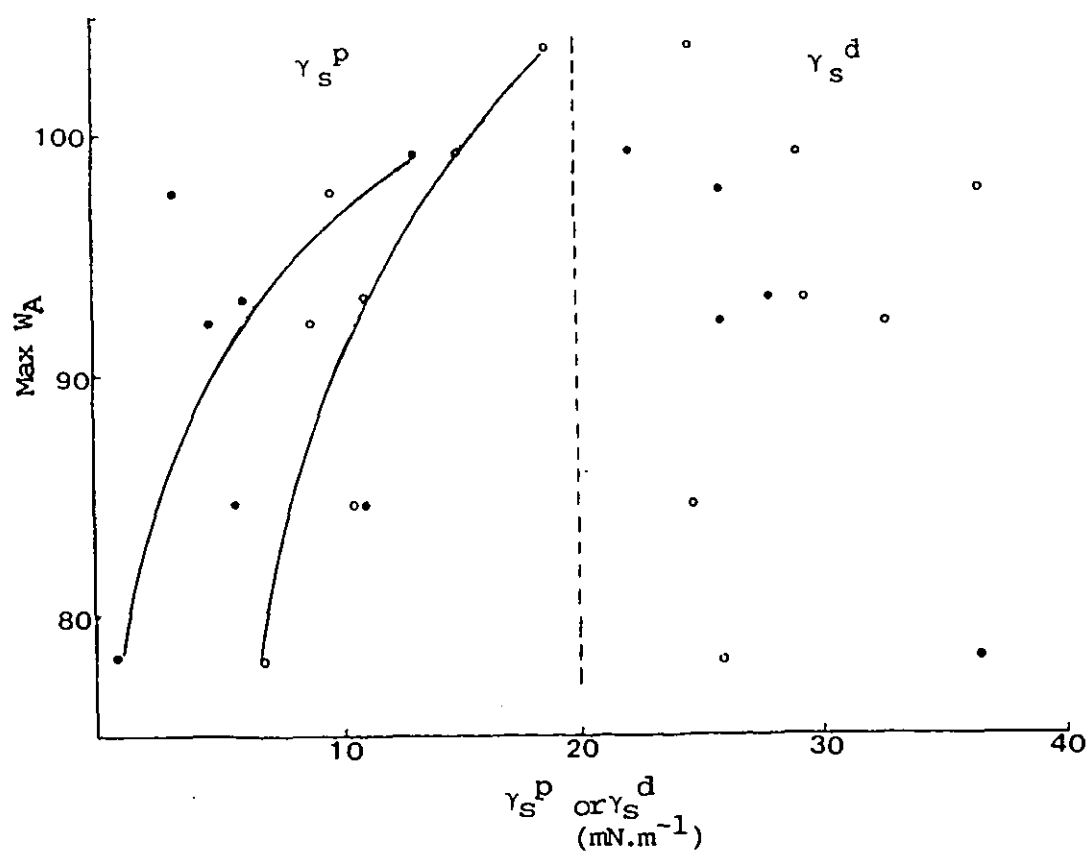
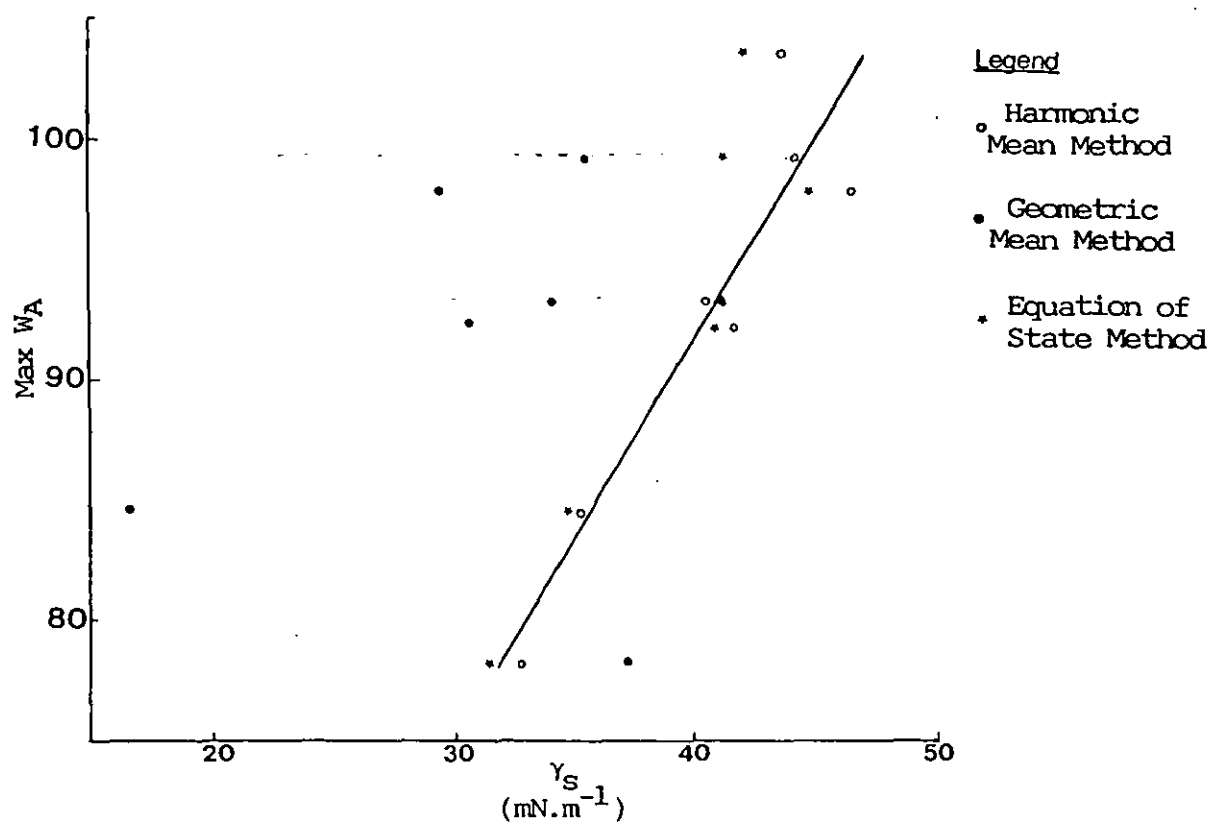


FIGURE 12.1: The relationship between Max  $W_A$ ,  $\gamma_S$ ,  $\gamma_S^p$  and  $\gamma_S^d$  for PU and polyester substrates



Chapter 5) show a direct relationship with corresponding  $\text{Max } W_A$ . Such a relationship is not found with scattered  $\gamma_S$  values calculated by the geometric mean method. Furthermore, it may be said that polar components of surface tension,  $\gamma_S^p$ , are better related to  $\text{Max } W_A$  than dispersive components,  $\gamma_S^d$ .

From the above findings it may be concluded that the effect of hydrogen donating (i.e. polar) liquids on PU and polyester substrates (i.e. polar surfaces) are different to those of less polar liquids. This relates to various wettability and consequent adhesion properties shown by different coatings (i.e. having different polarities) on polar PU and polyester substrates. These effects are best explained by diffusion theory differentiating between adhesion properties resulting from various levels of component polarity.

3. Similar views to the above discussion have been shown in a number of reports [387-389] on the effect of polarity of surfaces on increasing their thermodynamic properties. Critical surface tension and work of adhesion have been directly related to the polarity (i.e. cohesive energy density) of surfaces.

From our discussions in the preceding sections (see 5.7.1.2 and 12.2.1) and the arguments put forward in the above, it is noted that systems having similar wettability properties (measured by  $\gamma_C$ ) are more compatible (i.e. interfacial tension,  $\gamma_{12}$ , is reduced). this affinity between substrate and coating materials has been shown to be affected by the temperature (see Section 12.2.1). Therefore from a thermodynamic point of view, we can argue that temperature increase in IMC is reducing the

interfacial tension and resulting in a closer contact. This in effect explains the improved mechanical properties of in-mould coated samples.

Wu [390] has shown that interfacial tensions between a number of polymers varies over a temperature range, indicating that as temperature is increased there is a reduction in interfacial tension. It has also been discussed that a thermodynamic relationship based on the temperature coefficient of various regions (i.e. interfacial tension and the two corresponding surface tensions) may exist [391]:

$$x_2 = \frac{d \gamma_{12}/dT + d \gamma_1/dT}{d \gamma_1/dT + \frac{1}{2} d \gamma_2/dT}$$

where  $x_2$  is the mole fraction of component 2 in the interfacial zone.

4. The difficulties encountered in surface analysis of the original and IMC and PMC samples of PU and polyester substrates in this research (see Section 8.3) may be attributed to a number of facts. Polymers being generally non-conducting materials will charge up easily when treated with electrons and ions. They are very often not UHV compatible because they cannot be baked and usually contain additives which have high vapour pressures. Polymers are also much more sensitive to electron and ion-induced reactions than metals and oxides. It may also be noted that information about chemical analysis is much more difficult in composites rather than single polymers especially when the polymeric phases are chemically identical.

### 12.2.3 Discussion on Mechanical Properties of Coated Samples

The results obtained by the adhesion pull-off test, cross-cut hardness and scratch hardness test, and instrumented falling weight impact (IFWI) test have been presented and briefly discussed in Chapter 9. This section will attempt to discuss these results in more detail and explain their relations with each other and other parameters studied in this research.

1. Substrate materials had some effect on the mechanical properties of the joint. For PU substrates, the RIM surfaces proved to give best performance. This indicated that surface polarity and microcellular structure of the RIM PU surface provided a more desirable condition for stronger bonds to be established. Due to the very similar chemical ingredients for rigid and semi-flexible PU substrates and common processing conditions (see Chapter 2), these two surfaces showed similar results. Another reason could be due to having similar surface polarities and hence showing the same kind of affinity for certain coatings. Nevertheless, the geometry (topography) of these surfaces is different (see Sections 9.2.5 and 9.3.4) resulting in somewhat different modes of failure.
2. Generally, the IMC samples showed superiority to PMC. Therefore the coating processes have had some effect on the adhesion properties. This can be explained in terms of physical and chemical factors. The real area of contact is usually larger for IMC than corresponding PMC and this seems a more favourable condition for a stronger joint to be made.

The wetting equilibrium for IMC and PMC was different because of the geometry of the surfaces, the application and setting conditions, the viscosity of the participants and the environmental conditions. Therefore the thermodynamics of wetting (see Chapter 5 and Section 12.2.2) influencing the extent of interfacial/molecular contact between the substrate and coating has been different for IMC and PMC. As a result the adhesion properties have shown differences between the two systems. It is worth noting that in a few selected cases where the surface of the PU RIM specimens was deliberately not cleaned (i.e. either by a dry tissue or by solvent application), the traces of mould release agent (i.e. mainly silicone based having low surface energy values), the presence of adsorbed  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules, and other contaminants resulted in PMC samples showing very poor wettability and almost no adhesion affinity. It can be argued that mould release in effect has modified the coefficient of friction of substrate and hence reduced its adhesion properties.

3. It can be argued that in the case of probable effect of poor wetting the air pocket at the coating/substrate interface has been developed. The stress failure within some of the PMC and coated spray PU foam (especially those subjected to severe environmental conditions) occurred at a relatively small applied stress. This can be explained first because of air bubbles, voids, and surface defects. These occurred due to stress concentrations that are much higher than the mean stress applied across the specimen. Rance [247] showed similar views by stating that measured adhesion strength between substrate and coating is normally much lower than the ideal adhesion strength because of

flaws such as voids in the interfacial region or microcracks in the bulk phase. These flaws provided the locus of stress concentration so that on applying a modest stress to the interface, the local strength in different parts of the interface is exceeded and fracture is initiated.

Second, internal stresses which are attributed to incomplete relaxation processes, a delay in the rate of such processes due to unevenness of curing in the individual polymerisation, and a temperature gradient (i.e. variation in local air and substrate temperature) have resulted in a weaker interfacial region. Third, the decrease in adhesion failure is due to these surfaces being more highly crosslinked and rich in urethane and urea linkages. Therefore having fewer polar or hydrogen groups available for interfacial bonding, these substrates are less reactive, less adsorbent, and less affected by paint solvents. It can be concluded that high orders of crosslinking has reduced the potential for adsorptive interactions.

4. Typical tensile stress failure and impact peak energy results for spray rigid PU foam that had been allowed to age to different times and under various conditions did not show any significant trend from the random nature of results for samples prepared within the first hour of foam production. Further to our discussion in Chapter 9, it can be argued that on drying the PU paint film on newly prepared PU foams excellent cohesion strength within the coating and strong adhesion with the substrate is achieved. However the surfaces which had undergone prolonged ageing gave a sharp decrease in tensile stress and seemed to impose the worst impact resistance. In particular, the specimen

based on a substrate aged for six days was darkened showing probable UV attack and that a relatively thick weak boundary layer had been formed.

5. Although the ratio of adhesive strength values between a number of IMC and PMC samples ranging from 15 to 40 times (see Tables 9.2 to 9.7) can be explained due to a number of processing parameters, it is clear that such a large variation may be interpreted as different orders of bond energies involved in the interfacial region. In particular, the IMC combinations of two pack PU coatings with RIM-PU (almost impossible to delaminate) and polyester substrates gave superior results upon a number of PMC combinations of one pack PU based coatings with semi-flexible and rigid PU substrates. This observation points to the importance of lengths of the molecular chains composing an interfacial bond discussed in the preceding section (see Section 12.2.1). It can be argued that in a number of perfectly matched IMC samples, the conditions for molecular contact and forming long molecules resulted in a large number of bonds at the interface. Therefore we can presume that a larger amount of force (applied in tensile pull-off test) is needed since all these bonds must be highly stressed in order to break one of them (failure therefore is cohesive within the weaker of the two molecules). For many PMC samples the resultant interfacial region may be highly crosslinked and the molecular chains are short. Therefore less force is needed since this kind of interfacial formation is both less extensible and weaker (again cohesive failure but contamination and high proportions of crosslinking also exist). Similar views have been expressed by others [392,393] reporting that the ratio of bond dissociation energies

between covalent and Van der Waals attractions coincide with the ratio of their adhesive strength values.

6. From the above discussion it may be argued that Bikerman's shortcoming in explaining the adhesion phenomena by WBL effects (see Section 4.2.5) is more obvious. Bikerman's view is so narrowly focused on one aspect of adhesion theory that he improperly rejects the idea that molecular forces could have a significant effect on the interfacial bond formation and consequent breaking stress measurement. Although Bikerman is rightly presenting a number of examples where the mechanical separation never occurs along the interfacial layer, he fails to recognise that even so the molecular forces influence cannot be totally disregarded. After all even if factors such as improper wetting, surface irregularities and others are in existence in a number of PMC systems, these are basically due to the molecular forces being too small to allow the penetration (diffusion) of coating or substrate into the interfacial zone.
7. The effect of different coating materials on the mechanical properties results reported in Chapter 9 is not immediately separable except for the two pack PU coating (X-220/CO75/C770) which showed superiority in almost all combinations. It can be argued that generally thick coatings showed poorer adhesion than thin coatings. This effect was not directly investigated by the adhesion pull-off test because uniform spraying was applied in all cases producing an acceptable coating thickness. Nevertheless some SEM micrographs (see Chapter 11) revealed that with thin coatings a stronger bond is possibly formed. In addition, the tensile results for spray PU foam coated with a thick elastomeric

PU coating ( $1.2 \pm 0.1$  mm) showed the lowest failure stress values. This finding has also been observed by others [394] who have stated that the effect of coating thickness is more pronounced in thermosetting coatings than in thermoplastic types. It has been shown that different variables (i.e. substrates, coatings and coating processes) would have different effects on the cross-cut hardness values of coated specimens (see Section 9.4.2.2). This finding is contrary to Bikerman's view (see Section 9.4.2) stating that the same coating on different substrates would give similar cross-cut hardness values. Bikerman's argument may be generally true for very thick coatings as discussed above, but for thin coatings (i.e.  $< 50 \mu\text{m}$ ) and the type of coatings used in these experiments is not valid.

8. In instrumented impact testing and tensile adhesion pull-off testing, the consideration of the stress field is concentrated on the coating layer and upper portion of the substrate. It is noted that the measured strength of adhesion (i.e. failure stress) is generally larger for ductile and inelastic substrates (i.e. RIM-PU and Crystic polyester) than it is for more elastic surfaces (i.e. PU foams). This observation shown also by Gent [222], may be explained by the fact that any work expended in stressing the composite joint up to the point of failure is included in the total work of detachment (failure). Therefore it can be argued that failure stress and peak energy values of coated PU and polyester samples are dependent on dissipative properties of components in these systems.

Superior results (i.e. large amounts of energy absorbed prior to failure) with IMC and PMC samples of RIM-PU, indicate that



substrate and coating components do not dissipate much energy in internal deformation processes. This suggests a strong interfacial region. Contrary to this, the splitting caused by impact upon the elastomeric PU coating of rigid spray PU foam samples show that the elastic modulus of these materials affect the deformation process (i.e. less efficient energy absorber) and that dissipation energy is dependent on coating and foam thicknesses (i.e. kept constant for all samples).

The above argument is similarly observed with tensile adhesion measurement of a number of IMC and PMC systems. It is clearly revealed that by applying a low rate of extension the required energy for rupture is stored elastically in the bonded parts, and that initial failure is caused by a small detached region growing in size. Some differences observed in impact strengths of corresponding IMC and PMC samples may be attributed to the solvent action of coatings. A similar view has been stated by others [87], where mould stressed areas of the parts being attacked and revealed by the solvents was shown to give some reduction in impact strength.

9. The overall effects of substrates, coatings and coating processes upon the mechanical testing results of coated PU and polyester substrates reported in preceding chapters were further investigated and are presented in Figures 12.2 to 12.5. A generalised summary of these findings can be presented as follows:

---

(i)

Semi-flex PU < rigid PU < C<sub>199</sub> < C<sub>198</sub> < C<sub>196</sub> < RIM-PU  
MRC (120N) < X-226/C2885 < X-225/C2885 < X-220/C075/C770  
MRC (600) < MRC (200)  
PMC < IMC

---

increasing failure stress (tensile adhesion strength)

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(ii)

C<sub>199</sub> < C<sub>198</sub> < C<sub>196</sub> < rigid PU < semi-flex PU < RIM-PU  
X-226/C2885 < MRC (120N) < X-225/C1885 < X-220/C075/C770  
MRC (600) < MRC (200)  
PMC ≤ IMC

---

increasing peak energy (impact)

---

(iii)

rigid PU < semi-flex PU < C<sub>199</sub> < RIM-PU < C<sub>198</sub> < C<sub>196</sub>  
MRC (120N) < X-226/C2885 < X-225/C2885 < X-220/C075/C770  
MRC (600) < MRC (200)  
PMC < IMC

---

increasing cross-cut hardness

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(iv)

rigid PU < semi-flex PU < C<sub>199</sub> < RIM-PU < C<sub>198</sub> < C<sub>196</sub>  
MRC (120N) < X-226/C2885 < X-225/C2885 < X-220/C075/C770  
MRC (200) < MRC (600)  
PMC < IMC

---

increasing gouge hardness

---

(v)

rigid PU < semi-flex PU < C<sub>199</sub> < C<sub>196</sub> < C<sub>198</sub> < RIM-PU  
MRC (120N) < X-226/C2885 < X-220/C075/C770 < X-225/C1885  
MRC (600) ≤ MRC (200)  
PMC < IMC

---

increasing scratch hardness

---

10. From the discussions in 1 to 9, changes in state of PU surfaces can be summarised as follows:

- i) For a PU moulding, spray foam, or 100% solids two pack coating:
  - a) monomeric or/and oligomeric ingredients having been mixed and placed, will react by chain extension (foaming mechanism), crosslinking through gel state and to higher levels of cure
  - b) slower cure at the surface to tack-free state

- c) adsorbed molecules altering state of active species at surface, e.g. surface active additives migrating to surface, hydrogen bonding between PU side groups or chain ends or residual reactants, external contamination (e.g. moisture or dust from atmosphere, release agent from a mould surface)
  - d) eventually aromatic isocyanate based PUs will degrade in the presence of UV and oxygen to give a structurally weaker zone at the surface i.e. a weak surface layer.
- ii) For a solvent based two pack coating, a similar scheme of change as in (i) exists. However, until the solvent evaporates from the applied wet film of coating, the urethane reaction is relatively slow with residual solvent affecting its molecular structure and limiting its cohesive strength.
- iii) For a solvent based one pack fully reacted coating (i.e. a full PU in solution):
- a) initially the polymer is in a solvated, swollen molecular state
  - b) as solvent evaporates from the applied wet film, polymer chains move together and intermolecular attraction increases with internal adsorptive action, with development of the cohesive strength of the drying film. Solvent diffusion out of the body of the film escaping through the film's surface i.e. the surface is the last part of film free of solvent
  - c) a solvent-free surface will be exposed which is active to polar and dispersive interactions, either from a second surface or contaminations.

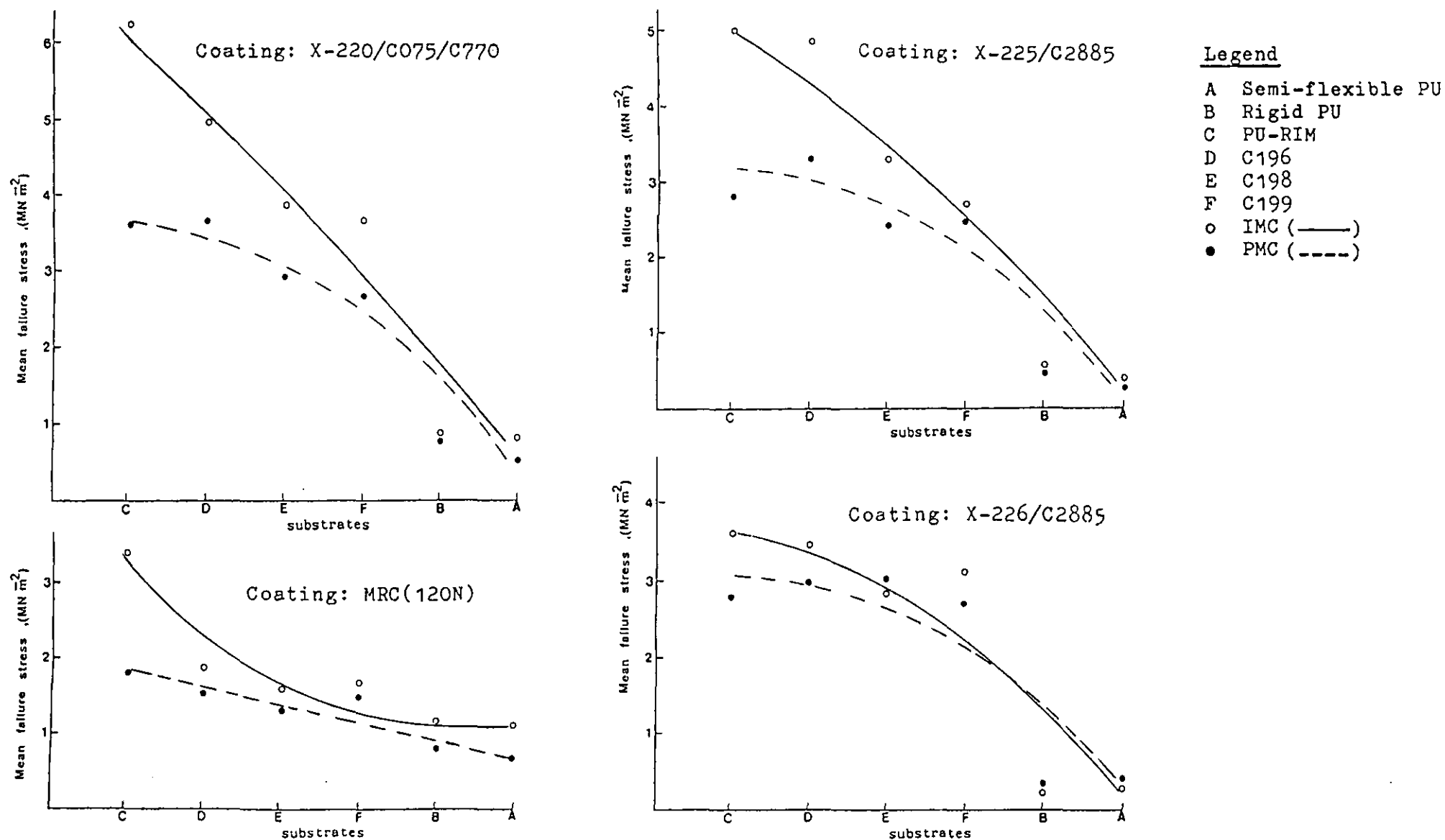


FIGURE 12.2: The overall effect of substrates, coatings and coating processes on mean failure stress of coated PU and polyester substrates

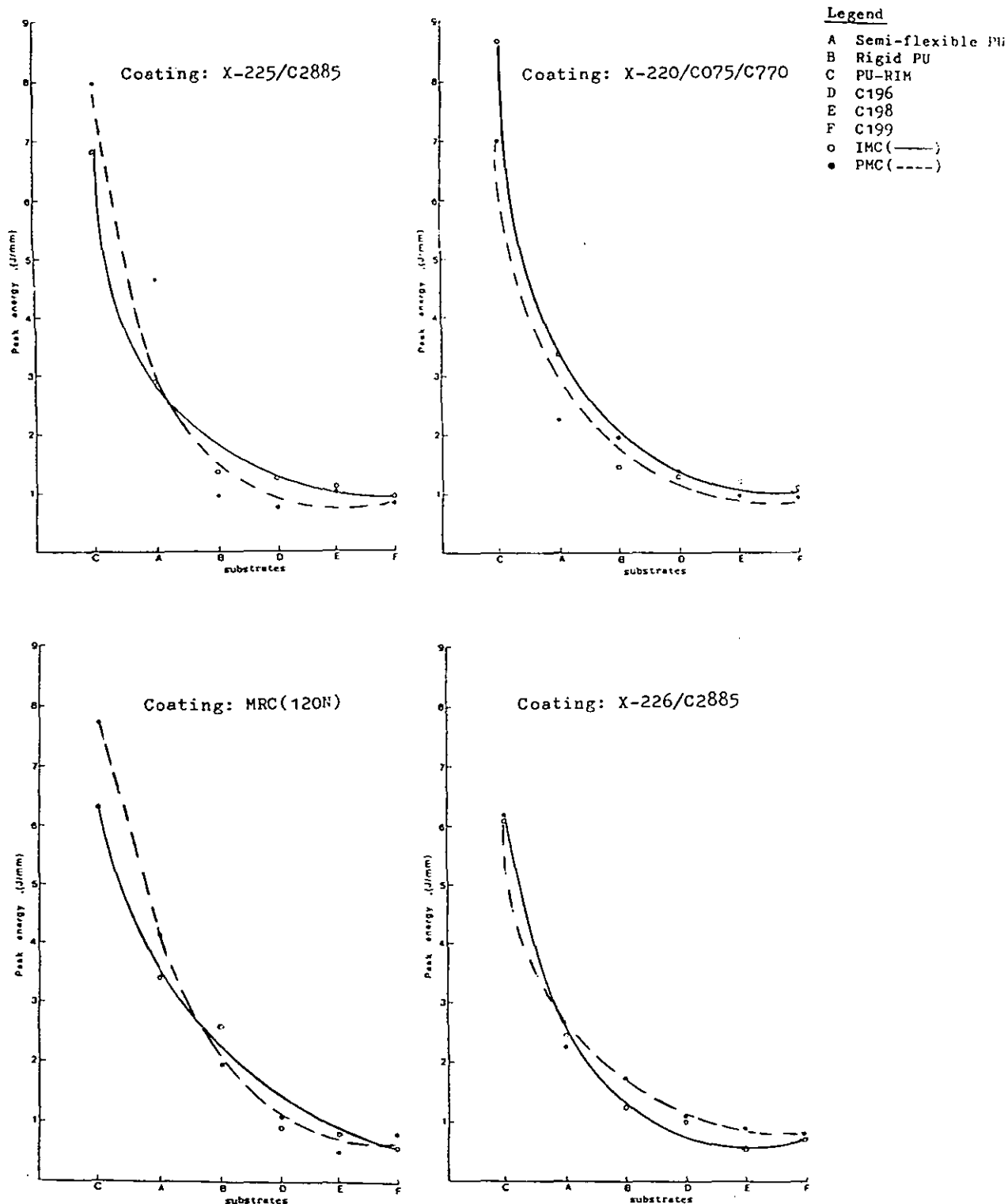
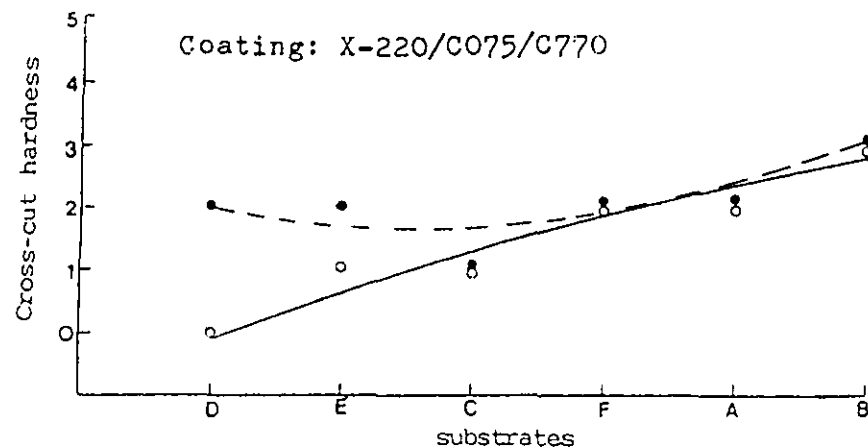
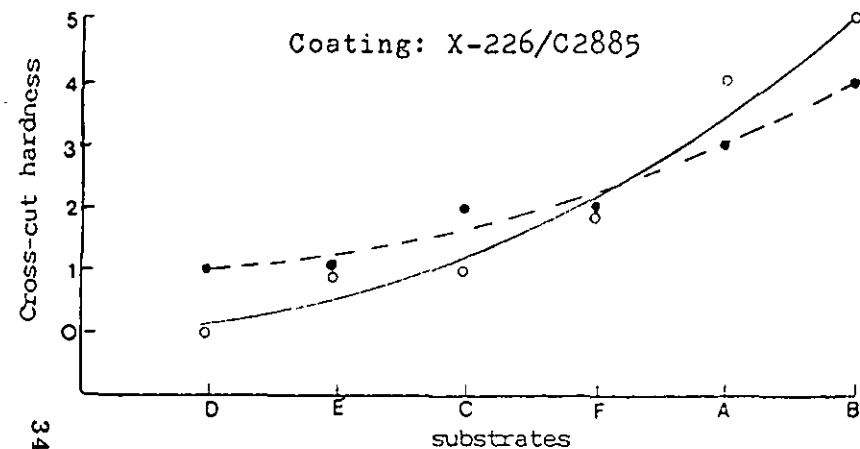


FIGURE 12.3: The overall effect of substrates, coatings and coating processes on average peak energy of coated PU and polyester substrates



#### Legend

- A Semi-flexible PU
- B Rigid PU
- C PU-RIM
- D C196
- E C198
- F C199
- IMC (—○—)
- PMC (---●---)

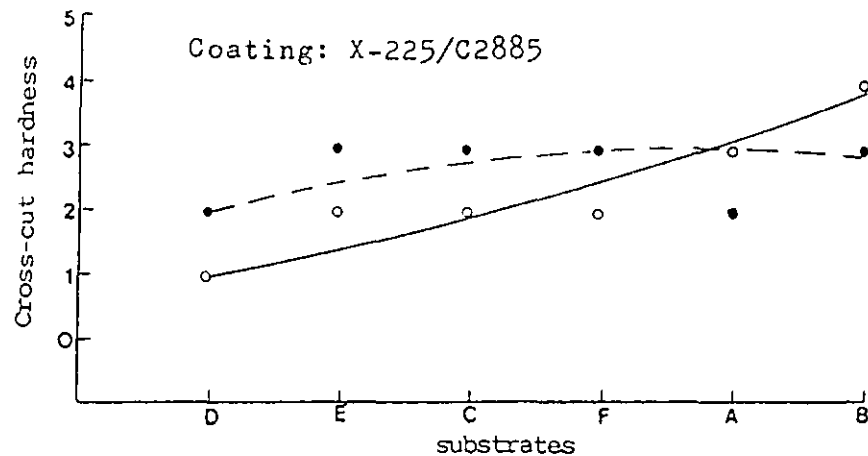
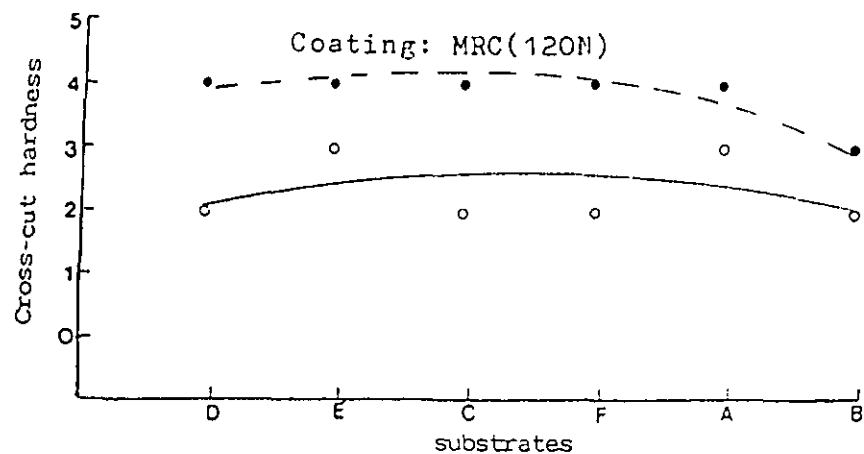


FIGURE 12.4: The overall effect of substrates, coatings and coating processes on cross-cut hardness of coated PU and polyester substrates

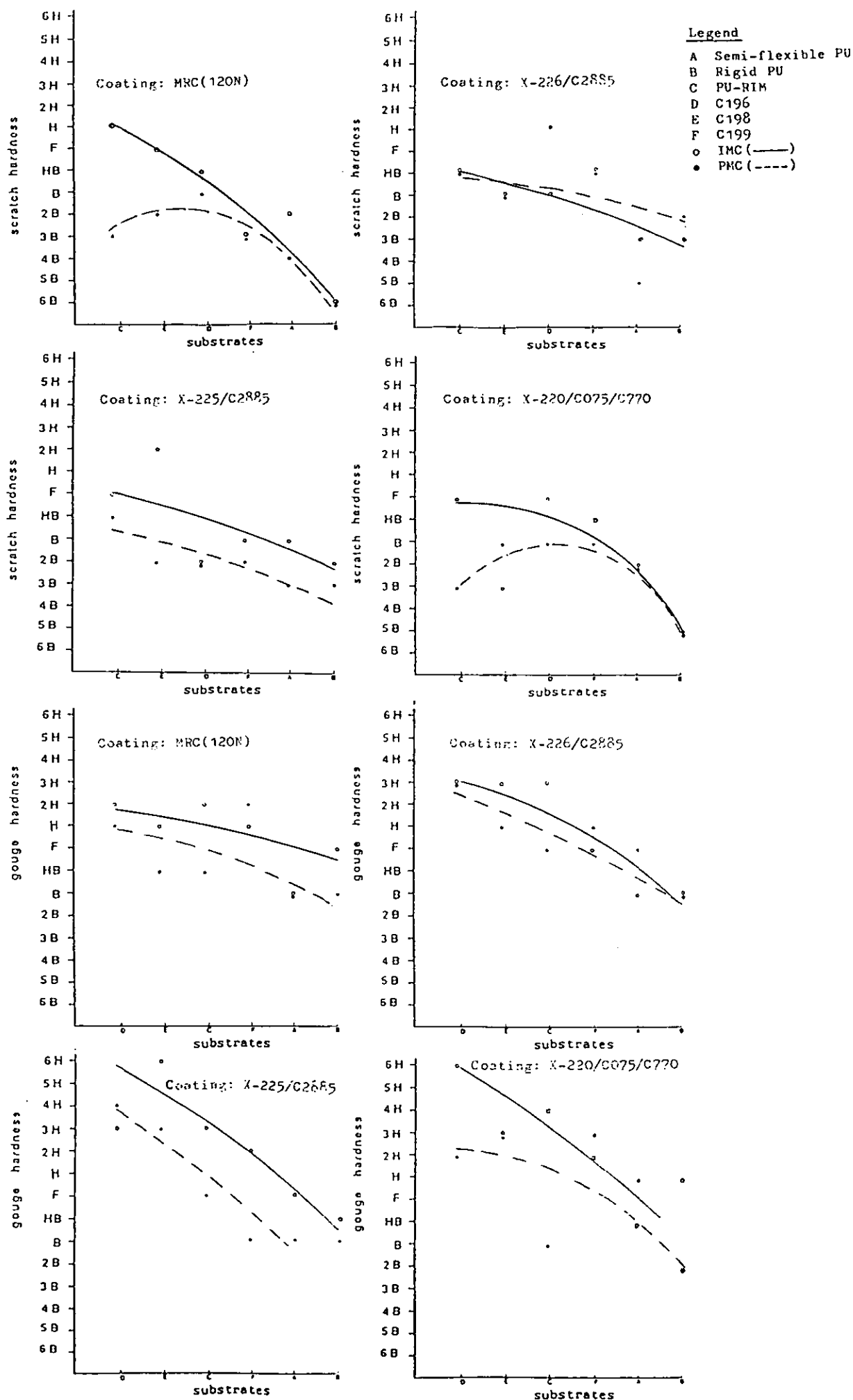


FIGURE 12.5: The overall effect of substrates, coatings and coating processes on scratch/gouge hardness of coated PU and polyester substrates



As a PU surface ages, its activity must inevitably lessen and subsequently any bond formed will be relatively weak. The rate of change of a free surface must be dependent on its chemistry, and the physical and chemical state of its environment.

#### 12.2.4 Discussion on Thermal Properties of Coated Samples

The results obtained by DSC and DMTA carried out on IMC and PMC samples of polyurethane and polyester substrates were presented and briefly discussed in Chapter 10. This section attempts to discuss the thermal properties results in more detail.

1. It may be argued that the differences in thermal properties of IMC and PMC samples are due to any mechanical, physical and chemical changes brought about during the production of these systems. It is clear that factors such as availability of free radicals, chemical affinity, processing temperature, ageing of the substrate and other effects detailed in the preceding sections have influenced the interfacial formation of coated systems and that subsequently has affected their transition temperatures. A similar view has been stated by Roller [395] that factors such as interchain stiffness, intermolecular polar forces, and comonomer compatibility, can affect the size of the transition region, and therefore, the behaviour of polymers. Nielsen and others [395-397] have also shown that the levels of crosslinking in thermosets affects the magnitude of accompanying physical changes and the temperature range of the glass transition. With increasing degrees of crosslinking, the relaxation peaks due to  $T_g$  in dynamic mechanical tests occur at higher temperatures, their intensities are lower and the peaks are broader.

2. From the above discussion it may be added that both DSC and DMTA results for PMC samples (especially those affected by adverse environmental conditions) show lower transition temperatures than corresponding IMCs. This is believed to be due to changes in surface polarity (i.e. urethane and urea linkages formation in humid conditions). Polar polymers such as polyamide substrates and epoxy thermoset coatings have been shown to absorb moisture and the appearance of relaxation peaks are therefore changed [397]. It has also been stated that in DMTA,  $T_g$  measured for vinyl based coatings are found to decrease with decreasing levels of hydrogen bonding [352].
3. It can be pointed out that the effect of polarity or cohesive energy density upon wettability and consequent adhesive strength discussed in preceding sections is also shown in the thermal energy difference of these systems. This increase in  $T_g$  may be explained in terms of the reduced expansion of a polymeric system with strong intermolecular attractions. It has been shown [398] that upon heating, the required fractional free volume for  $T_g$  to occur is achieved at an elevated temperature.
4. It may be argued that preparation of coating films and their affinity for certain substrates can have a significant effect on the morphology of the interfacial region. It is clear from the DMTA results of coated PU and polyester substrates that due to the effect of interfacial orientation  $\tan \delta$  observed by PMC samples resembles that of corresponding free films. This is contrary to the results obtained for IMCs (particularly with RIM-PU coated with two pack PU coating). A similar view has been expressed by many authors [399-401] stating that preparation of a

polymer film by evaporation of a solvent from a solution on a substrate results in orientation of the molecular chain segments near the solid interface.

#### 12.2.5 Discussion on SEM and EDX Studies of Coated Samples

The scanning electron microscopy and X-ray microanalysis results of coated polyurethane and polyester substrates were presented and briefly discussed in Chapter 11. This section attempts to further discuss the information already obtained from SEM/EDX studies of the interfacial region and the types of locus of failure occurring and tries to relate these findings to measured mechanical properties of corresponding coated samples.

1. The interface between substrates and coating shown in SEM micrographs (see Figures 11.2(a), 11.2(c), 11.3(b), 11.3(c), 11.4(a), 11.5(c), 11.5(d), 11.6(a), 11.7(c), 11.7(d), 11.8(a), 11.11(b)) appear as a diffusive layer in which some penetration from one phase to the other, indicating an intermixing of the two components in the interfacial zone, is observed. This observation is reinforced by EDX analysis of IMC samples where the penetration of elements from substrate and coating into the interfacial region and diffusing into the first few microns of the adjacent layers is detected.

It may be pointed out that the porosity of these surfaces (especially the microcellular structure of RIM) are providing a mechanical keying and also the possible presence of unreacted isocyanate groups (especially with the IMC process) on the surface enables some form of chemical interaction. Shutov et al [365] have expressed similar views on SEM studies of cell

morphology of PU based foams. They showed that macrocells (size up to 1 mm) are of some aid in mechanical interlocking but the most useful structures are microcells being less than 1 micron in size.

It may further be added that some partial solubility between chemically similar coating and substrate (see Section 12.2.1) resulted in diffusion and consequent molecular entanglement across the interface. We may argue that the development of adhesion between substrate and coating by a diffusional mechanism (i.e. potential for molecular penetration) resulted in a strong interface irrespective of the type of molecular interactions involved.

With IMC prepared PU foam mouldings where the surface air traps are formed, it was observed that the coating adhered completely at the line of the trapped air bubbles and no clean interfacial delamination could be achieved. The tensile adhesion failure results associated with these systems showed either superiority (particularly with RIM specimens) and/or revealed traces of coating or substrate on the other phase. The peak energy values for these samples were also high. These observations detailed in the preceding section and also the SEM micrographs (revealing apparent intimacy of surfaces) and EDX analysis of these samples, suggested some possible chemical interaction at the interface.

2. In a similar manner to the above observation, the SEM and EDX results for a number of PMC samples of PU and polyester substrates (see Figures 11.2(b), 11.2(d), 11.4(b), 11.4(d), 11.6(b), 11.7(b), 11.10(c)) were examined. It is clear that the

cellular structure of foam samples provided ideal conditions for mechanical interlocking to take place. It may also be argued that with paints having adequate viscosity and surface tension for PMC application the surface imperfections were adequately covered and substrates more completely wet out. The interfacial area and its adjacent neighbouring system shown in Figure 11.7(b) suggested some penetration of paint resin molecules in the substrate's matrix. This can be explained by solvent action of the two pack PU coating on the surface layer of the substrate and the eventual evaporation loss of solvent.

The above argument is supported by the consequent high mechanical strength values reported on these systems and indicates a strong interface. It may be concluded that the differences between IMC and PMC samples shown above are largely due to the processing effects such as temperature and viscosity discussed in preceding sections. Similar views have been shown by Heskkula et al [402] studying the diffusion of some miscible polymers in multilayer films. Although at room temperature sharp boundaries between the components of these structures were formed, heating the films provided mobility that allowed interdiffusion of systems. The extent of this diffusion depended on the value of the mutual diffusion coefficient and the time at the heat treatment temperature.

3. It may be argued that sharp interfaces observed by SEM micrographs of IMC and PMC PU and polyester substrates coated with one pack PU coatings (see Figures 11.6(c), 11.6(d), 11.8(c), 11.8(d), 11.9(d), 11.11(c), 11.11(d)) are indicating less compatibility, inadequate wetting, and even the possible presence

of WB layers on these surfaces. This type of interface is in effect formed by mechanical interlocking of porous surfaces where limited dispersion molecular forces are the only interaction forces present. It is clear that for IMC samples, the SEM section across the interface showed no evidence of voiding. This shows that wetting and spreading was an imposed mechanical rather than physical type. It is presumed that with PMCs, the presence of voids and cracks in the interfacial region as well as in the body of the coating or substrate provide points of stress concentration. The relatively low adhesion strength (with no or very little residue left on either phase) and also inferior impact failure values observed by these samples is indicating a weak interface and reflects on their small viscoelastic dissipation energies. This is additional evidence supporting the SEM results of these samples.

4. The SEM results for spray PU rigid foam coated with one pack PU based elastomeric coatings were discussed in Chapter 11. It may be added that microscopic observation of the fracture surfaces did not reveal any real differences in their interfacial areas. An exception to this was seen with two extreme cases of either very early application of coating (i.e. within minutes of the substrate foam production) or with the coating being applied after the PU foam was left for a considerable time under severe environmental conditions. This can be explained due to the possible presence of free  $-N=C=O$  in the early stages and formation of less reactive, more crosslinked structure of surfaces after being subjected to adverse conditions.

### 12.3 PROPOSED SCENARIOS FOR CHANGE IN STATE OF INTERFACES

From the experimental observations made in the laboratory and production and the discussions outlined above, a number of scenarios for the interfacial interaction of a coating on a polymer substrate may be proposed:

- i) wetting and spreading should be expected to occur if the correct combination of surface energetics in substrate and coating (i.e. formulations choice), can be brought together under desirable process conditions. The resulting maximum area of contact between the surfaces, whilst minimising stress concentrations create the correct environment to maximise interfacial bonding and hence good adhesive strengths.

However, the cohesive forces within a liquid (measured as viscosity), may limit the degree of spreading on a substrate. With reduced area of wetting, more material may have to be employed to achieve uniform coverage, increasing the risk of air entrapment at the interface. If possible paint thinners must be selected to reduce the carrier resin's viscosity, whilst having a positive effect on the resulting coating's surface free energy, i.e. to increase its potential to spread over and into the surface imperfections of the solid. Similarly, the formulation of a 100% solids coating must be tailored to produce good wetting of substrates. In either case surfactants may be employed as 'flow aids to help wetting', but it is important these materials do not give rise to weak boundary layer effects. Alternatively process conditions must be provided to promote mechanically imposed wetting.

Having achieved uniform coverage, the wet coating should have the physico-chemical potential to maximise interfacial bonding.

- ii) interfacial bonding by adsorptive mechanisms will occur if the two molecular structures of surfaces are close enough (at 10 to 30Å), for atomic interactions. With PU systems there will be an expectation for dispersive force and polar-polar interaction. Further, if free isocyanate and hydroxyl groups are present there is also the potential for chemisorptive bonding. In increasing order of desirability for bond strength and resistance to ageing: dispersive < polar-polar < covalent bonding.
- iii) roughening of a surface produces increased real surface area: this increases the potential for mechanical interlocking between coating and substrate. To separate such joined surfaces means that more work has to be done to overcome the friction and interlocking networks at the interface. Abrasive treatment of PUs and to a limited extent vapour or solvent wash degreasing may increase the real area of a surface. However, cutting through skin into the cellular structure of a foam has disadvantages.
- iv) diffusion may arise, due to the action of paint thinners solvating the surface layer of the substrate. As most paint films are thin and volatiles loss is rapid, solvent attack on the substrate may be limited. Even so, with limited swelling of the substrate's surface layer, there is a possibility for molecules of the paint resin binder to diffuse into it. Following evaporative loss of solvent, paint resin molecules will remain entangled in the substrate's matrix. The more mobile oligomer molecules (i.e. in 2-pack systems), are more likely to be involved in diffusion mechanisms.



v) several potential weak boundary layer effects should be avoided in coated PU systems:

- a) external release agent left on the surface, or internal release agent migrating to the surface of a moulded substrate;
- b) other mobile additives migrating to the surface of a moulded substrate, having poor compatibility with PU and relatively low molecular weight;
- c) adsorbed atmospheric moisture on the surface molecular layers as a surface ages;
- d) oxidised/UV degraded PU at the surface which will give a weak cohesive layer in the finished (coated) product;
- e) certain polar solvents used as thinners, being more mobile than the PU paint resins will form preferential polar bonds at an interface;
- f) thinners action releasing surface active reagents from the substrate;
- g) non-volatile but mobile surface active materials in the coating.

Removal of boundary layer materials can be carried out in several ways for PU substrates, including vapour degreasing, washing with solvent, treatment with abrasive or plasma.

CHAPTER 13  
CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

13.1 INTRODUCTION

The structure of this Chapter is as follows: the first section brings together a number of points which emerge from the above chapters. The second section gives some suggestions for further work.

13.2 CONCLUSIONS

Based on tests, observations and interfacial theories, and discussions detailed in the preceding chapters, a number of conclusions may be presented. These include:

1. Considerable potential for dispersive forces in bonding.
2. Considerable potential for polar bonding, e.g. between two adjacent urethane groups, other N-H containing groups with urethane, urea, etc, or unreacted hydroxyl groups.
3. Some potential for chemisorptive bonding if free isocyanate and hydroxyl are present on both surfaces.
4. Paint solvents may carry paint resin into the substrate's surface layer by diffusion mechanisms, even during the short drying and curing period of a paint.

5. High critical surface energy of PU and polyester substrates should encourage wetting and spreading of a broader range of surface coating types, over most topographies of substrate surfaces. However, the cohesive forces in the paint may limit the degree of spreading and area of wetting. Thinness dilution or mechanically imposed wetting of high viscosity coatings will minimise voiding at an interface. This will reduce surface tension and viscosity and in effect will increase its potential to flow over and into the surface imperfections of the solid.
6. Moulding forces involved in the IMC process are likely to encourage near complete wetting of the maximum area of paint film by liquid moulding ingredients. The potential of interfacial bonding by the phenomena listed above will be maximised, while boundary layer effects may be expected to be minimised.
7. The potential for good adhesive properties will lessen as an active surface ages. Ageing rates will be dependent on the chemical and physical properties of the substrate and its environment.
8. The mechanical and thermal properties of coated substrates are influenced to some extent by the thermal and mechanical history induced during processing. In other words, the exact state of chain interaction during processing will influence the properties of the solidified material.
9. The maximum contact area between coating and substrate will tend to increase total adhesive strength, since in part the potential for adsorptive and chemisorptive interaction is increased.

10. Keeping the molecular weight of the components maintained below a certain size, while being free of bulky side groups, is likely to encourage penetration into the adjacent phases by diffusion.
11. Any local increase in stress level, which would be the consequence of a stress concentration, may considerably exceed the average stress on which the coated polymer is processed, leading to failure even at a fairly low intensity of mechanical loading.
12. A proposed model based on surface tension of the testing liquids and corresponding contact angles formed on a solid surface (i.e.  $\gamma_{LV}$  relationship with  $\cos^2 \theta/2$ ) gives direct measurements of a number of thermodynamic parameters.
13. The identification of the relaxation transitions (temperatures) exhibited by substrate and coating components in various IMC and PMC coated systems provides the starting point for interpretation and improvement of the interfacial/adhesion performance characteristics.

### 13.3 SUGGESTIONS FOR FURTHER WORK

A fuller understanding of adhesion phenomena and the nature of the bonding in coated polymeric materials might be gained by considering:

1. Application of test methods and analytical techniques employed in this research to a broad range of surface coating/substrate combinations, especially less compatible systems.

2. Examination of the effect of various surface treatments on PU and other polymeric substrates prior to coating application (i.e. PMC) and investigation of the factors such as temperature, pressure and injection velocity (therefore shear rate over surfaces) during the IMC process.
3. Evaluation of the effects of molecular structure of the PUs, the additives and the choice of solvent carriers.
4. Studying the effect of deliberately changing the surface coatings' physical and chemical properties by introducing thinners and paint additives.

## APPENDIX 1

### SURFACE ENERGY AND SURFACE TENSION

The surface energy of a liquid or solid is the amount of energy required to form a unit area of a new surface.

The surface tension is the force acting in plane of the surface. The surface tension of a liquid can also be defined as the work done per unit area in increasing the surface area of a liquid under isothermal conditions. This is also called the surface free energy because the mechanical work done can be released when the surface contracts. Unlike a liquid, atoms at the surface of a solid are not mobile. The solid is likely to have a considerable range of values of surface free energy, varying from region to region on the surface, and also at any one point, unlike the surface of a liquid, the surface tension need not be the same in all directions. Contrary to the surface tension of a liquid, the surface tension of a solid is not susceptible to direct measurement.

For a pure liquid, surface tension is numerically equal to surface free energy. For solid surfaces this is not the case. Therefore, for a pure liquid, it is possible to switch from one concept to the other, using them interchangeably.

## APPENDIX 2

### HEALTH PRECAUTIONS ASSOCIATED WITH THE USE OF POLYURETHANE INTERMEDIATES\*

#### A. Safety Control

1. Apply stringent good housekeeping
2. Wear protective clothing
3. Use equipment designed to minimise aerosols
4. Ensure good extract facilities at crucial areas
5. Decontaminate residues
6. Dispose of waste safely
7. Carry out atmospheric checks and keep records
8. Check staff for (FEV) lung function on a regular basis
9. Study hazard sheets on all the chemicals used.

#### B. Decontaminants

Spillages should always be mopped up without delay, and decontaminants can be valuable in such situations. Suitable recipes are given below:

Liquid I	( Water 45% by wt. ( Ethanol 50% by wt. ( 0.880 Ammonia 5% by wt.
Liquid II	( Water 90% by vol. ( Surfactant 2% by vol. ( 0.880 Ammonia 8% by vol.
Solid	( Sawdust 20 parts by wt. ( Kieselguhr, China Clay 40 (        parts by wt. ( Liquid decontaminant II (        mixed in as required

Empty drums should be decontaminated before disposal - a caustic wash ( $\text{Na}_2\text{CO}_3$ ) usually being employed for isocyanate drums. Suitable solutions can be selected from the instructions in the suppliers' literature. All items of waste should be rendered innocuous before disposal through normal channels.

### C. Control Limits

TLV - Threshold Limit Value

STEL - Short Term Exposure Limit

TWA - Time Weighted Average

$\text{TLV}_c$  - Ceiling Value - should not be exceeded even instantaneously.

Two levels of control limits are usually quoted for isocyanates:

8 h TWA 0.02 mgs NCO groups/ $\text{m}^3$   
 10 min TWA 0.07 mgs NCO groups/ $\text{m}^3$

### D. Isocyanate Control Limits

	TWA 8h mgs $\text{NCO}_3$ group/ $\text{m}^3$	(ppm by vol.)	TWA 10 min mgs $\text{NCO}_3$ group/ $\text{m}^3$	(ppm)
TDI	↑	(0.0058)	↑	(0.02)
MDI		(0.0058)		(0.02)
NDI		(0.0058)		(0.02)
HDI		(0.0058)		(0.02)
IPDI	0.02	(0.0058)	0.07	(0.02)
Methyl Isocyanate	↓	(0.0116)	↓	(0.04)
Prepolymers		(-)		(-)
CHMDI		(0.0058)		(0.02)


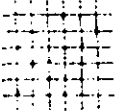
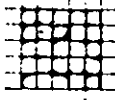

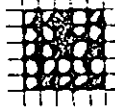
\* Data from British Rigid Urethane Foam Manufacturers' Association Limited (BRUFMA).



APPENDIX 3

CLASSIFICATION OF CROSS-CUT TEST RESULTS AS SPECIFIED IN

BS 3900: PART E6: 1974

Classifi- cation	Description	Appearance of surface of cross-cut area from which flaking has occurred (example for six parallel cuts)
0	The edges of the cuts are completely smooth; none of the squares of the lattice is detached	
1	Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not distinctly greater than 5% is affected.	
2	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area distinctly greater than 5%, but not distinctly greater than 15% is affected.	
3	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area distinctly greater than 15%, but not distinctly greater than 35% is affected.	
4	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area distinctly greater than 35%, but not distinctly greater than 65% is affected.	
5	Any degree of flaking that cannot even be classified by classification 4.	

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