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**THERMALLY STABLE POLYURETHANE ELASTOMERS :
THEIR SYNTHESIS AND PROPERTIES**

by

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**A Doctoral Thesis submitted in partial fulfilment
of the requirements for the award of
Doctor of Philosophy
of the
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This thesis is respectfully dedicated to:

My parents

My wife

and our sons Meysam and Majid

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ABSTRACT

Polyurethane elastomers have demonstrated unusually excellent physical and mechanical properties, but these advantages are considerably diminished at elevated temperatures.

This research was carried out to prepare thermally stable polyurethane elastomers. The investigation has led to methods of synthesising heat resistant castable polyurethanes. These polymers were prepared by chain extension of a polycaprolactone diol/trans cyclohexane diisocyanate (CHDI) or paraphenylene diisocyanate (PPDI), as prepolymer systems, with a variety of diol and diamine chain extension agents. A further study concerned the use of a large excess diisocyanate (10-50%) as a means of producing isocyanurate crosslinking in these polymers. This technique resulted in enhanced thermal stability. It is interesting to mention that the conventional PU system possessing typically 0-0.2% of free NCO has a maximum service temperature of approximately 120°C; this is raised to about 240°C by the use of this excess diisocyanate technique.

The occurrence of this enhanced thermal stability in polyurethane elastomers has been investigated by studying their morphology, using Dynamic Mechanical Thermal Analysis (DMTA) and Differential Scanning Calorimetry (DSC) techniques.

Infrared analysis has shown evidence of hydrogen bonding and the extent of this hydrogen bonding was measured. Thermal analysis and X-ray diffraction data showed support for a phase separated morphological structure where hard segment interactions led to the formation of non-crystalline domains.

Physical and mechanical properties of polyurethane elastomers were used as the criteria of their quality.

Measurements were made of ultimate tensile strength, elongation at break, modulus, hardness, tear strength, compression set, tension set, hysteresis, density, crosslink-density, fatigue life, internal heat generation and hot air ageing.

To evaluate the stability of these materials at high temperature, the tensile properties of some of the new polymers were investigated at elevated temperature.

CONTENTS

					<u>Page No</u>
Acknowledgements	i
Abstract	ii
Contents	iv
List of Figures	ix
List of Tables	xv
CHAPTER 1:	1
1A:	POLYURETHANES	1
1A.1	Introduction	1
1A.2	Fundamental Chemistry of the Polyure- thanes	2
1A.3	Chemistry of Polyurethane Elastomers				11
1A.4	Raw Materials	11
	1A.4.1 Diisocyanates		11
	1A.4.2 Polyols		13
	1A.4.2.1 Polyester			13
	1A.4.2.2 Polyether			15
	1A.4.3 Chain Extenders		16
	1A.4.4 Catalysts		17
1A.5	Synthesis	19
1A.6	Classification of Polyurethane Elastomers				23
	1A.6.1 Castable Polyurethanes			23
	1A.6.2 Millable Polyurethanes			24
	1A.6.3 Thermoplastic Polyurethanes				24
1B:	GENERAL STRUCTURE-PROPERTY RELATIONSHIPS IN POLYURETHANE ELASTOMERS..			27
1B.1	Introduction	27
1B.2	Morphological Structure in Polyurethane Elastomers	28
1B.3	Structure-Property Correlations in Seg- mented Polyurethane Elastomers			38

	<u>Page No</u>
1B.3.1 Effect of Soft Segment	40
1B.3.2 Effect of Hard Segment	43
1B.3.2.1 Effect of Diisocyanate	44
1B.3.2.2 Effect of Chain Extender	46
1B.3.3 Effect of Segment Size	48
1B.3.4 Effect of Crosslinking	49
1C: THERMAL STABILITY OF POLYMERS	53
1C.1 Introduction	53
1C.2 Thermal Stability of Polyurethanes	56
1C.3 Effect of Chemical Structure	56
1C.3.1 Effect of Hard Segment	58
1C.3.2 Effect of Polyols	62
1C.3.3 Effect of Crosslinking	63
1C.3.4 Effect of Isocyanurate Cross- linking	63
1D: OBJECTIVE OF THE RESEARCH	66
CHAPTER 2: PREPARATION (SYNTHESIS) OF POLYURETHANES	67
2.1 Introduction	67
2.2 Experimental	68
2.2.1 Selection of Raw Materials	68
2.2.1.1 Polyols	70
2.2.1.2 Diisocyanates	71
2.2.1.3 Chain Extenders	72
2.2.1.4 Catalyst	73
2.3 Synthesis	73
2.3.1 Prepolymer Method	74
2.3.1.1 Casting	75
2.3.1.2 Curing and Postcuring	75
2.3.2 Quasi-Method	76

		<u>Page No</u>
2.4	Crosslinking	76
2.5	Hazards	77
2.6	Summary of Polyurethane Materials Prepared	77
CHAPTER 3:	CHARACTERISATION AND PROPERTIES OF THE POLYMERS	88
3.1	Characterisation	88
	3.1.1 Dynamic Mechanical Analysis	88
	3.1.2 Thermal Analysis	90
	3.1.3 Infrared Analysis	93
	3.1.4 X-ray Analysis	96
	3.1.5 Electron Microscopy	99
3.2	Experimental	100
	3.2.1 Dynamic Mechanical Thermal Analysis (DMTA)	100
	3.2.1.1 Introduction	100
	3.2.1.2 Experimental Procedure	103
	3.2.1.3 Results and Discussion	104
	3.2.2 Differential Scanning Calorimetry (DSC)	143
	3.2.2.1 Introduction	143
	3.2.2.2 Experimental Procedure	145
	3.2.2.3 Results and Discussion	146
	3.2.3 Infrared Spectroscopy (IR)	172
	3.2.3.1 Introduction	172
	3.2.3.2 Infrared Technique	173
	3.2.3.3 Infrared Reflection Spectroscopy	173
	3.2.3.4 Experimental Procedure	174
	3.2.3.5 Extent of Hydrogen Bonding	175
	3.2.3.6 Results and Discussion	177
	3.2.4 X-ray Diffraction	189
	3.2.4.1 Introduction	189
	3.2.4.2 Experimental Procedure	190
	3.2.4.3 Results and Discussion	191

	<u>Page No</u>
3.2.5 Scanning Electron Microscopy (SEM)	192
3.2.5.1 Introduction	192
3.2.5.2 Experimental Procedure	193
3.2.5.3 Results and Discussion	194
3.2.6 Determination of Crosslink Density by Swelling	201
3.2.6.1 Introduction	201
3.2.6.2 Experimental Procedure	203
3.2.6.3 Results and Discussion	204
 CHAPTER 4: GENERAL PHYSICAL AND MECHANICAL PROPERTIES	 210
4.1 Tensile Strength Properties	210
4.1.1 Results and Discussion	211
4.2 Hardness	214
4.2.1 Results and Discussion	214
4.3 Tear Strength	226
4.3.1 Results and Discussion	227
4.4 Compression Set	227
4.4.1 Results and Discussion	228
4.5 Tension Set	232
4.5.1 Results and Discussion	233
4.6 Density	238
4.6.1 Results and Discussion	238
4.7 Skid Resistance	241
4.8 Determination of Heat Generation and Resistance to Fatigue	242
4.8.1 Flex Cracking and Crack Growth	242
4.8.2 Experimental Procedure	242
4.8.3 Results and Discussion	243
4.9 Hysteresis	252
4.9.1 Introduction	252
4.9.2 Experimental Procedure	252
4.9.3 Results and Discussion	254

	<u>Page No</u>
4.10 Heat Ageing of Polyurethane Elastomers	262
4.10.1 Introduction	262
4.10.2 Experimental Procedure	262
4.10.3 Results and Discussion	263
CHAPTER 5: GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK	278
5.1 Discussion and Conclusion	278
5.2 Recommendations for Further Work	287
APPENDICES:	
Appendix I: A. Structural Formula of Industrially Important Diisocyanate	289
B. Basic Physical Properties of PPDI and CHDI	291
C. Name, Formula and Basic Technical Information of the Raw Material Used in Polyurethane Elastomers	292
Appendix II: Precautions Necessary in the Handling of Raw Materials	301
Appendix III: Formulation of Rubber Used for Comparison Purposes	303
Appendix IV: PL Dynamic Mechanical Thermal Analyser	305
References	307

LIST OF FIGURES

<u>Figure No</u>		<u>Page No</u>
1A.1	Schematic representation of preparation techniques for polyurethane elastomers	23
1B.1	Hard and soft segments in polyurethane elastomer	29
1B.2	Diagrammatic representation of hydrogen bonding	31
1B.3	Schematic drawing of the structure of a polyether polyurethane	34
1B.4	Segmented polyurethane elastomer at 500% extension and placed in warm water at 80°C	35
1B.5	Possible models of spherulitic structure	36
1B.6	Diagrammatic representation of the three-dimensional crosslinking structure	37
1B.7	Schematic model depicting the morphology before and after heat treatment	37
1C.1	Intermittent stress relaxation of polyester and polyether urethane at 130°C	62
1C.2	Different types of polyurethane crosslink.....	65
2.1	Typical laboratory apparatus for the preparation of a polyurethane elastomer	87
3.1	The model series of segmented urethanes used in electron microscopic study by Wilkes et al	99
3.2	General form of the effect of temperature on storage modulus and $\tan \delta$	101
3.3	The effect of increasing or decreasing frequency on storage modulus and $\tan \delta$	102
3.4	Styrene-butadiene block copolymer phase separated	103
3.5	Compatible blend exhibiting one T_g relaxation	103
3.6	A typical DMTA (1 Hz) scan for a polyurethane sample heated at 4°C/min	125

<u>Figure No</u>		<u>Page No</u>
3.7	Storage modulus as a means of observing the dependence of temperature stability on diisocyanate	126
3.8	The temperature dependence of the loss tangent ($\tan \delta$) of different diisocyanate based polyurethanes	127
3.9	Storage modulus and $\tan \delta$ as a means of observing the dependence of temperature stability on mixed diisocyanate structure	128
3.10	Storage modulus and $\tan \delta$ as a means of observing the dependence of temperature stability on molar ratios	129
3.11	Storage modulus as a means of observing the dependence of temperature stability on chain extenders structure	130
3.12	Temperature dependence of the loss tangent ($\tan \delta$) of different chain extender based polyurethanes	131
3.13	Storage modulus and $\tan \delta$ as a means of observing the dependence of temperature stability with respect to the structure of various chain extenders	132
3.14	Storage modulus and $\tan \delta$ as a means of observing the dependence of the temperature stability on chain extender structure	133
3.15	An illustration of using a DMTA scan as a means of observing the dependence of temperature stability on crosslink density in a PU (1,4-BD system)	134
3.16	An illustration of using a DMTA scan as a means of observing the dependence of temperature stability on crosslink density in a PU (1,4-BD+1,4-CHDM system)	135
3.17	DMTA scan of PPDI based polyurethanes	136
3.18	DMTA scan as a means of observing the dependence of temperature stability on crosslink density in PU elastomer (1,4-BD system with block ratio of 1/3/2)	137

<u>Figure No</u>		<u>Page No</u>
3.19	DMTA scan as a means of observing the dependence of temperature stability on both chain extenders structure and crosslink density in the case of using 30% excess CHDI	138
3.20	DMTA scan of crosslinked PU elastomer (soft series)	139
3.21	DMTA scan as a means of observing the dependence of glass transition temperature on polyol structure in soft series PU	140
3.22	DMTA scan as a means of observing the dependence of glass transition temperature on polyol structure in hard series PU	141
3.23	A schematic view of the mechanical heat - cut away view	142
3.24	Urethane sample clamped in the PL-DMTA prior to measurement	142
3.25	Schematic representation of two types of hard segment domain order	145
3.26	Block diagram of the thermal analysis apparatus	146
3.27	DSC scans of various diisocyanate based PU elastomers	158
3.28	DSC scans of mixed diisocyanate based polyurethane elastomers	159
3.29	DSC scans of polyurethane elastomers with different block ratios	160
3.30	DSC scans of different chain extender based PU elastomers (block ratio 1/2/1)	161
3.31	DSC scans of different chain extender based PU elastomers (block ratio 1/2.6/1)	162
3.32	DSC scans of diamine and diol extended polyurethane elastomers	163
3.33	DSC scans of crosslinked PU elastomers in the case of using excess diisocyanate (1,4-BD system)	164

<u>Figure No</u>		<u>Page No</u>
3.34	DSC scans of crosslinked PU elastomer in the case of using excess CHDI (1,4-BD+1,4-CHDM system)	165
3.35	DSC scans of 1,4-BD based PU elastomer with block ratio of 1/3/2	166
3.36	DSC scans of Polacure based polyurethane elastomers	167
3.37	DSC scans of mixed chain extender based PU elastomer as a means of observing soft and hard segment transitions	168
3.38	DSC scans of PPDI based PU elastomers	169
3.39	DSC scans of crosslinked PU elastomer based on different diamine and diols chain extenders	170
3.40	DSC scans of PU elastomer of soft polymer series	171
3.41	The optical path in a simple ATR unit and totally internally reflected IR radiation....	175
3.42	Infrared spectrum of 1,4-cyclohexane diisocyanate (CHDI)	184
3.43	A typical infrared spectra of Capa 225/CHDI/1,4-BD based PU elastomer	185
3.44	A typical infrared spectra of Capa 225/CHDI/Polacure based PU elastomer	186
3.45	A typical infrared spectra of Capa 231/CHDI/Capa 305 based PU elastomer	187
3.46	A typical infrared spectra of Capa 230/CHDI/305 based PU elastomer	188
3.47	Showing base line density method in a typical NH absorption band of PU elastomer	179
3.49	Essential feature of the X-ray diffraction instrument (WAXS)	189
3.50	Wide angle X-ray diffraction patterns of Capa 225/CHDI/1,4-BD series with different percentage of CHDI	196
3.51	Wide angle X-ray diffraction patterns of Capa 225/CHDI/1,4-BD+1,4-CHDM series with different percentage of CHDI	197

<u>Figure No</u>		<u>Page No</u>
3.52	Wide angle X-ray diffraction patterns of Capa 225/CHDI/Polacure series	198
3.53	Wide angle X-ray diffraction pattern of Capa 225/CHDI/1,4-BD+1,4-CHDM series with 30% CHDI at 300% extension	198
3.54	A schematic diagram showing the operation of a scanning electron microscope	193
3.55	SEM micrographs (2000x magnification) showing the surface morphologies of Capa 225/CHDI/1,4-BD+1,4-CHDM based PU elastomer having different percentages of excess CHDI	199
3.56	SEM micrographs (2000x magnification) showing the surface morphologies of Capa 225/CHDI/1,4-BD based PU elastomer having different percentages of excess CHDI	200
3.57	Crosslink density vs % excess CHDI for the polyurethane elastomer	209
4.1	Relationship between tensile strength at different temperatures and the excess amount of diisocyanate used for crosslinking CHDI based polyurethane	222
4.2	Relationship between 300% modulus and excess amount of diisocyanate in CHDI based polyurethane	223
4.3	Relationship between tensile strength and temperature for polyurethanes of different crosslinking density	224
4.4	Effect of crosslinking on tensile properties of soft series polyurethanes	225
4.5	Tear testing sample and tearing mode	226
4.6	Relationship between tension set and percentage excess CHDI used for crosslinking of polyurethane elastomer	237
4.7	Relationship between density and % excess CHDI in PU elastomers	240
4.8	De Mattia type machine with sample in its original form, under strain and under stress....	245

<u>Figure No</u>		<u>Page No</u>
4.9	Relationship between fatigue life and percentage excess diisocyanate and % strain of PU elastomer	249
4.10	Heat generation against time for PU elastomers with different amounts of excess CHDI at 100% strain	250
4.11	Heat generation against time for PU elastomers with 30% excess CHDI at different % strains	251
4.12	Typical hysteresis curve	256
4.13	Typical example of hysteresis curve of a PU chain extended with 1,4-BD+1,4-CHDM at room temperature	256
4.14	Relationship between hysteresis and % excess diisocyanate in Capa 225 based polymers chain extended with 1,4-BD and 1,4-BD+1,4-CHDM	261
4.15	Effect of ageing time at 150°C on Capa 225/CHDI/1,4-BD based PU elastomer	273
4.16	Effect of ageing time at 150°C on Capa 225/CHDI/1,4-BD+1,4-CHDM based PU elastomers	274
4.17	Effect of ageing time on Polacure based PU elastomer at 150°C	275
4.18	Comparing the effect of ageing time and diol and diamine cured PU elastomer at 150°C	276
4.19	Effect of ageing time on soft polymer series at 150°C	277
5.2	Summary of research investigation	288
5.1	The reaction sequence used for the synthesis of isocyanurate modified urethane elastomer preparation	281
A3.1	Curing behaviour of NR/SBR compound	304

LIST OF TABLES

<u>Table No</u>		<u>Page No</u>
1A.1	The variety of systems and applications of polyurethane elastomers	26
1B.1	Estimated cohesion energies of common groups in urethane elastomers	28
1B.2	Effect of polyol on hydrolysis properties of polyurethane	41
1B.3	Effect of polyether and polyester on properties of urethane elastomer - a comparison	42
1B.4	Effect of molecular weight of polycaprolactone on the Tg of polyurethanes	43
1B.5	Effect of diisocyanate structure on physical properties of segmented polyurethane elastomers	44
1B.6	Effect of different diisocyanates on Tg of the polyurethane elastomer	45
1B.7	Effect of diamine structure on physical properties of polyurethane elastomers	47
1B.8	Effect of diol structure on physical properties of polyurethane elastomers	48
1B.9	Some typical millable polyurethane elastomers	52
1C.1	The effect of hard segment symmetry on the temperature resistance of polyester-MDI-butane diol elastomers	59
1C.2	The influence of the type of urethane group on heat stability	60
1C.3	Thermal stability of model urethanes in argon	61
1C.4	Melting point of some isocyanurate structures	64
2.1	Typical example of the selection of raw materials for preparation of polyurethane elastomers	74
2.2	List of raw materials abbreviations	78

<u>Table No</u>		<u>Page No</u>
2.3	List of prepared polyurethane elastomers	79
2.4	List of prepared polyurethane elastomers (using excess amounts of diisocyanate)	82
3.2	Maximum temperature to which storage modulus (log E') values of polyurethane elastomer will remain constant	114
3.3	α and β transition temperatures of polyurethane elastomers based on different diisocyanates	114
3.4	Maximum temperature to which storage modulus values of polyurethane elastomer will remain constant in the case of using mixed diisocyanate	116
3.5	Maximum temperature to which storage modulus values of PU elastomer will remain constant in the case of using different block ratios	115
3.6	Maximum temperature to which storage modulus values will remain constant in the case of using different chain extenders	116
3.7	α , β and γ transition temperature of polyure- thanes in the case of using different diol chain extenders	116
3.8	Maximum temperature to which storage modulus values of PU elastomer will remain constant in the case of using different chain extenders	117
3.9	α , β and γ transition temperature of polyure- thanes in the case of using different diol chain extenders	117
3.10	Maximum temperature to which storage modulus values of PU elastomers will remain constant in the case of using diols and diamine chain extenders	118
3.11	α and β transition temperatures of polyure- thane elastomers based on various chain extenders	118
3.12	Maximum temperature to which storage modulus values of the crosslinked PU elastomer will remain constant (BD based)	119
3.13	Maximum temperature to which storage modulus values of the crosslinked PU elastomer will remain constant (BD+CHDM based)	120

<u>Table No</u>		<u>Page No</u>
3.14	Maximum temperature to which storage modulus values of the crosslinked PU elastomers will remain constant (PPDI based)	121
3.15	Maximum temperature to which storage modulus values of crosslinked polyurethane elastomers will remain constant (BD based with 1/3/2 block ratio)	121
3.16	Maximum temperature to which storage modulus ($\log E'$) values of the PU elastomer will remain constant in the case of using excess CHDI and different chain extenders	122
3.17	Maximum temperature to which storage modulus ($\log E'$) values of PU elastomer will remain constant in the case of using excess PPDI and different chain extenders	123
3.18	Temperature dependence of the α and β transition for Capa 225/PPDI type polyurethanes based on various chain extenders	123
3.19	Temperature dependence of the α -transition for the various polyol containing polyurethanes in PPDI/TMP based polymers	124
3.20	Temperature dependence of the α -transition for the various polyol containing polyurethanes in CHDI/Polacure based polymers	124
3.21	Transition temperature of various diisocyanate based polyurethane elastomers	153
3.22	Transition temperature of mixed diisocyanate based PU elastomers as a means of observing the effect of CHDI on thermal property	153
3.23	Transition temperature of PU elastomers as a means of observing the effect of block ratio on thermal property	154
3.24	Transition temperature of different chain extender based PU elastomer	154
3.25	Transition temperature of different chain extender based PU elastomers in the case of using excess diisocyanate	154

<u>Table No</u>		<u>Page No</u>
3.26	Transition temperature of diamine and diols based PU elastomers as a means of observing the influence of their structure on thermal property	155
3.27	Transition temperature of crosslinked PU elastomers as a means of observing the influence of excess diisocyanate on thermal property (1,4-BD system)	155
3.28	Transition temperature of crosslinked PU elastomers as a means of observing the influence of excess CHDI on thermal property (1,4-BD+1,4-CHDM system)	155
3.29	Transition temperatures of mixed chain extender based PU elastomers as a means of observing soft and hard segment transitions	156
3.30	Transition temperature of PPDI based PU elastomers	156
3.31	Transition temperature of crosslinked PU elastomer based on various diols and diamine chain extenders	156
3.32	Transition temperature of soft polymer series PU elastomers	157
3.33	Major infrared band assignment for prepared PU elastomers	180
3.34	Extent of hydrogen bonding in polyurethane elastomer, chain extended with 1,4-BD	181
3.35	Extent of hydrogen bonding in PU elastomers chain extended with 1,4-BD+1,4-CHDM	182
3.36	Extent of hydrogen bonding in Polacure chain extended based PU elastomer	183
3.37	Extent of hydrogen bonding in PPDI based polyurethane elastomers	183
3.38	Crosslink density and swollen volume of polyurethane elastomer based on Capa 225/CHDI/1,4-BD	205

<u>Table No</u>		<u>Page No</u>
3.39	Crosslink density and swollen volume of polyurethane elastomer based on Capa 225/CHDI/1,4-BD+1,4-CHDM	206
3.40	Crosslink density and swollen volume of PU elastomer based on Capa 225/CHDI/Polacure....	207
3.41	Crosslink density and swollen volume of PU elastomer based on Capa 225/PPDI/1,4-BD	207
3.42	Crosslink density and swollen volume of soft polyurethane elastomer	208
4.1	Tensile properties of polyurethane elastomers based on Capa 225/CHDI/chain extender with 1/2/1 molar ratio	215
4.2	Tensile properties of polyurethane elastomers based on Capa 225/CHDI/1,4-BD with 1/3/2 molar ratio	216
4.3	Tensile properties of PU elastomers based on Capa 225/CHDI/1,4-BD with 1/2/1 molar ratio	216
4.4	Tensile properties of PU elastomers based on Capa 225/CHDI/1,4-BD with 1/2/1 molar ratio at room and elevated temperature	217
4.5	Tensile properties of polyurethane elastomers based on Capa 225/CHDI/1,4-BD+1,4-CHDM with 1/3/2 molar ratio at room and elevated temperature	219
4.6	Tensile properties of polyurethane elastomers based on Capa 225/CHDI/chain extender with 1/3/9/2 molar ratio	221
4.7	Tensile properties of the soft series of PU elastomers	221
4.8	Tear strength of polyurethane elastomers (1,4-BD and 1,4-BD+1,4-CHDM series)	229
4.9	Tear strength of PU elastomers (Polacure extended and PPDI based polymers)	230
4.10	Tear strength of polyurethane elastomers (soft series)	230
4.11	Compression set of polyurethane elastomers	231

<u>Table No</u>		<u>Page No</u>
4.12	Tension set of polyurethane elastomers (1,4-BD series)	234
4.13	Tension set of polyurethane elastomers (1,4-BD+1,4-CHDM series)	235
4.14	Tension set of polyurethane elastomers (PPDI based)	236
4.15	Tension set of polyurethane elastomers (soft series)	236
4.16	Density value of polyurethane elastomers	239
4.17	Skid resistance data of some soft PU elasto- mers	241
4.18	Flex-cracking resistance of polyurethane elasto- mer based on Capa 225/CHDI/1,4-BD+1,4-CHDM	246
4.19	Crack propagation resistance of PU elastomer based on Capa 225/CHDI/1,4-BD+1,4-CHDM	246
4.20	Heat generation observed by flexing of PU elastomers at 100% strain	247
4.21	Heat generation observed by flexing of PU elastomers at 150% strain	248
4.22	Hysteresis properties of PU elastomers based on Capa 225/CHDI/1,4-BD with block ratio 1/2/1	257
4.23	Hysteresis properties of PU elastomers based on Capa 225/CHDI/1,4-BD+1,4-CHDM with the block ratio 1/3/2	258
4.24	Hysteresis properties of PU elastomers based on Capa 225/PPDI/1,4-BD with the block ratio 1/2/1	259
4.25	Hysteresis properties of PU elastomers based on Capa 225 with different diisocyanate and chain extenders	260
4.26	Heat ageing properties of PU elastomer based on Capa 225/CHDI/1,4-BD with block ratio 1/3/2 at 150°C	266
4.27	Heat ageing properties of PU elastomers based on Capa 225/CHDI/1,4-BD+1,4-CHDM with block ratio of 1/3/2 at 150°C	267

<u>Table No</u>		<u>Page No</u>
4.28	Heat ageing properties of PU elastomer based on Capa 225/CHDI or PPDI/1,4-BD with block ratio 1/2/1 at 150°C	269
4.29	Heat ageing properties of soft series PU elastomer at 150°C	271
A2.1	Threshold unit values (TLV) for some commonly used diisocyanates	301
A3.1	Formulation of rubber used throughout the compression set, tear and skid resistance investigation	303

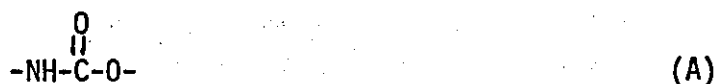
CHAPTER 1

1A POLYURETHANES

1A.1 INTRODUCTION

Polyurethanes, also referred to as "urethanes" refer to a relatively new group of most important class of polymers that have found wide-spread commercial application over the last thirty years or so.

These polymers are manufactured in various forms including foams, fibres, surface coatings, adhesives and elastomers. Polyurethanes are characterised by the linkage (A)¹ regardless of the constitution



of the rest of the molecule, although a variety of other structurally important groups, in addition to urethane, such as ester, ether, amide, biuret, allophanate and others may be present in the polymer chain.

The history of urethane goes back to 1849 when Wurtz² first synthesised an aliphatic isocyanate by reacting organic sulphates with cyanates. A number of isocyanates were prepared following his work, but much of the early development work dates back to as far as 1937 when Dr Otto Bayer experimented with addition products of diisocyanates³. He discovered that the reaction between aliphatic diisocyanates and aliphatic diols (glycols) went smoothly under reflux conditions to build linear polymers of high molecular weight⁴. In 1941, these materials were marketed as Perlon U, a fibre forming polymer, and Igamid U, for plastic moulding uses. Potential was also shown for use as adhesives, foams, lacquers, coatings and synthetic leathers. In 1942 German patent No 728981 was published⁵, covering the basic principles of their work. By 1952 the vulkollan class of castable polyurethane elastomers had been established. Vulkollan⁶ is the original urethane rubber developed in Germany. This group of polyurethanes is based on the reaction

products of various diisocyanates and polyesters. Two major reviews of the work on the 'Vulkollan' development have appeared in the literature^{7,8} describing the variations of composition possible and other effects on the properties of resulting materials. Elastomers with excellent tear and abrasion resistance together with high tensile strengths and good oil resistance, are typical of the vulkollans, which form the basis of the majority of the present day polyurethane composites. As well as solid elastomeric compositions, polyurethanes have been widely developed to include foams (rigid, semi-rigid and flexible), surface coatings, plastics, adhesives, sealants and textiles, and their properties depend primarily on the nature of the intermediates⁹ employed, the degree of crosslinking in the molecules, and the method of fabrication.

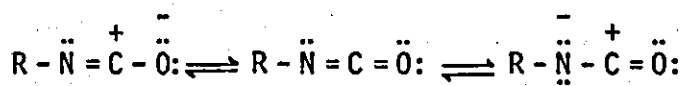
1A.2 FUNDAMENTAL CHEMISTRY OF THE POLYURETHANES

The ability of the isocyanate group (-NCO) to react with compounds containing active hydrogen, and with itself, forms the basis of polyurethane chemistry. Reaction of the isocyanate group falls into three main categories:

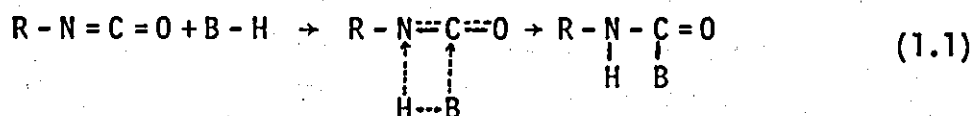
- a) Intermolecular hydrogen transfer reactions
- b) Self-addition reactions
- c) Miscellaneous reactions.

a) Intermolecular hydrogen transfer reactions

The isocyanate group is highly reactive towards compounds containing an active hydrogen atom and the carbon-nitrogen double bond of the isocyanate group undergoes ionic addition reactions with a variety of functional groups which contain an active hydrogen atom. This is known as addition polymerisation by rearrangement of the molecules¹⁰. No by-products are given off unless water or a carboxyl group is present, in which case carbon dioxide gas is given off. The reactivity of the isocyanate group can be explained by its electronic structure¹¹:



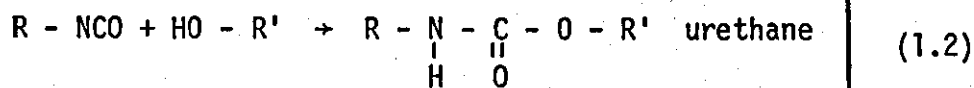
The resonance possibilities indicate the electron density is greatest on the oxygen and least on the carbon resulting in the oxygen having the highest net negative charge, the carbon having the highest net positive charge and the nitrogen being intermediate with a net negative charge. The reaction of isocyanates with active hydrogen compounds proceeded by the attack of a nucleophilic centre upon the electrophilic carbon atom, equation 1.1:



attention here being focussed on the most important primary reactions.

Reaction with alcohols:

Isocyanates react with alcohol to give urethanes in the following manner:

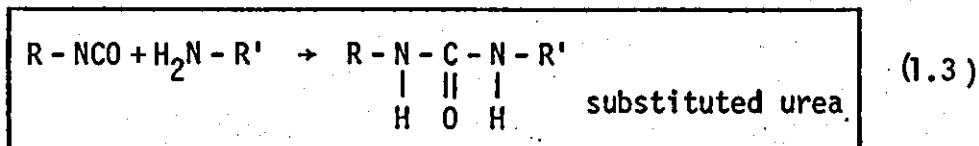


This is the most important reaction in the polyurethane preparation as the backbone polyols are OH terminated and also now the most widely used chain extenders are diols e.g. 1,4-butanediol. The reactivity order of alcohols is:

Primary > secondary > tertiary

Reaction with amines:

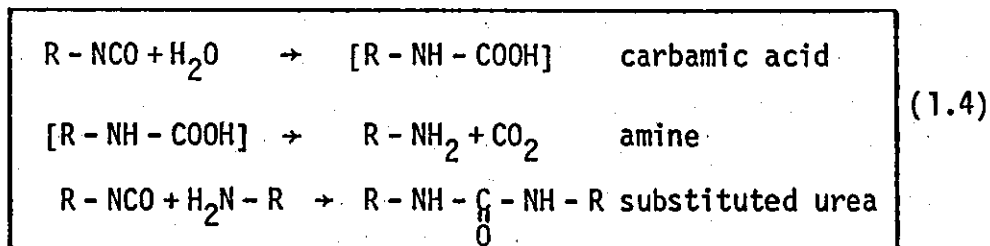
Isocyanate reacts with amines to form ureas:



This reaction is particularly valuable in chain extensions of isocyanate terminated prepolymers, forming urethane-urea elastomers.

Reaction with water:

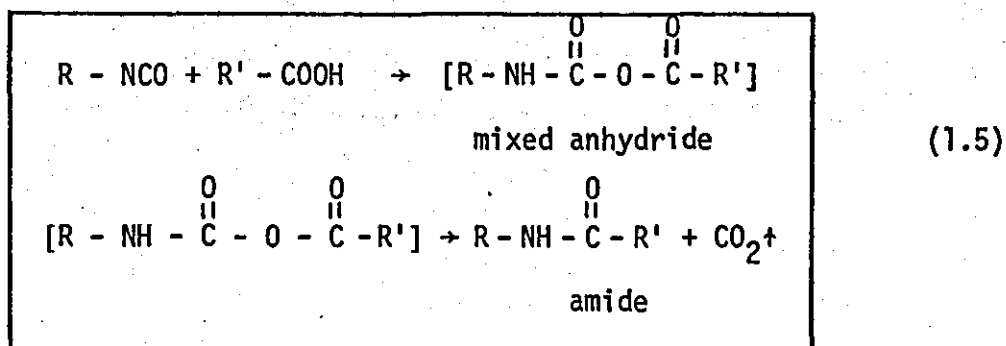
Isocyanate reacts with water to give an unstable intermediate product of carbamic acid followed by amines and carbon dioxide. The amine immediately reacts with additional isocyanate to form a substituted urea, equation 1.4:



The reaction of isocyanate and water is particularly important in low density flexible foam manufacture¹² and moisture curing of one component isocyanate terminated coatings. The above reaction shows the importance of handling urethane raw materials in perfectly dry conditions during the formation of solid elastomers, in order to avoid undesirable bubble formation due to formation of carbon dioxide¹³.

Reaction with carboxylic acids:

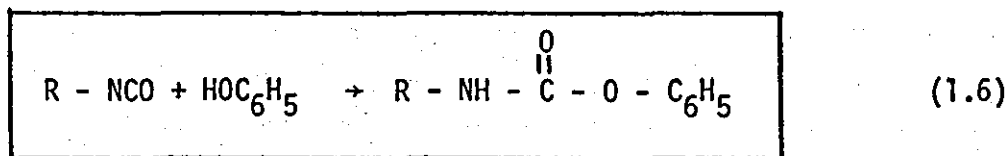
Isocyanates react readily with carboxylic acids, and the reaction proceeds via an unstable intermediate (mixed anhydride) whose decomposition products depend on the type of isocyanate and carboxylic acid, yielding the corresponding acid amide with loss of carbon dioxide, equation 1.5:



the reaction rate between carboxylic acid and isocyanate being dependent on the acid strength¹¹.

Reaction with phenols:

Phenols are acidic and react more slowly with isocyanates than do aliphatic alcohols, to form urethanes. Catalysts in the form of tertiary amines are usually required.

Reaction with amides:

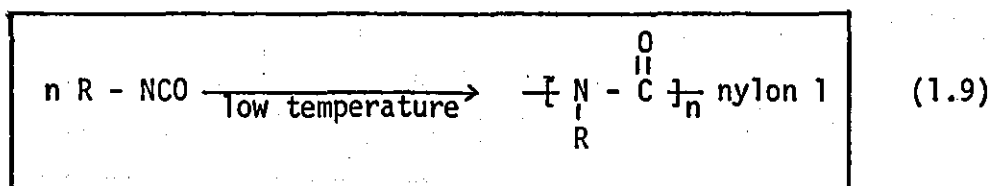
Amides, and substituted amides can also react under certain conditions¹⁹ with isocyanate to give acyl ureas, equation 1.7:

b) Self-Addition Reactions

In addition to the above mentioned reactions, isocyanates can react with themselves under certain catalytic conditions. The four most important reactions of this type are as follows:

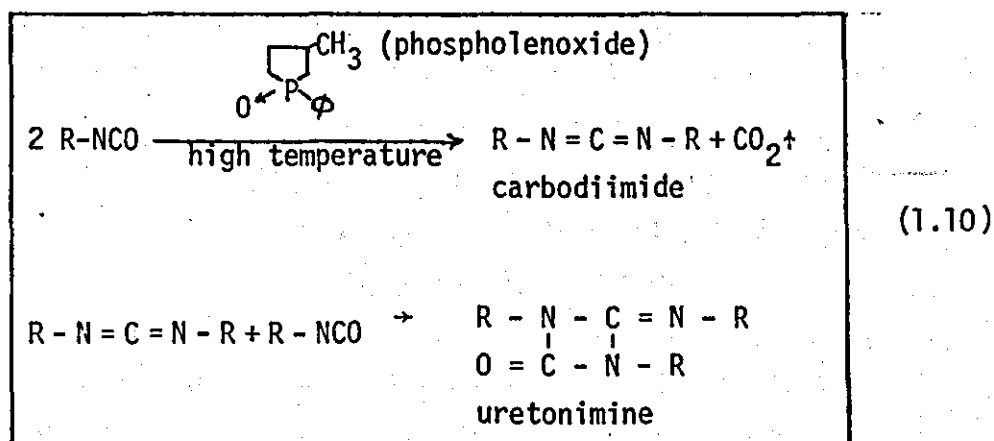
i) Linear polymerisation:

The linear polymerisation of isocyanates is obtained in a manner similar to vinyl polymerisation with anionic catalysts (such as sodium cyanide in N,N-dimethyl formamide) at temperatures of -20°C to -100°C . However, this reaction is usually not observed in normal urethane polymerisation reactions¹⁴.



ii) Carbodiimide formation:

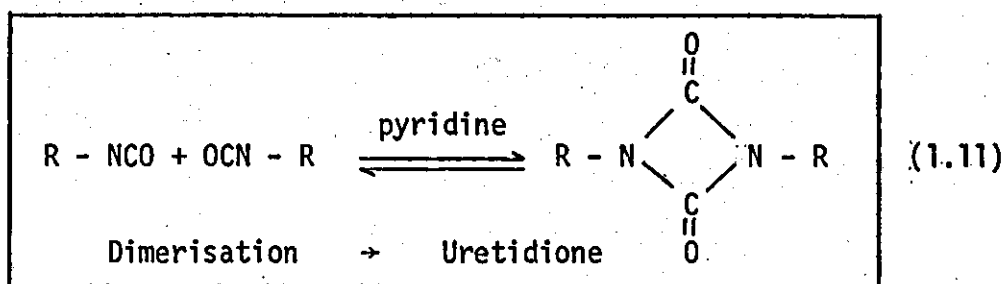
Isocyanates condense easily to form carbodiimides with evolution of carbon dioxide¹⁵. The reaction occurs easily on heating but the products react with further isocyanate, during and after cooling, to yield a substituted uretonimine. Traces of uretonimine are thus present in many modified isocyanates.



Carbodiimides are used as anti-hydrolysis additives in polyester based urethanes¹⁶.

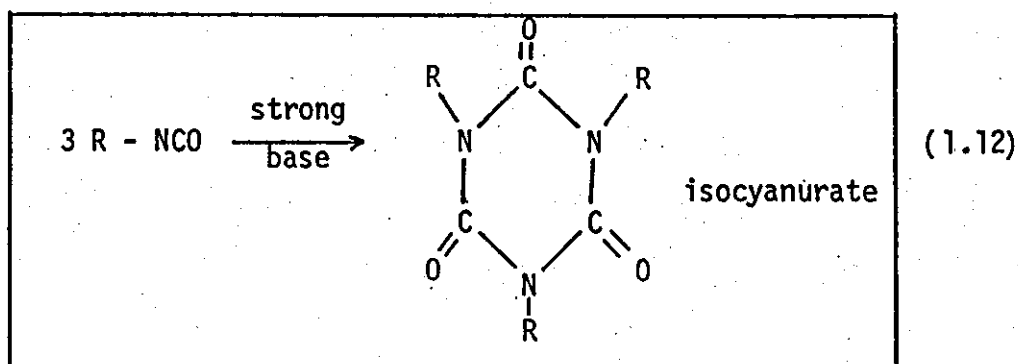
iii) Dimerisation:

Dimerisation of isocyanates takes place in the presence of pyridine giving rise to uretidione rings. This reaction is an equilibrium reaction and can be reversed by heat, equation 1.11:



iv) Trimerisation:

Trimerisation of isocyanates takes place in the presence of a basic catalyst such as sodium methoxide or a strong organic base giving rise to isocyanurate rings¹⁷.



Both uretidione and isocyanurate formation are important in isocyanate chemistry, but isocyanurate formation is significant in a wider range of polyurethane applications¹⁸. Isocyanurate structures are extremely

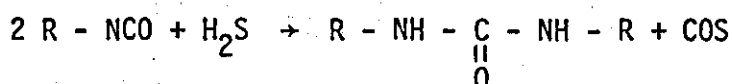
stable to both thermal and hydrolytic attack, and decomposition does not begin until well above 300°C.

c) Miscellaneous Reactions:

Although the reactions covered above are the most important reactions in polyurethane formation, the isocyanate group can take part in many other types of reaction¹⁹:

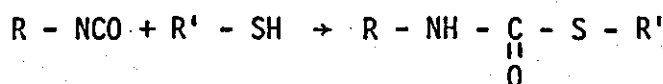
i) Reaction with S-H groups:

Sulphur compounds react with isocyanates in a similar manner to their oxygen analogues. Hydrogen sulphide for example reacts similarly to water.



1.13

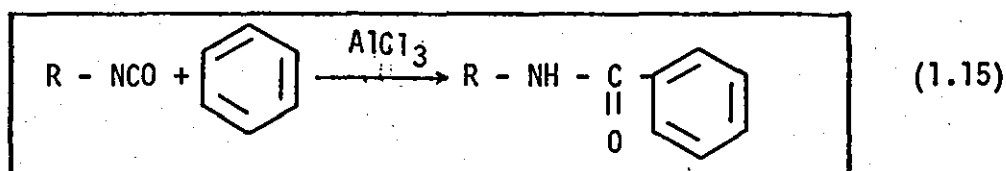
Similarly mercaptans give thiourethanes.



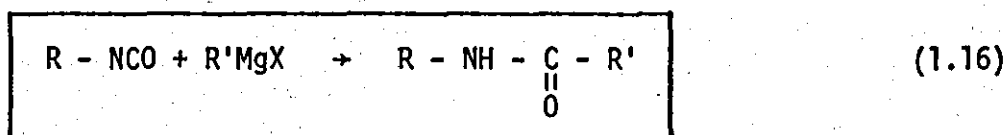
1.14

ii) Friedel-Crafts and Grignard reactions:

Isocyanates react to form amides under Friedel-Crafts conditions in the presence of aluminium chloride.

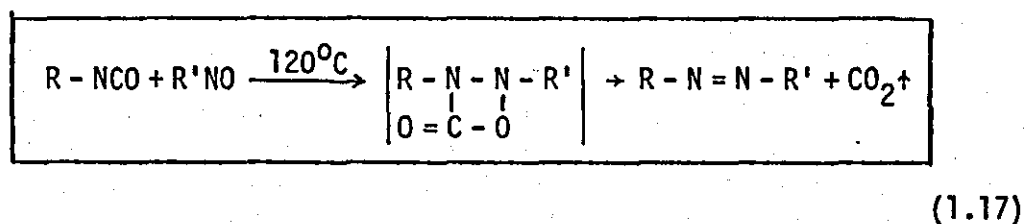


Reaction with Grignard reagents also occurs under relatively mild conditions.



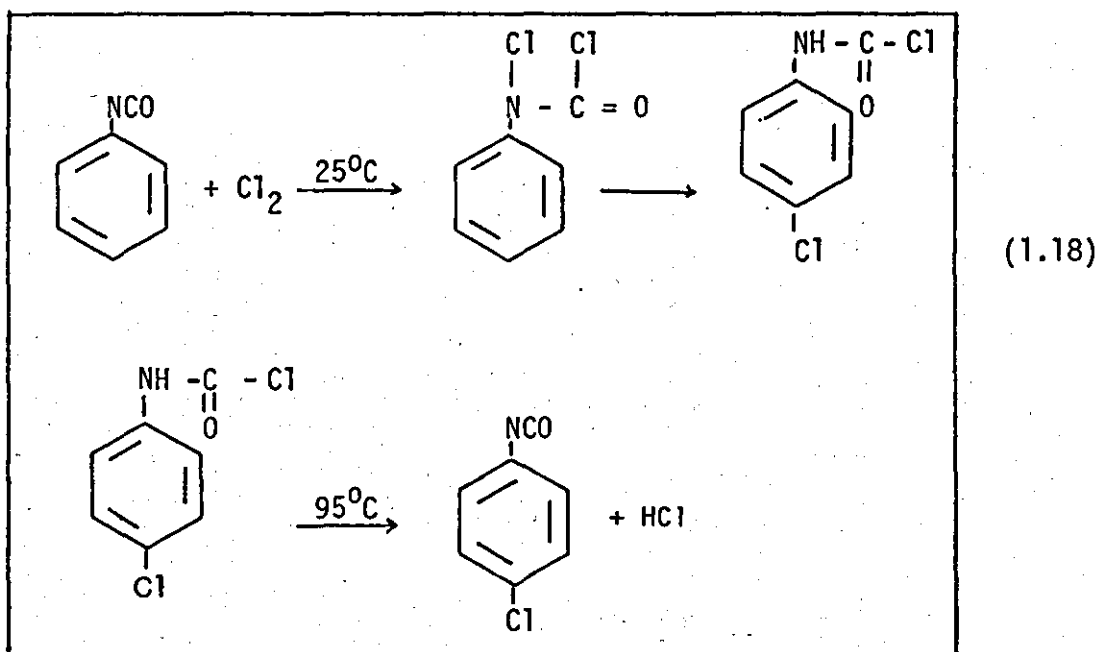
iii) Reaction with unsaturated compounds:

Isocyanates react with unsaturated groups such as the nitroso or aldehyde groups.



iv) Reaction with halogens:

Chlorine and bromine form addition products with isocyanates, followed by rearrangement to yield chlorinated (brominated) - carbamoyl chloride (bromide). Hydrogen chloride is removed at higher temperature.



1A.3 CHEMISTRY OF POLYURETHANE ELASTOMERS

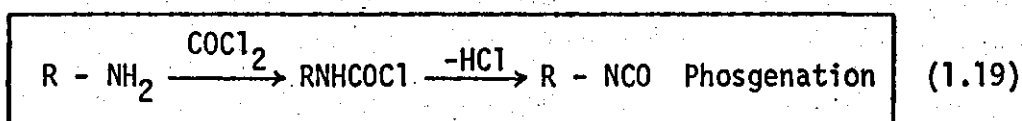
Elastomers with a high level of mechanical properties are usually based on block copolymer systems having alternating flexible and rigid segments in the polymer chain. The flexible segments are composed of polyols, generally polyether or polyester, while the hard segments are made up of urethane or urea units formed by the reaction of diisocyanate with diol or diamines. Therefore, polyurethane elastomers are prepared from three basic raw materials, such as diisocyanates (aromatic or aliphatic), polyols (polyether or polyester), and chain extenders (diamine or diol). The feedstock of basic raw material for polyurethanes is petroleum.

1A.4 RAW MATERIALS

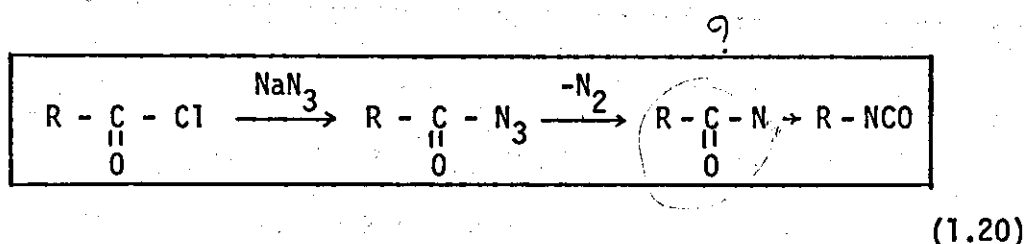
1A.4.1 Diisocyanates

The most widely used diisocyanate in elastomer manufacture are the isomers of 2,4- and 2,6-toluene diisocyanates (TDI), in a ratio of 80:20 or 65:35; 4,4'-diphenylmethane diisocyanate (MDI) and its aliphatic analogue 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI); 1,5-naphthalene diisocyanate (NDI); 1,6-hexamethylene diisocyanate (HDI); xylene diisocyanate; and 1-isocyanato-3,5,5-trimethyl-5-isocyanato-

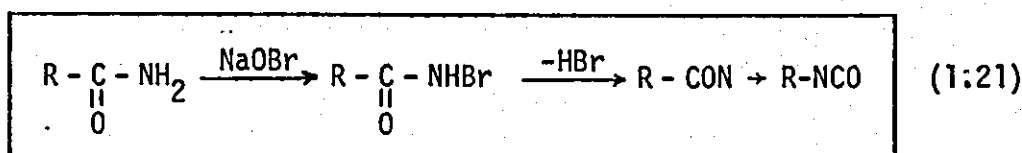
methyl-cyclohexane (isophorone diisocyanate) (IPDI). All these isocyanates are generally prepared by reaction of the corresponding amines with phosgene in an inert solvent like ortho dichlorobenzene at temperatures of 25-100°C, via a number of intermediate steps. This is at present the most widely commercially used method for the manufacture of isocyanates, equation 1.19:



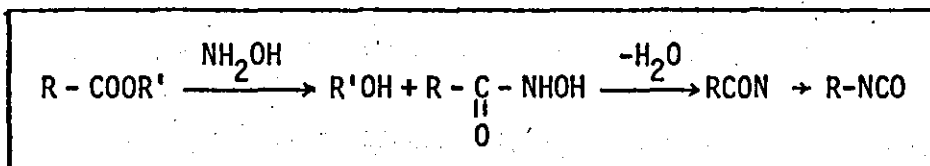
Other preparative methods include the Curtius, Hoffman and Lossen rearrangement reactions, which may involve nitrene as an intermediate, are not satisfactory for large scale operation. Although the use of azides is hazardous, the Curtius rearrangement of an acid azide can be considered next in importance to the phosgenation reaction²⁰.



The Hoffman rearrangement involves the reaction of an amide with sodium hypobromite in aqueous solution.



The Lossen rearrangement involves the rearrangement of hydroxamic acids in the presence of thionyl chloride.



(1.22)

The structural formula of industrially important diisocyanates is given in Appendix 1.

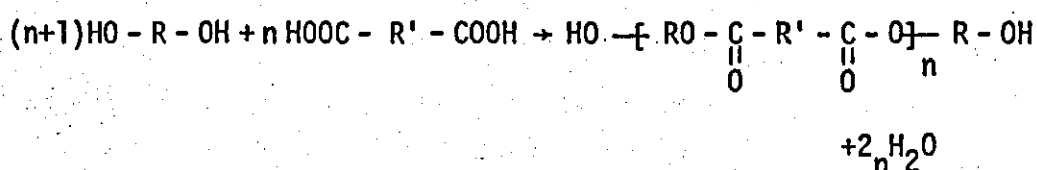
1A.4.2 Polyols

The two different types of polyols, polyester or polyether, are widely used as intermediates in the manufacture of all types of polyurethanes and the choice of polyol strongly influences the final properties of urethanes. In general, polyesters provide better mechanical properties than the polyethers which yield more hydrolytically stable polyurethanes. Hydroxy-polyethers, which are obtained by alkoxylation, are used in far greater quantities than hydroxy-polyesters obtained by esterification²¹. Polyols may have molecular weights of the order of 500-3000, be crystalline or amorphous, contain atoms or groups which contribute to molecular flexibility or stiffness, and be linear or branched according to the requirements for use.

1A.4.2.1 Polyesters

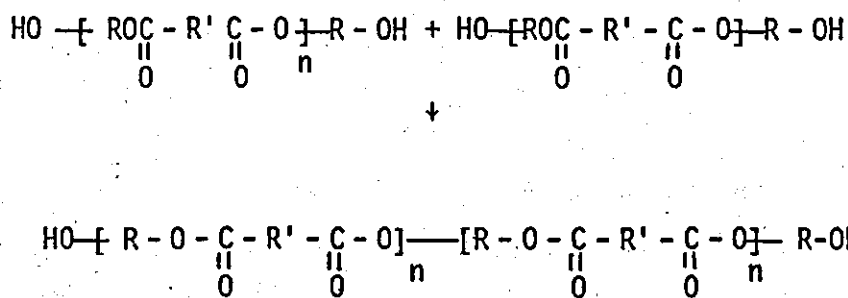
The polyesters are usually prepared by reaction of dibasic acids with excess diols. The most common raw materials used in polyesters for the urethane polymers are adipic acid, sebacic or phthalic acid with ethylene glycol, 1,2-propylene glycol, and diethylene glycol, where linear polymer segments are required, and glycerol, trimethylolpropane, pentaerythritol, and sorbitol, if chain branching or ultimate crosslinking is sought.

For the preparation of the polyesters, conventional methods of polyesterification are used. As the polyesters are required to be hydroxyl terminated, it is usual to react an excess of the stoichiometric amount of the glycol with the acid.



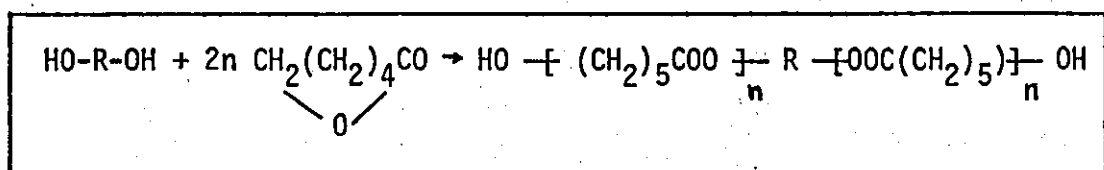
(1.23)

This esterification reaction results in a mixture of low molecular weight polymers. Continued reaction at high temperatures and, in some cases, reduced pressures leads to the elimination of some glycol with the formation of higher molecular weight polyesters.



(1.24)

Another type of polyester which is of interest in the field of solid polyurethanes is polycaprolactone, which is obtained by the addition polymerisation of ϵ -caprolactone in the presence of an initiator.

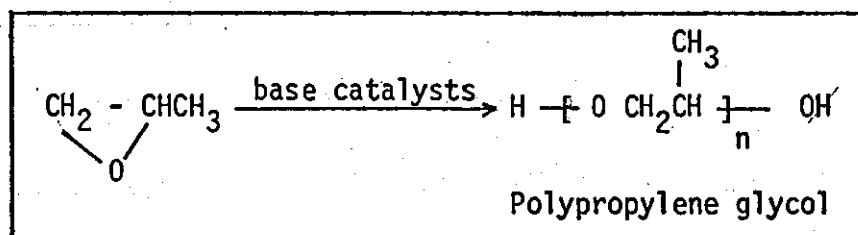


(1.25)

In some cases, copolyesters are employed to overcome the cold hardening effect in the final elastomer which occurs due to crystallisation.

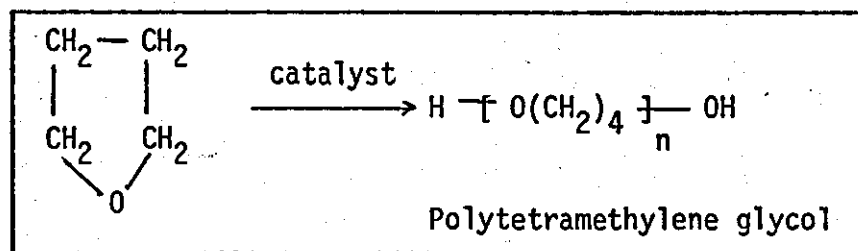
1A.4.2.2 Polyethers

The polyethers are commercially the most important of the polyhydroxy compounds used to prepare polyurethanes. They are generally prepared by catalytic polymerisation of the epoxide group in the alkylene oxide with suitable initiators.



(1.26)

The first polyether designed specifically for preparing polyurethanes was a polytetramethylene glycol derived from tetrahydrofuran.



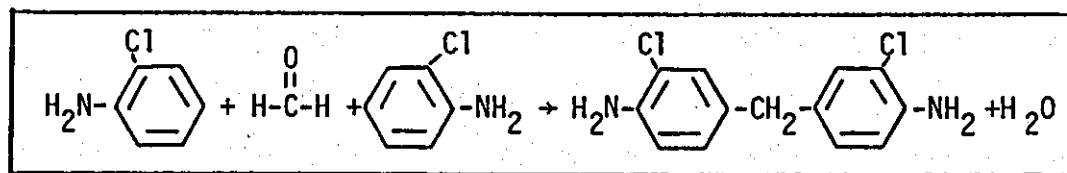
(1.27)

The catalysts used are Lewis acids and bases and salts. For the manufacture of polypropylene glycols, the catalyst is usually sodium or potassium hydroxide in aqueous solution, although sodium methoxide, potassium carbonate and sodium acetate are also used²². A polymerisation initiator is employed to control the type of polyether produced. Bivalent glycols (ethylene-, propylene-, diethylene-, and dipropylene-) can be used as initiators in the manufacture of difunctional polyethers, whereas trivalent or multivalent alcohols (trimethylolpropane, glycerol, pentaerythritol, sorbitol, etc) are general initiators for trifunctional or multifunctional polyethers. In general polyether glycols are light coloured viscous liquids. They are non-volatile and soluble in common organic solvents.

1A.4.3 Chain Extenders

There are many glycols and diamines which are used as chain extenders in the manufacture of solid polyurethanes and the most widely used chain extension agents are 1,4-butanediol and MOCA²³ (3,3'-dichloro-4,4'-diaminodiphenylmethane).

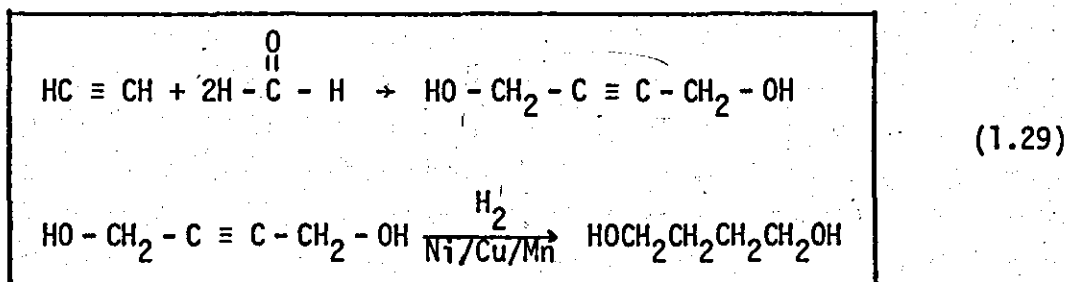
MOCA is manufactured by the condensation of ortho-chloroaniline with formaldehyde in acid medium:



(1.28)

The condensation is started at low temperature, which is gradually increased to about 80°C. After reaction the mixture is made alkaline, washed with water, filtered and dried.

The manufacture of 1,4-butanediol involves the high pressure hydrogenation of 1,4-butyne diol using a nickel-copper-manganese catalyst. The 1,4-butyne diol is obtained by the reaction between acetylene and formaldehyde²⁴.

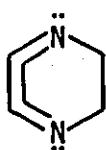


1A.4.4 Catalysis

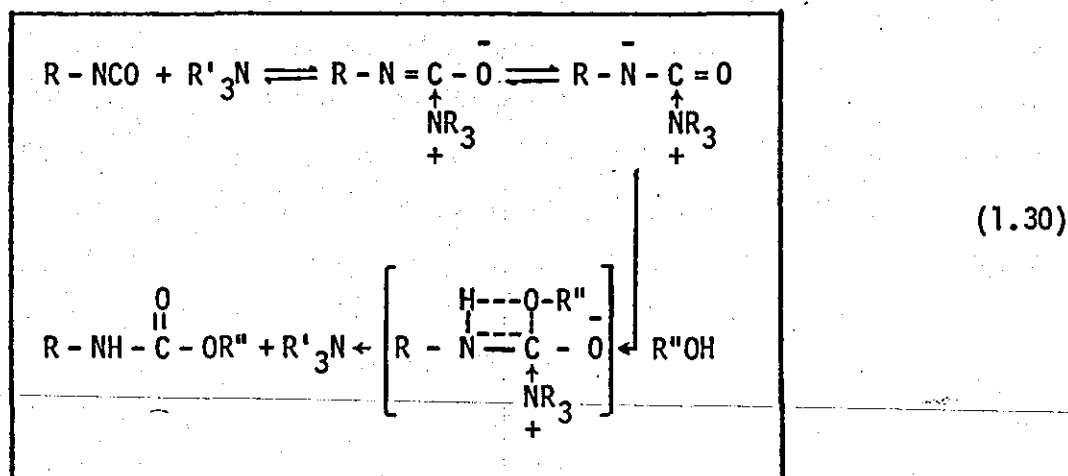
The purpose of catalysts in polyurethane chemistry is to accelerate the reaction rate, reduce reaction time, and achieve a balanced reaction rate in the system where various reactants differ widely in activity. The catalysts usually employed in polyurethane synthesis are: acids, bases and metal compounds such as tin and mercury.

Acids accelerate the chain extension mildly but retard the crosslinking reactions. The only reaction strongly catalysed is that with water which ideally should not be present in solid polyurethanes¹¹. Due to its selective action acid halides e.g. p-nitrobenzoyl chloride or benzoyl chloride can be usefully employed as a stabiliser for polyurethane prepolymer systems²⁵.

Bases accelerate all the isocyanate reactions and in general their catalytic effect increases with increasing strength of the base. Tertiary amines are relatively more powerful catalysts due to the accessibility of their nitrogen atoms and lack of steric hindrance e.g. 1,4-diazo-[2,2,2]-bicyclo-octane (DABCO).



The tertiary amine catalysis is thought to proceed as follows²⁶



By the base catalytic reaction an isocyanate-base complex is formed, which then reacts with the alcohol and gives the urethane²⁷⁻²⁹.

Although many organometallic compounds have a catalytic effect on reactions of the isocyanate group, organotin compounds are extremely effective catalysts and usually preferred for use in polyurethanes. They include stannous octoate, stannous oleate, dibutyltin dilaurate, and, dibutyltin di-2-ethylhexoate. Catalysis by metals such as tin has been explained by the formation of ternary complexes³⁰⁻³¹. Other explanations³² are based on the formation of bridge complexes between metal-alcohol and metal-isocyanate complexes. However the most widely used catalysts commercially available in polyurethane processes are tertiary amines and organotin compounds.

1A.5 SYNTHESIS

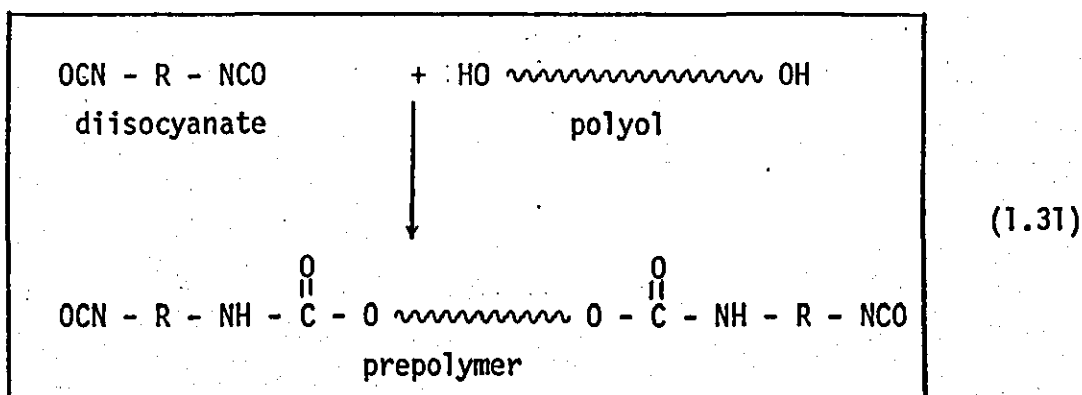
The term block ratio (NCO/OH ratio) is frequently used in the synthesis of polyurethanes as a basis of controlling the synthesis and relating the stoichiometric proportion of starting materials with that of final physical properties. The stoichiometric efficiency between reactants is known to proceed with 100% efficiency and hence the reaction of diisocyanates with hydroxyl groups is carried out using a selected molar ratio or block ratio of NCO/OH to produce a urethane of predetermined structure. For example a polyurethane based on the 1:2:1 ratio signifies the stoichiometric equivalent weight ratio by which the polyol, the diisocyanate and chain extenders are respectively reacted to give the final product.

The techniques commonly employed in the synthesis of polyurethanes are:

- a) prepolymer
- b) semi- or quasi-prepolymer
- c) one-shot.

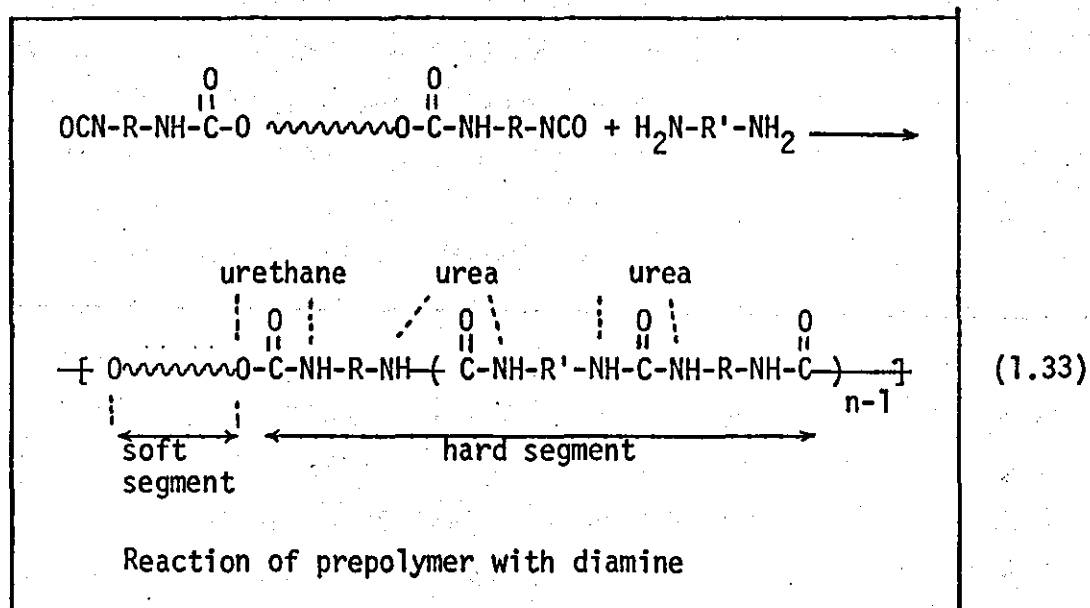
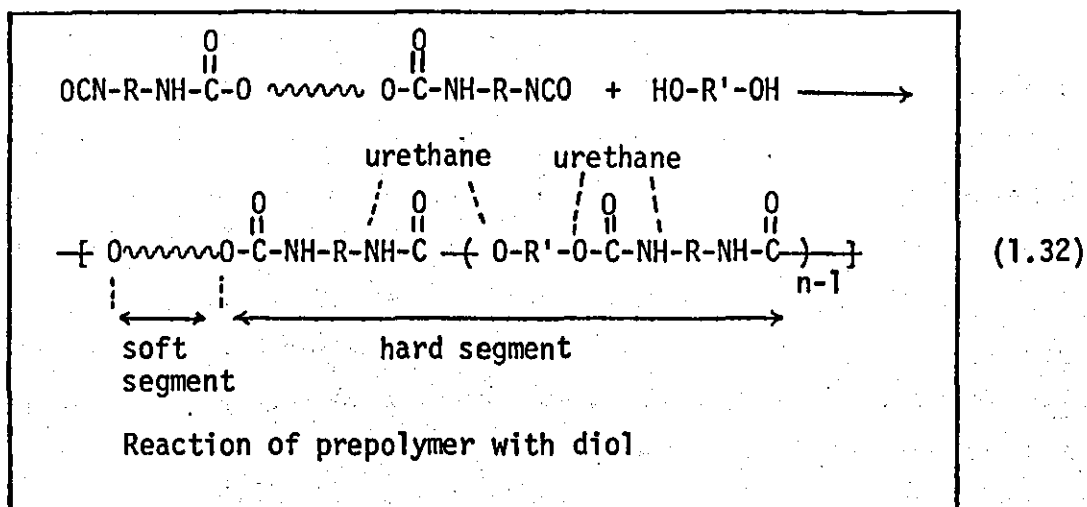
a) Prepolymer

Most commercial solid polyurethane elastomer systems are based on the prepolymer technique and the prepolymer route is by far the most widely used and provides better handling, controlled processing and consequently better properties. The prepolymer is obtained by reacting a long chain polyol (polyether or polyester) with an excess of diisocyanate to give an isocyanate-terminated polymer of moderate molecular weight, which in the second stage can be chain-extended with low molecular weight diol or diamine to yield the final product. A typical prepolymer reaction can be represented schematically as follows:



The prepolymer can be prepared either by melt polymerisation or solution polymerisation. In melt polymerisation the predried diisocyanate and a polyol at NCO/OH ratio greater than one, are mixed in molten form with vigorous stirring. As with other chemical reactions, temperature, time and rate of mixing are very important variables to control the reaction and achieve desired end product properties. The prepolymers are relatively stable high viscosity liquids or low melting solids at room temperature, which should be stored in the dark under nitrogen to prevent photodegradation, dimerisation or moisture contact with NCO groups.

Further reaction of the prepolymer with chain extension agent (low molecular weight diol or diamine) proceeds to give a higher molecular weight, soluble or insoluble polymer. Diols are comparatively less reactive than diamines and sometimes necessitate the use of catalysts which should be added to the prepolymer before mixing. As the pot life of melt polymerised urethanes is short the reacting mix is quickly cast into a mould after mixing. The cast urethane is then cured in an oven in the temperature range 50-120°C for several hours. A typical chain extension reaction with diol and diamine are schematically shown below³³:



The technique of solution polymerisation is similar to melt polymerisation, except that the process is carried out in a common non-reactive solvent. Although the properties of polymers are not good as melt polymerisation, this technique has the following advantages over melt polymerisation³⁴:

1. Possibility of using high melting points and highly reactive diisocyanates and chain extension agents;

2. Rapid and efficient dispersion of reactants;
3. Overcome the disadvantages of short pot life;
4. Easier casting to form thin film by solvent evaporation.

b) Semi-prepolymer

The semi- or quasi-prepolymer method is also used in some cases. In this method only part of the polyol (polyether or polyester) component is reacted with all of the diisocyanate to form the semi- or partial (quasi) prepolymer. This prepolymer is then reacted with the remainder of the polyol which was mixed with chain extension agent, to give the final polymer.

c) One-shot

The one-shot system basically involves the simultaneous mixing together of stoichiometric quantities of polyol, diisocyanate and chain extender. In practice the polyol and chain extender are first mixed, dried and then added to diisocyanate. There is no control over the reaction priority, hence random polyurethane structures are produced. Sometimes for solid polyurethanes one-shot systems are used due to economical reasons in the production of segmented thermoplastic materials where the three starting ingredients are mixed and extruded in a continuous process, but generally this technique is used more in the production of foam than elastomers (e.g. the reaction injection moulded or RIM process).

Techniques common in the synthesis of polyurethane elastomers are depicted below:

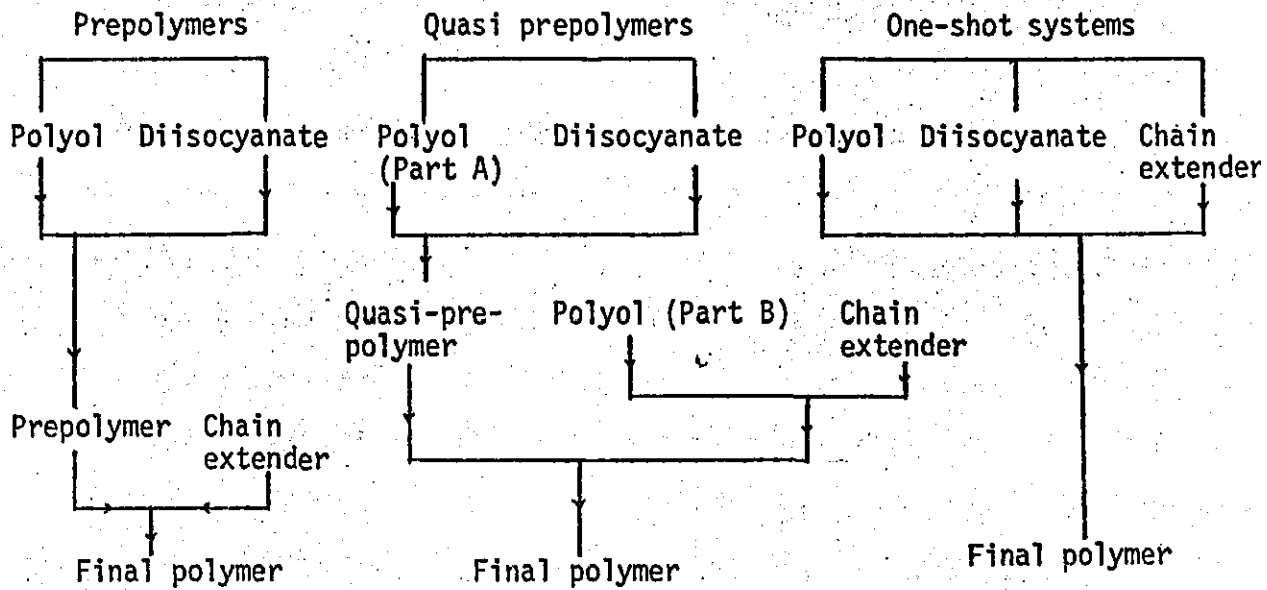


FIGURE 1.1: Schematic Representation of Preparation Techniques for Polyurethane Elastomers

1A.6 CLASSIFICATION OF POLYURETHANE ELASTOMERS

On the basis of their processing characteristics polyurethane elastomers fall into three main categories:³⁵

1. Castable polyurethanes
2. Millable polyurethanes
3. Thermoplastic polyurethanes.

1A.6.1 Castable Polyurethanes

Castable polyurethanes are by far the largest class of polyurethane elastomers presently used and can be manufactured by either the prepolymer or one-shot route³⁶. The fabrication techniques include open casting, centrifugal and rotational casting, compression and transfer

moulding from plastic gum, spray coating either reaction or solvent techniques, and reaction injection moulding. By variation of the three major ingredients (polyol, diisocyanate and chain extender), cast elastomers manufactured by the techniques mentioned cover a wide range of physical properties. They vary from very soft gelatine like materials, to hard products of outstanding strength. They also exhibit excellent oil and abrasion resistance. Because of these outstanding properties cast elastomers have found successful applications as solid tyres for industrial vehicles, rollers, especially those used in the printing industry³⁷, pulleys, bearings, gear wheels and other articles which could be produced conveniently by injection moulding.

1A.6.2 Millable Polyurethanes

Millable polyurethane elastomers are composed of the storage-stable millable gums. These are essentially based on the prepolymer concept described for cast polyurethane elastomers. They are rubbery in character but require processing on conventional rubber machinery with curing agents. Crosslinking can be effected either by the addition on the mill of more diisocyanate, peroxide or sulphur. Fillers such as carbon black can also be added on the mill, and the whole process including the high temperature press cure, is analogous to the manufacture of conventional rubber products. The properties of the final product are inferior in strength to those from the castable polyurethanes but have superior compression set and creep. The millable urethanes have mainly been used for products which could not be satisfactorily produced using the cast systems, for example, thin walled flexible gaiters, diaphragms and other similar components most easily manufactured by compression and similar moulding techniques³⁸.

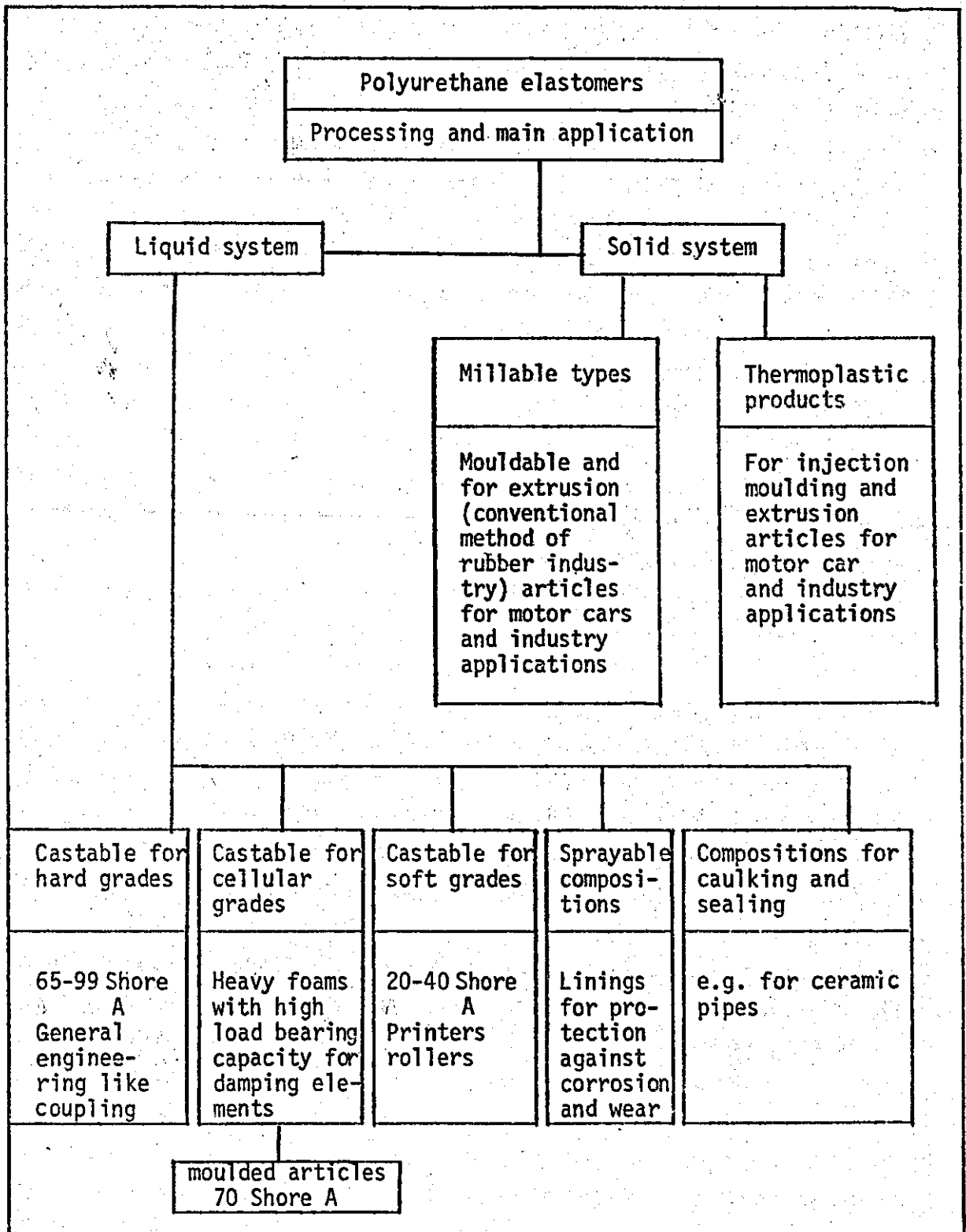
1A.6.3 Thermoplastic Polyurethanes

Thermoplastic polyurethane elastomers are a relatively recent development in the field of polyurethane technology. They are typically formed as the reaction product of a diisocyanate with a hydroxyl terminated

polyether or polyester polyol and a low molecular weight glycol chain extender. The NCO/OH ratio is kept at 1.0 so that no crosslinking between the chains occur or chain branching results. Thermoplastic polyurethanes are defined as materials having elastomeric properties at ambient temperatures but they are readily fabricated at elevated temperatures by such melt-processible techniques as injection moulding or extrusion which are characteristic of plastic materials. The outstanding characteristics of thermoplastic urethane are excellent abrasion resistance, high tensile strength and elongation with relatively low permanent set, high tear strength, low compression set, environmental and chemical resistance, flexibility at low temperatures and high load bearing capacity³⁹. Owing to their excellent mechanical strength and ease of processing thermoplastic polyurethanes have found widespread application in exterior automotive body parts, cable jacketing, industrial hose, tubing, gears, seals, belting, ski boots and wheels.

The following Table 1A.1 shows the variety of systems and applications of polyurethane elastomers.

TABLE 1A.1: The variety of systems and application of polyurethane elastomers



1B: GENERAL STRUCTURE-PROPERTY RELATIONSHIPS IN POLYURETHANE ELASTOMERS

1B.1 INTRODUCTION

Polyurethane elastomers are block copolymers with relatively inflexible regions containing short polyurethane segments interspread between long and flexible polyester or polyether sequences. The latter structures give the materials their elastic quality, while the former provide sites for inter-molecular ties through secondary bonding. It is these interactions which give these materials retention of useful moduli particularly at elevated temperatures due to their intermolecular hydrogen bonding properties. These different sequences are termed the hard and soft segments of polyurethanes with the flexible polyester or polyether regions being the soft segments.

Polyurethanes can contain a high concentration of polar groups, in particular the urethane groups resulting from isocyanate-hydroxyl reactions, as well as ester, urea and other groups. The interactions between these polar entities are of great importance in determining the properties of polyurethanes of all types, and especially the polyurethane block copolymers where local concentrations of polar groups occur together. Such strong polar interactions in polyurethane block copolymers can lead to a supra-molecular organisation resulting in aggregated structures, which may be in the form of glassy domains or crystallites. An empirical estimate of the energies of interactions between some common groups can be seen in Table 1B.1, and the high cohesion energy of the urethane group will be noted. The summed interactions between hard segments containing many urethane groups can be great enough to provide a pseudo crosslinked network structure between linear polyurethane chains by means of hydrogen bonding and dipole-dipole interactions, so that the polymer has the physical characteristics and mechanical behaviour at room temperature of a covalently cross-linked network.

TABLE 1B.1: Estimated Cohesion Energies of Common Groups in Urethane Elastomers

Group		Energy of Cohesion kJ.mole ⁻¹
Methylene	- CH ₂ -	2.85 2.8
Oxygen	- O -	4.18 4.2
Carbonyl	$\begin{array}{c} \text{O} \\ \parallel \\ - \text{C} - \end{array}$	11.10
Carboxyl	$\begin{array}{c} \text{O} \\ \parallel \\ - \text{C} - \text{O} - \end{array}$	12.10
Phenylene	- C ₆ H ₄ -	16.30
Urea	$\begin{array}{cc} \text{O} & \text{H} \\ \parallel & \\ - \text{C} & - \text{N} - \end{array}$	35.30
Urethane	$\begin{array}{ccc} & \text{O} & \text{H} \\ & \parallel & \\ - \text{O} & - \text{C} & - \text{N} - \end{array}$	36.60

The hard segments in polyurethane block copolymers particularly affect the physical properties i.e. modulus, hardness and tear strength, and determine the upper use temperature by their ability to remain associated at elevated temperatures. The flexible blocks primarily influence the elastic nature of the product and its low temperature performance, and they make important contributions towards the hardness, tear strength and modulus.

1B.2 MORPHOLOGICAL STRUCTURE IN POLYURETHANE ELASTOMERS

The morphology and properties of polyurethane block copolymers have been subjected to extensive investigations over the past decade⁴⁰⁻⁴⁵. Phase

separation of the urethane hard segments into microregions, termed domains, has been observed even when the segment length is relatively short. The primary drive force for domain formation is the strong intermolecular interaction between the urethane units which are usually aromatic and have the capability of forming interurethane hydrogen bonds. Additional factors which affect the degree of microphase separation are segment length, copolymer composition, crystallizability of either segment, and the method of sample fabrication. Hard segment domains can consist of semicrystalline or glassy segments. They are separated by a rubbery matrix which is rich in soft segment though this soft phase may contain some hard segments due to incomplete microphase separation. Typical structures which result from the hard and soft segment combination are shown in Figure 1B.1:

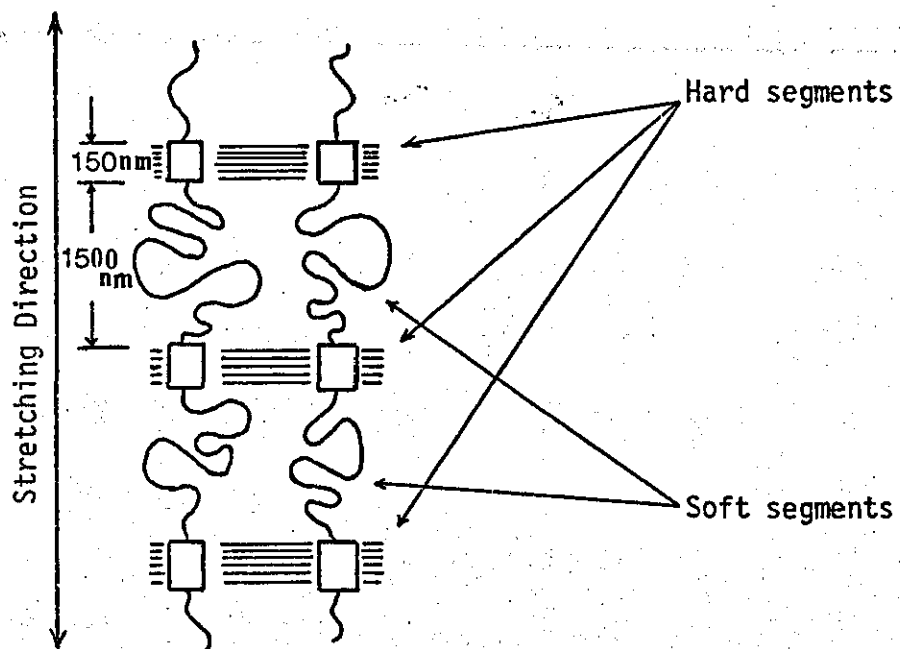


FIGURE 1B.1: Hard and Soft Segments in Polyurethane Elastomer

The structure and organisation of the hard segment blocks have most influence on the physical and mechanical properties. Clough and

Schnieder⁴⁰ have summarised the evidence indicating that in certain elastomeric systems the hard segments undergo phase separation into regions which are now termed domains. Work by Clough, Schneider and King⁴¹ using differential scanning calorimetry, thermomechanical analysis and small angle X-ray scattering provides further evidence for both crystalline and non-crystalline domains in various elastomers. Phase separation occurs to a larger extent in polyether based polyurethanes than in those with a polyester soft segment⁴⁰.

As previously described the urethane group is a highly polar group which is associated with a high energy of cohesion and is capable of forming hydrogen bonds. The extent and possible forms of hydrogen bonding is dependent on many factors including the electron donating ability, relative proportions and special arrangements of the proton-acceptor groups in the polymer chains. The groups which can function as proton-acceptors in the formation of hydrogen bonds are the carbonyl groups of the urethane and ester groups, and the ether oxygens⁵². Typical hydrogen bonding will take place at ester-urethane, ether-urethane, and urethane-urethane linkages as shown in Figure 1B.2.

Seymour et al⁴⁶ have concluded that essentially all the NH groups involved in hydrogen bonding in both polyether (PTMG) and polyester (PTMA) polyurethanes are derived from MDI and butane diol. It was estimated that about 60% of the NH groups in the polyether system were associated with the hard block urethane carbonyls (urethane-urethane hydrogen bonding). The rest being associated with the soft block ether oxygens (urethane-ether hydrogen bonding). Because of several unresolved peaks in the carbonyl region of the spectrum of the polyester polyurethane it was not possible to assess the relative contribution made to the hydrogen bonding in such systems by the two potential acceptors, ester and urethane carbonyl, Figure 1B.2. However the degree of phase separation would be expected to be less with the more polar polyester than polyether and this would give rise to a lower level of urethane-urethane bonding than the 60% observed with the polyether⁴⁸. The degree

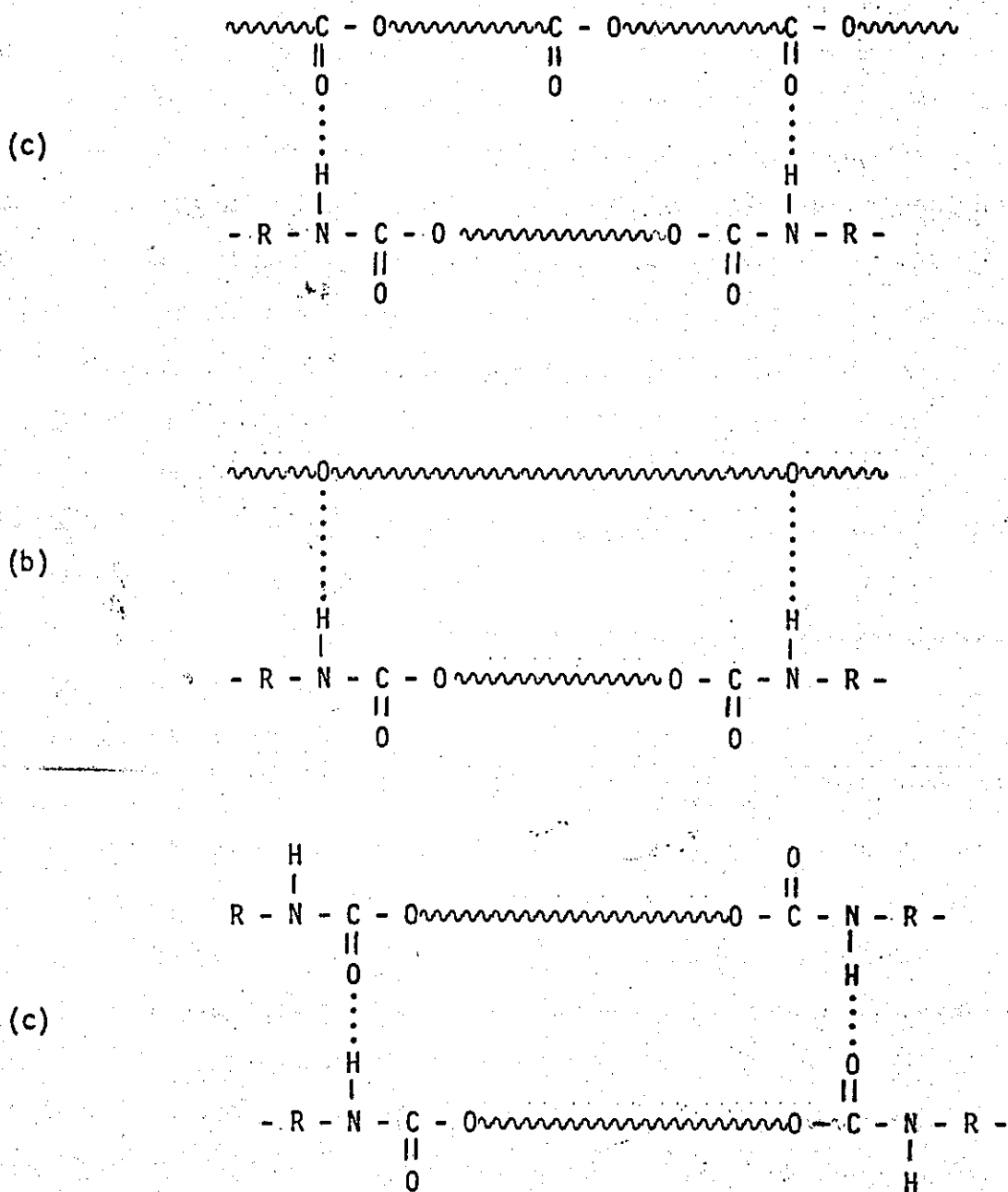


FIGURE 1B.2: Diagrammatic representation of hydrogen bonding:

- a) ester-urethane
- b) ether-urethane
- c) urethane-urethane.

to which the hydrogen bonding contributes to the physical properties of the polymer is uncertain. It is believed that hydrogen bonding decreases as temperature increases. However, it is observed that even at 200°C there is still some hydrogen bonding present⁴⁶.

Other similar studies on polyurethane⁴⁹ and poly(urethane-urea)⁵⁰ block copolymers support the view of incomplete segregation of the blocks. These general conclusions are further reinforced by many studies of the thermal and thermo-mechanical behaviour of polyurethane block copolymers⁵¹.

Thermal analysis techniques^{53,54} have been widely used to determine the extent of polymer chain interactions and phase separation in polyurethane elastomers. Among them differential scanning calorimetry (DSC) has been the most widely used technique, and generally the observed transitions fall into three main groups: low temperature transitions (below -30°C) associated with the glass transition temperature of the soft block; transitions in the region 80-150°C; and higher temperature transitions (above 160°C) associated with the thermal dissociation of the hard block aggregates which may be crystalline or paracrystalline.

The endotherms occurring in the region of 80°C are usually ascribed to the dissociation of the urethane soft block hydrogen bonds and those in the region of 150°C to the break-up of urethane hydrogen bonds^{40,54,55}. It was found by Seymour⁵⁶ that annealing history will cause some increase in soft segment transition temperature from 80°C to 150°C. At higher annealing temperatures this transition is itself moved and it eventually merges with the transition above 160°C associated with the break-up of the hard block aggregates. It is considered that the endotherms observed in the DSC traces can be attributed to the loss of long and short range order. Different degrees of short range order may exist simultaneously due to the distribution of hard block lengths. The short range ordering may be continuously improved by annealing as shown

by the merging of the endotherms. The thermal behaviour of the hydrogen bonds is insensitive to the degree of ordering present and is affected primarily by the T_g of the hard block. Hydrogen bond dissociation only occurs above the T_g of the hard block. For a pure MDI/butane diol homopolymer this T_g is known to be 109°C ⁵⁷, but because of the short block lengths in polyurethane copolymers it is usually somewhat lower than this (80°C for the samples examined by Seymour) and for a given chemical composition is very dependent on the hard block length.

Another feature of polyurethane elastomers which is worthy of mention, is elongation crystallisation. Segments that are essentially amorphous in the isotropic undeformed state may develop crystallinity, upon deformation (Figure 1B.3). This phenomenon is commonly referred to as "stress induced crystallisation" and its result is to produce excellent ultimate tensile strength properties. The fact that some polyurethanes e.g. those based on polycaprolactone exhibit high tensile strength and excellent wear and abrasion resistance, is attributed to the ability of the soft segments to stress crystallise. The phenomena can be usually observed when the polymer is elongated during tensile testing by the appearance of stress **whitening**.

The extension and subsequent relaxation processes in an elastomeric polyurethane block copolymer probably involves orientation and restructuring of the molecular organisation initially present⁵⁸. Upon a limited elongation, stress induced crystallisation of the soft segment may occur. In the case of polyether based elastomers, extension beyond approximately 150% gives rise to marked elongation crystallisation of the soft segments. Polyester based elastomers show a lower level of crystalline order, presumably due to the more irregular chemical structure present. In their case, as the elastomer is further elongated up to 500% extension, the orientation of soft segments improves only to a small extent (because of the crystalline force) while the hard segments turn themselves with their longitudinal axes into the direction of

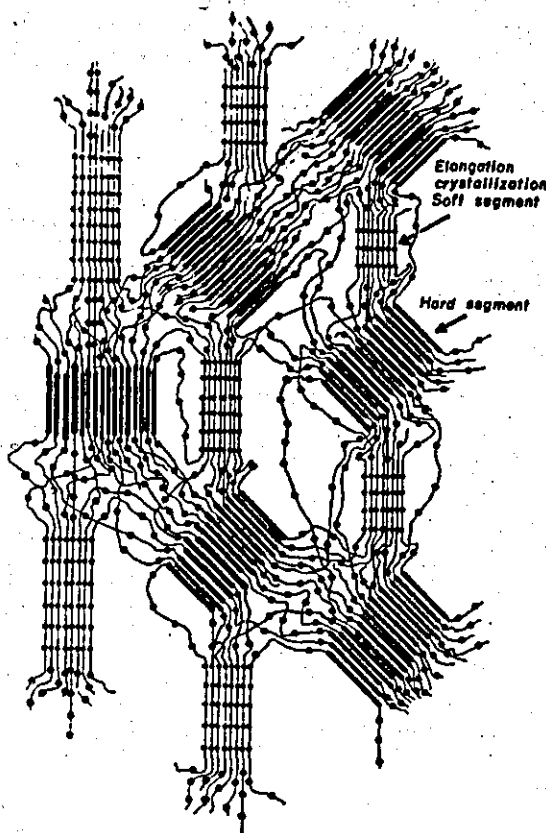


FIGURE 1B.3: Schematic drawing of the structure of a polyether polyurethane elastomer stretched to approximately 200%⁵⁸. The thick strokes represent hard segments and the thin strokes soft segments. Individual particularly strong stretched soft segments are considered to act as nuclei around which crystallisation can occur during elongation

elongation. This effect is explained in terms of force strands, i.e. maximally loaded chains in the soft segment which oppose any further extension. Further extension therefore requires sliding processes between hard segments to take place, resulting in the formation of new force strands. Continuation of this process will result in the restructuring of the hard blocks in new arrangements, a process which will be accelerated by heat treatment (Figure 1B.4).

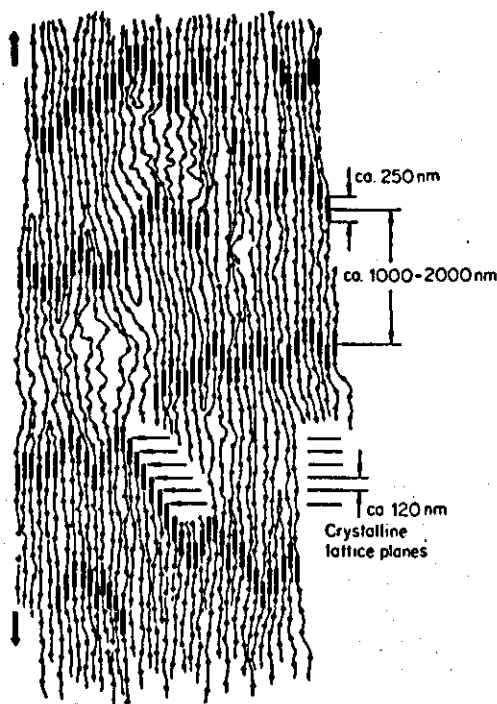


FIGURE 1B.4: Segmented polyurethane elastomer at 500% extension and placed in warm water at 80°C ⁵⁸

The phenomenon of microphase separation has been clearly demonstrated by electron microscope techniques where the presence of domains in polyester and polyether based elastomers is revealed by staining samples with iodine and observing darkened areas by transmission electron microscopy⁵⁹. The presence of a crystallisable segment in a segmented polyurethane elastomer system can lead to the development of large scale structures (termed 'superstructures'). Wilkes⁶⁰ et al have demonstrated this phenomenon in materials incapable of hydrogen bonding as well as hydrogen-bonded elastomers⁶¹. It appears that the superstructure entities (spherulites) contain preferentially orientated domains (Figure 1B.5). Spherulitic structure of the soft segment is readily apparent at high soft segment content, whereas at lower soft segment content, spherulites are formed by aggregation of hard segment domains. Slowikowska⁶² et al reported the formation of radial spherulites in polyurethane elastomer systems, and showed that increased degree of crosslinking in these systems impedes the ability to crystallise.

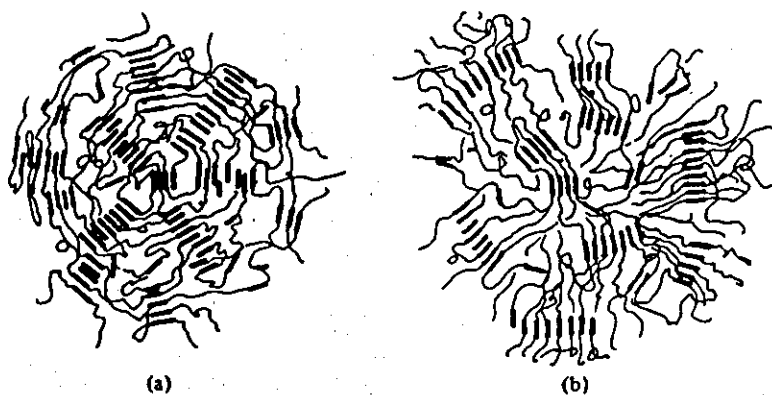


FIGURE 1B.5: Possible models of spherulitic structure⁶¹

The morphology and structure of polyurethane block copolymers has been reviewed in some detail⁶³ and present views can be summarised as follows:

1. Due to the dissimilar nature of hard and soft blocks which are partly incompatible with each other, the elastomers show a two phase morphology, although there is a significant level of mixing of the hard and soft blocks.
2. Hydrogen bonding can occur between hard and soft blocks, although its contribution to physical properties is not certain.
3. Hydrogen bonding occurs between individual hard blocks giving rise to a three-dimensional molecular domain structure (Figure 1B.6).
4. These domains may themselves be in a larger, ordered arrangement including both soft and hard blocks, the hard blocks being built up in a transverse orientation to their molecular axis leading, in cases, to the appearance of spherulites in the polymer.
5. The morphology is unstable with respect to temperature and is dependent on both the chemical constitution and thermal history of the polymer (Figure 1B.7).

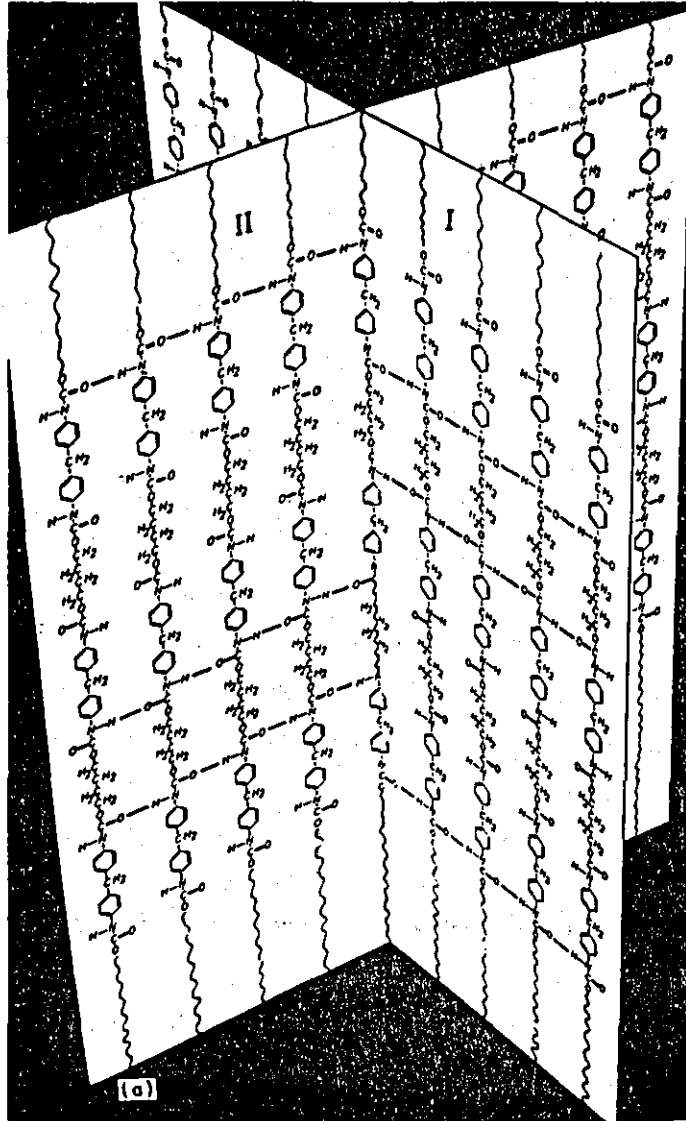


FIGURE 1B.6: Diagrammatic representation of the three-dimensional crosslinking structure (a) extended with butane diol⁶³

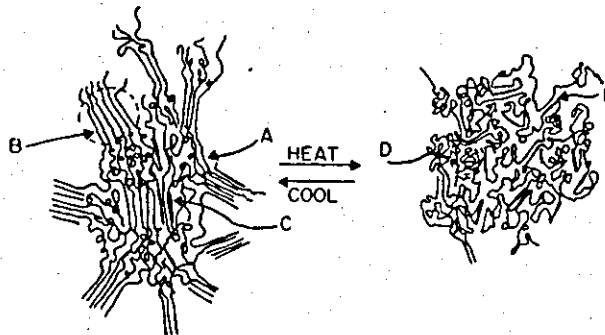


FIGURE 1B.7: Schematic model depicting the morphology before and after heat treatment⁶³

1B.3: STRUCTURE-PROPERTY CORRELATIONS IN SEGMENTED POLYURETHANE ELASTOMERS

The dependence of the structure-property relationship of polyurethane block copolymer elastomers on their chemical composition (nature of the polyether or polyester soft block, type of diisocyanate and chain extender, etc) and principal physical properties are now well recognised and have been extensively reviewed⁵¹. The physical and mechanical properties of segmented polyurethane elastomers can often be explained most easily in terms of morphological structure as described in the last section i.e. hard domains dispersed in a soft segment matrix. The soft matrix having a low T_g influences properties particularly at low temperatures. Hard segments in the domains, act as tie points as well as reinforcing filler and multifunctional cross-link, and govern the performance of the material at elevated temperature. The analogy between hard segment domains in polyurethane elastomers and reinforcing fillers in conventional rubbers, provides a useful means of interpreting structure-property relationships in segmented polyurethane elastomers. It is now generally recognised that thermoplastic elastomers based on certain block copolymers derive their excellent physical properties from their domain structures. For example, in such polymers as SBS poly(styrene_n-butadiene_m-styrene_n) and SIS poly(styrene_n-isoprene_m-styrene_n) incompatibility of the two different blocks results in rigid segment segregation of the styrene segments and thus in the formation of discrete glassy polystyrene domains embedded in a continuous soft segment matrix which is rubbery at room temperature. These structures are very similar to those observed in segment polyurethanes and it is, therefore, not surprising that their structure-properties relationship is based on the same principles. Like SBS or SIS structures, segmented polyurethanes have been shown to exhibit micro-phase separation whereby the rigid segment aggregates are embedded in the soft segment matrix. Direct comparisons of domain structure reinforcement in phase separated elastomeric block copolymers and filler reinforcement in conventional rubbers have been made by Bishop⁶⁴ et al. They showed that the reinforcement activity of a polystyrene domain is comparable to (i)

comparable to that of a good reinforcing carbon black (e.g. HAF black). Increased proportion of hard segment in segmented polyurethane elastomers is known to give materials of higher modulus⁶⁵, an effect also observed on increasing the filler content of conventional rubbers.

The phenomenon of stress softening on repeated extension is demonstrated in segmented polyurethane elastomers⁶⁶ and has been attributed to disruption of domain structure, leading to a decrease in the number of effective crosslinking sites^{67,68}. Smith⁶⁹ et al have demonstrated that at a given strain level, the stress in phase separated elastomeric block copolymers decreases as the temperature is raised, due to melting or softening of domain structures, which therefore become ineffective as tie points and filler particles. Introduction of chemical crosslinking, particularly between hard segments, has been shown to lead to less aggregation of hard segments into domains⁷⁰, resulting in decrease of physical properties, particularly a lowering of modulus (reflecting the reduced filler reinforcement effect).

Factors which contribute to strength and toughness in polyurethane elastomers lay particular emphasis on the role of the dispersed phase, and it should be noted that, as a general rule, for an elastomer to retain strength over an extended range of temperatures, presence of a dispersed phase is necessary. Such a dispersed phase may consist of high-temperature melting crystalline entities, finely dispersed filler particles, or rigid segmented domain structures such as exist in polyurethane elastomers. It is important to note that maximum physical properties are obtained in such polyurethane elastomer if a high degree of perfection of microphase separation exists.

The chemical structure present in a segmented polyurethane elastomer system can be varied in several distinct ways:

1. Variation of the chemical structure of the soft segment;
2. Variation of the chemical structure of the hard segment;
3. Variation of the relative sizes of the hard and soft segments;
4. Variation of the degree and type of covalent crosslinking.

From the above discussion, it is quite clear that selection of reactants, their ratio and controlled manner of introduction will control the structure of polyurethane elastomers. The effect of reactants, segment size, and crosslinking on properties of polyurethanes is discussed in the following section.

1B.3.1 Effect of Soft Segment Structure

The soft segments in polyurethane elastomers greatly influence the elastic nature of the material and also, its low temperature properties. There are two major classes of polyols used in polyurethane synthesis:

1. Polyether - linear polyether with or without pendant chain;
2. Polyester - linear polyester with or without pendant chain.

These aliphatic polyols have low glass transition temperatures (below room temperature) and are generally amorphous or have low melting points. Selection of polyol depends on the requirement of the physical property of products. Polyethers generally give elastomers having a lower level of physical properties than the polyester based materials due to the weaker interchain attraction. Many polyether or polyester materials crystallise on extension due to their structural regularity and this is thought to be an important factor contributing to their high tensile strengths. The higher elongation at break shown by the polyether material can also be explained by the weaker interchain attractive forces present, allowing increased chain slippage and disentanglement. Low molecular weight polyols or short sequence lengths of soft segments tend to increase the concentration of urethane

groups and consequently polyurethanes with a greater degree of physical bonding and high mechanical properties will be obtained. Introduction of a pendant group onto the polyol chain, causes increase in chain separation, reduces interchain packing and finally results in inferior physical strength property.

Polyethers generally have better low temperature properties than polyesters due to low glass transition temperatures⁵¹. Polyether based materials also show far superior hydrolytic stability⁷¹ as shown by the following values (Table 1B.2), because the ether groups are more resistant to hydrolytic attack than the ester groups.

TABLE 1B.2: Effect of polyol on hydrolysis properties of polyurethane

Polyol		Type	% Tensile Strength* Retained on Hydrolysis
Polyethylene adipate glycol	PEA	Polyester	40
Polyhexamethylene adipate glycol	PHA	Polyester	30
Poly-oxytetramethylene glycol	POTM	Polyether	88
Poly-oxypropylene glycol	POP	Polyether	88

*21 days in water at 70°C

The effects of polyol type and urethane-urea components have been discussed by Ferrari⁷². A summary of his results is given in the following Table 1B.3.

TABLE 1B.3: Effect of polyether and polyester on properties of urethane elastomer - a comparison

Type	I	II	III	IV
Cost	2	2	2	1
Processing ease	2	2	1	1
Toughness	1	1	2	3
Abrasion resistance	1	1	2	3
Solvent resistance	1	2	3	3
Heat and oxidative resistance	1	1	2	3
Brittle point	3	1	1	3
Resilience	3	2	1	3
Heat build-up	3	2	1	1-2
Humidity resistance	3	3	2	2

Key: 1 is very good
2 is good
3 is fair or poor

I is polyethylene adipate
II is mixed-glycol adipate
III is polytetramethyleneether glycol
IV is polyoxypropylene glycol

Variation of polyester structure⁷³ has much the same effect on properties as was shown for polyethers, i.e. the general effect of side groups is to prevent or hinder crystallisation on extension and to decrease inter-chain attractive forces, resulting in lower tensile strength and modulus. Decreased ester group content and the presence of pendant groups on the polyester backbone cause a decrease in tear strength. Permanent set has been shown to increase with increasing ester group content⁷⁴. This has been explained by the presence of residual polyester crystallinity on relaxation. The undesirable tendency of some polyesters to crystallise and produce cold hardening in polyurethane elastomers can be avoided by the use of copolyesters which possess structural irregularity.

The molecular weight of the soft segment has a marked influence over the final elastomer properties. In a study of polycaprolactone based elastomers, Seefried⁷⁵ et al showed that the Tg of the soft segment shifted to higher temperatures as the molecular weight of the polycaprolactone decreased. This is indicative of the restriction on the mobility of the soft segment by the rigid hard segments as the compatibility increases at the lower molecular weights (Table 1B.4). Very low molecular weight of soft segment (below 600) gives poorly elastic, hard materials, whereas high molecular weights give soft materials having poor physical properties.

TABLE 1B.4: Effect of molecular weight of polycaprolactone on the Tg of polyurethanes

MW	340	530	830	1250	2100	3130
Tg °C	53	25	-10	-27	-40	-45

The polymer used was based on polycaprolactone/MDI/1,4-BD with molar ratio 1/2/1.

1B.3.2 Effect of Hard Segment Structure

As mentioned earlier, hard segments in elastomeric polyurethanes are usually formed by the reaction of a diisocyanate with a diol or diamine chain extender to give a rigid polyurethane or polyurea, structure. The properties of the hard segments determine the interchain interactions in the elastomers to a large extent, due to the high concentration of polar groups and so determine the network 'structure' in these materials. Hard segments significantly affect mechanical properties, particularly modulus, hardness and tear strength. The performance of elastomers at elevated temperatures is very much dependent on the structure of the hard segment and its ability to remain associated at

these temperatures. In this section, the influence of individual hard segment components i.e. diisocyanates and chain extenders on the general mechanical properties of polyurethane elastomers will be considered respectively.

1B.3.2.1 Effect of Diisocyanates

The diisocyanate component can exert a significant influence on polyurethane elastomer properties. The effect of the diisocyanate structure on the physical properties of these materials has been investigated by several workers^{7,71,73,75a}. Polyurethanes having the highest levels of modulus, tear and tensile strengths are obtained by the use of the most rigid, bulky and symmetrical diisocyanate. Table 1B.5 illustrates this general relationship⁷³.

TABLE 1B.5: Effect of diisocyanate structure on physical properties of segmented polyurethane elastomers

Diisocyanate	Tensile Strength (MPa)	Elongation at Break %	Tear Strength (kN/m)	300% Modulus (MPa)	Hardness (Shore A)
p-phenylene diisocyanate (PPDI)	44.1	600	52.5	115.8	72
1,5-naphthalene diisocyanate (NDI)	29.4	500	35.3	20.6	80
Mixed isomer of toluene diisocyanate (2,4- and 2,6-TDI)	31.4	600	26.5	2.5	40
4,4'-diphenyl methane diisocyanate (MDI)	54.4	600	47.1	11.0	61

The data of Table 1B.5 shows that the bulky 1,5-NDI yields a polyurethane with higher modulus and hardness than the single aromatic ring PPDI and the more flexible MDI molecules. Asymmetrical molecules, as represented

by the 2,4/2,6-TDI combination, give elastomers of low modulus and hardness. Tensile strength and tear strength are also shown to be greater in the case of symmetrical molecules, particularly those based on the 1,4-substituted benzene ring system (PPDI and MDI).

The diisocyanate **blocks** in polyurethane elastomers apparently influence the ability of the polymer chains to align themselves and will clearly affect the development of interchain structure by hydrogen bonding. The low temperature properties of polyurethane elastomers are, however, only moderately affected by the diisocyanate used⁷³. The effect of different diisocyanates on the Tg of poly(ethylene adipate) and butane diol based elastomers has been reported by Aitken and Jeffs⁷⁶ (Table 1B.6). The isocyanates used were MDI, TDI (mixed 2,4 and 2,6 isomers), HDI, H₁₂MDI and IPDI.

TABLE 1B.6: Effect of different diisocyanates on Tg of the polyurethane elastomer

Diisocyanate	TDI	HDI	H ₁₂ MDI	IPDI	MDI
Tg °C	-16	-42	-39	-32 to -35	-31

The PU polymer was based on polyethylene adipate (MW = 2000)/diisocyanate/1,4-BD with molar ratio 1/4/3.

The Tg of the TDI based system (-16°C) was higher than the MDI based system (-31°C), indicative of reduced phase separation in the TDI based system. However, the Tgs of the aliphatic diisocyanate based systems were lower than the MDI, suggesting increased phase separation and this was attributed to the stronger hydrogen bonding in the hard segment domain with aliphatic diisocyanates.

1B.3.2.2 Effect of Chain Extenders

Chain extenders most commonly employed in polyurethane elastomers are diols and diamines. Diols give elastomers having polyurethane hard segments, whereas diamines form polyurea hard segments. This fundamental structural difference between diol and diamine extended materials generally leads to differences in physical properties between the two classes. When a diamine is employed as chain extender a higher level of physical properties often results than if a diol were used, probably due to introduction of urea linkages which enter into strong hydrogen-bonded interactions. A diamine is usually chosen as the chain extender when a relatively unsymmetrical diisocyanate (e.g. 2,4-TDI) is employed in a polyurethane elastomer system. Strong intermolecular attractive forces between urea groups compensate for structural irregularities due to the diisocyanate. The effect of diamine structure on properties of a polyoxytetramethylene diol/TDI elastomer system was investigated by Samson and Blaich⁷⁷. The reported data are given in the Table 1B.7.

Many diamines are too reactive for use as chain extenders in the preparation of bulk elastomers, as insufficient time is available for adequate mixing and pouring before gelation occurs. The most commonly used diamine chain extender in commercial elastomer systems is MOCA, which combines a practical reactivity rate with a high level of physical properties in the final elastomer. A major disadvantage in the use of aromatic diamines is the suspected carcinogenic activity associated with many of these materials, particularly 4,4'-diamino biphenyl (benzidine) and its derivatives, although giving elastomers having excellent physical properties.

Diols are often preferred as chain extenders in systems based on symmetrical diisocyanate (e.g. MDI), where intermolecular attraction forces are favoured. The effect of different glycol chain extenders on physical properties of polyurethane elastomers is given in Table 1B.8,

TABLE 1B.7: Effect of diamine structure on physical properties of polyurethane elastomers*

Diamine	Tensile Strength (MPa)	100% Modulus (MPa)	300% Modulus (MPa)	Elongation at Break (%)	Grave treat (kN/m)	Hardness Shore A
3,3'-dichloro-4,4'-diamino-diphenylmethane (MOCA)	34.5	6.4	14.5	450	83.4	91
4,4'-diaminodiphenylmethane	30.5	7.9	14.1	520	94.2	86
1,4-diaminobenzene	16.0	10.8	16.0	300	112.8	91
3,3'-dimethoxy-4,4'-diaminobiphenyl	17.0	5.1	7.6	550	72.6	93
3,3'-dimethyl-4,4'-diaminobiphenyl	48.3	12.7	21.6	550	118.7	95
4,4'-diaminobiphenyl	29.9	8.2	16.1	470	99.1	86
3,3'-dichloro-4,4'-diaminobiphenyl	37.6	11.7	28.1	390	109.9	94

* Prepared from Adiprene L100 (a polyether/TDI prepolymer by Du Pont) and ca 85% of the theoretical diamine based on NCO content.

TABLE 1B.8: Effect of diol structure on physical properties of polyurethane elastomers

Diol	Tensile Strength (MPa)	300% Modulus (MPa)	Elongation at Break (%)	Hardness Shore A
Ethylene glycol	44.8	13.8	500	61
1,3-propane diol	45.5	6.6	600	61
1,4-butane diol	54.5	6.9	600	61
1,5-pentane diol	49.0	6.2	600	62
1,6-hexane diol	51.0	5.9	500	60

which compares the physical properties of chain extended polyethylene adipate/MDI prepolymer with a homologous series of diols⁷⁵.

The high modulus of the ethylene glycol extended material is thought to be due to the presence of the $-(CH_2)_2$ group in both the hard and soft blocks, allowing increased structural regularity. A similar effect is pointed out by Schollenberger⁷¹ in the case of a polytetramethylene/MDI material extended with 1,4-butane diol. In the case of diol extended materials a significant proportion of crosslinking is often introduced by the use of a triol such as trimethylol propane (TMP).

1B.3.3 Effect of Segment Size

Several investigations have been made into the effect of varying the size of hard and soft segments in polyurethane elastomers. In an attempt to investigate the effect of segment size and polydispersity on hard segment crystallinity and material properties, Ng et al⁷⁸ conducted a thorough characterisation of piperazine/BD/PTMO-based polyurethanes which possessed a well-defined segment molecular weight and molecular weight distribution and no possibility for intermolecular hydrogen bonding. They found that copolymers with a narrow hard segment length distribution exhibited better microphase separation, higher modulus, and higher elongation at break than equivalent materials containing polydispersed hard segments. Harrell⁷⁹ reported that a hard segment consisting of two piperazine units extended by BD exhibited a sharp and distinct melting point at about 50°C. The melting point of the family of piperazine-based polyurethanes increased as the hard segment length increased. In a POP/TDI/MOCA-based polyurethane⁸⁰, increased molecular weight of the polyether soft segment is found to give a decrease in tensile strength, modulus, hardness and tear strength, but increased abrasion resistance. In a water extended poly(ethylene-co-propylene adipate)/MDI system increased polyester molecular weight is accompanied by a decrease in modulus⁸¹. The effect of urethane

concentration on properties of polyurethane elastomers has been studied by Smith and Magnusson^{82,83}. They showed that the increase in T_g with increasing urethane concentration for polyoxypropylene diol based elastomers, gives rise to an increase in tensile strength, measured at ambient temperature. The effect of variation in polyurethane concentration on tensile strength in a system based on POP/TDI gives increased tensile strength, a correlation which is not found between degree of crosslinking and tensile strength. Tear strength was found to increase to a maximum and then decrease with further increase in urethane concentration into a polyester/MDI system extended with 1,4-butane diol⁸⁴, presumably due to the disruptive effect of excessive bulky MDI groups. These results indicate the general increase in strength properties (tensile strength, modulus, hardness, tear strength) associated with increased urethane concentration in polyurethane elastomers.

1B.3.4 Effect of Crosslinking

The crosslinking of polymer chains is of primary importance in controlling many polymer properties. Large increases in the degree of crosslinking make amorphous polymers more rigid and cause them to have higher softening points and higher modulus, reduce elongation and swelling by solvents, and raise the glass transition temperatures. Chemical crosslinking in segmented polyurethane elastomers can be produced by the following ways:

1. The use of an excess of the diisocyanate which can react with chain backbone urethane or urea linkages to give allophanate, biuret and isocyanurate groups.
2. The use of a branched polyether or polyester having hydroxyl functionality greater than two.

3. The incorporation of a low molecular weight triol in the reactions, e.g. trimethylolpropane (TMP).

Pigott et al⁷³ investigated the effect of chemical crosslinking on properties in a polyethylene adipate/MDI/1,4-BDO based polyurethane elastomer. The extent of crosslinking was increased by using varying amounts of TMP combined with 1,4-BDO chain extender. Results showed that increased degree of crosslinking in this system is accompanied by a decrease in tensile strength, elongation at break, modulus, hardness and tear strength. Modulus and tensile strength were found to decrease to a minimum and then increase (sharply in the case of modulus) at very high degrees of crosslinking. Volume swelling of elastomers in dimethyl acetamide decreased as expected with increasing degree of crosslinking.

Smith and Magnusson⁸² investigated the effect of crosslinking on T_g in a series of POP/TDI/TMP-based elastomers. They found no significant effect on T_g as the degree of crosslinking increased. Tensile strength was found to vary only slightly, whereas the modulus increased and the elongation at break decreased. Polyether based elastomers extended with diols also have been found to show increased hardness and modulus with increased degree of crosslinking⁷³.

From the above considerations, it is seen that elastomers having strong secondary interactions (e.g. polyester based materials), tend to suffer a general decrease in physical properties as the extent of crosslinking increases, whereas elastomers which have relatively weak secondary interchain interactions (e.g. polyether based materials), show a general increase in physical properties with increasing crosslink density. This is due largely to the influence of non-covalent intermolecular attractive forces such as hydrogen bonding, which lose their effectiveness as increased chemical crosslinking causes increased chain separation in the linear polymer. Havlik and Smith⁸⁵ demonstrated the

importance of these non-covalent interactions in a soluble polyurethane elastomer based on polyoxypropylene diol/2,4-TDI extended with 2,4-toluene diamine. This material showed a high modulus compared with a chemically crosslinked elastomer based on the same system. This effect has been explained by the disruption of non-covalent intermolecular forces by the introduction of chemical crosslinks which cause spatial separation of polymer chains.

Sasaki et al⁸⁶ have investigated the effect of isocyanurate crosslinks in a polyoxypropylene diol based elastomer. Modulus was found to increase linearly with crosslink density, and it was suggested that this effect was due to formation of isocyanurate rings into rigid domain aggregations.

In addition to the items already mentioned, peroxides and sulphur are also used as methods of crosslinking specialised types of polyurethane elastomers.

The presence of $-C=C-$ groups as a pendant group to the main chain structure of PU elastomers provide sites for conventional sulphur crosslinking to occur. Sulphur is combined in the vulcanisation network in a number of ways. As crosslinks, it may be present as monosulphide, disulphide, polysulphide, pendant sulphide, cyclic monosulphide and cyclic disulphide¹⁵⁸.

Peroxide curing is a universal method of crosslinking all elastomers and is applicable to the millable urethane grades which do not need the unsaturated groups added which are essential in the sulphur curing process and hence both saturated and unsaturated millable urethane types can utilise peroxide curing. The reaction mechanism is essentially free radical in type giving rise to short length, thermally stable, carbon-carbon crosslinks between the high molecule chains¹⁵⁹.

Some commercially available millable polyurethane elastomers are given in Table 1B.9. The millable crosslinkable urethane rubber listed in Table 1B.9 can be modified with a variety of compounding ingredients such as fillers and plasticisers to meet specific processing and end-use requirements, just as with other rubbers.

TABLE 1B.9: Some typical millable polyurethane elastomers

Trade Name of Series	Supplier
Millathane Urepan Adiprene Vibrathane	TSE (USA) Notedone Ltd (UK) Bayer Uniroyal Uniroyal

1C: THERMAL STABILITY OF POLYMERS

The present section contains first a brief general discussion on the thermal stability of polymers, and this is followed by a review of the effect of different chemical structures and crosslinking on the thermal stability of polyurethanes. The final part outlines the objective of the research as related to the relationships discussed.

1C.1 INTRODUCTION

One of the newest speciality areas within polymer science is that of high temperature or thermally stable materials. It has been recognised as a separate area within polymer chemistry for nearly 25 years.

Polymers, during their normal service life, are frequently exposed to a variety of deteriorating influences such as heat, oxidative attack and solvolytic degradation. The stability of a material to those destructive forces can be interpreted in the retention of a given set of mechanical properties under specified test conditions, or in the capability of the polymer to retain its chemical structure under severe conditions over extended periods of time.

Thermal stability of a polymeric material is normally expressed in terms of a specific temperature or temperature-time limit within which the polymer can be used without excessive loss of properties. There are two fundamentally different mechanisms of property loss⁸⁷:

1. Physical or reversible changes;
2. Chemical or irreversible processes.

The physical changes, consisting specifically of glass transition, melting or crystallisation phenomena and changes in polymer morphology are self-evident controlling the performance of thermoplastic materials which ordinarily melt and become useless before finally decomposing.

These changes are primarily temperature dependent, for example the thermal instability of polystyrene occurs between 70-110°C, the limitation of its use therefore is totally determined by softening before decomposition occurs.

Irreversible changes are of importance in the determination of the high temperature endurance of thermosets and crosslinked polymers, as well as in those linear materials in which melting does not take place before scission of primary bonds has occurred to a considerable degree. These processes are both temperature and time dependent and stability is therefore generally expressed in terms of rates of decomposition (or property loss) at a given temperature. Since chemical bond breaking and bond formation play dominant roles in this type of degradation, it is extremely sensitive to environmental conditions. As an example, decomposition in vacuum or in an inert atmosphere will be different from degradation in oxidising mediums, and a polymer will behave differently if heated in a closed system where the degradation products can take part in secondary reactions rather than in an open system which provides for continuous removal of in situ formed volatile compounds. Irregularities in the polymer structure, branching, chain ends, peroxides, impurities or abstractable hydrogen as well as neighbouring group effects leading to the formation of transition states with low activation energies nearly always cause breakage of polymer chains at considerably lower temperature than theoretical considerations would predict.

Both oxidative and solvolytic stability of polymers have been a matter of great concern in many of their applications. Attack by oxygen is one of the most important deteriorating influences a polymer may have to endure. Polymers containing ester, amide, urethane or urea groups are sensitive to hydrolytic cleavage. Both acidic and basic contaminations are catalysts for this type of breakdown and their presence generally reduces polymer stability markedly.

The requirements for use of a polymer at high temperatures may be very simply stated⁸⁸:

1. Retention of mechanical properties, high (melting) softening point.
2. High resistance to thermal breakdown.
3. High resistance to chemical attack, i.e. oxidative, hydrolysis.

The softening point can be raised by increasing the intermolecular forces between chains. This can be done by incorporating polar side groups, by increasing the opportunities for hydrogen bonding, and by actual chemical crosslinking of the chains. Other methods are to increase the regularity of the chain with possible consequent increase in the degree of crystallinity by incorporation of bulky cyclic groups, especially para-linked, in the main backbone⁸⁹.

Simple thermal stability is influenced by the strength of chemical bonds and it is axiomatic that combination of atoms with known weak bond strengths should not be used. Perhaps the most useful data guiding the search for heat resistant polymers has come from the study of the thermal stabilities and mechanisms of thermal breakdown of sets of polymers of closely related structures. Considering the total data the following generalisations can be made⁸⁸:

To attain high thermal stability:

- a) only the strongest chemical bonds should be used;
- b) the structure should allow no easy paths for rearrangement reactions;
- c) there should be a maximum use of resonance stabilisation;
- d) all ring structures should have normal bond angles;
- e) polybonding should be utilised as much as possible.

1C.2. THERMAL STABILITY OF POLYURETHANES

Polyurethanes are an extremely complex class of polymers. This is not only because of the enormous structural diversity in the isocyanate and glycol portions of the polymers but also because of the presence, in many of the commercially most important polymers, of a variety of chemical entities, other than urethanes. Notable among these entities are isocyanate-derived groups: urea, isocyanurate, allophanate, biuret, uretidion and carbodiimide which can form in varying amounts during polyurethane preparation, as well as the two linkages most commonly present in urethane polymers which are not isocyanate-derived: the ester and the ether bond.

A number of reviews, describing the thermal stability of specific classes of polyurethanes, have been published in the technical literature⁹⁰⁻⁹³. The relative thermal stability of polymer model compounds was investigated by Sheehan et al⁹⁴. They demonstrated that S-triazine derivatives are thermally stable compounds.

Backus et al⁹³ investigated the flammability and thermal stability of isocyanate-based polymers in a series of model polyurethanes and polyureas by reacting 4,4'-diphenyl-methane diisocyanate or polyisocyanates having similar polybenzyl structures with aliphatic or aromatic coreactants. Flame resistant polymers were prepared by use of structural elements which were thermally stable and non-volatile or which formed non-flammable decomposition products. The main factors determining the thermal stability of polyurethanes are the nature of the starting material and the conditions of polymer preparation.

1C.3. EFFECT OF CHEMICAL STRUCTURE

As mentioned above, the thermal stability of polyurethanes depends on the chemical composition of the materials used in polyurethane formulations. This is true not only for thermal stability in the physical meaning of the term, i.e. the stability that is reflected in such

reversible changes as melting or softening, but also in the chemical stability that is connected with the dissociation of urethane linkages and which commonly takes place in the range of 200-250°C⁹⁵. To a certain degree the nature of the soft segment (ether or ester groups) also affects the chemical stability of these polymers.

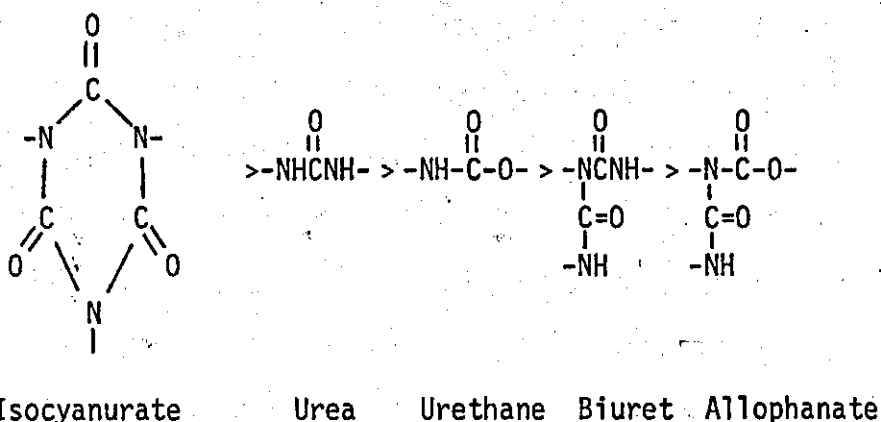
The melting point of linear polyurethanes can, in some cases, exceed 200°C. It depends not only on the nature and molar ratios of the components, but also on the way in which the synthesis is carried out since the existence and magnitude of microcrystalline domains formed by hard segments is influenced by the synthesis conditions⁹⁶. The dependence of thermal stability of poly(ester-urethane) elastomers on their composition was investigated by Masiulanis⁹⁷. He reported that for polyurethanes of hard segment content above 30%, the best choice of chain extender was hydroquinone di(β -hydroxy-ethyl)ether (HQEE) where good thermomechanical stability is needed; he also found that the stability of bisphenol-A-based PU polymers is rather poor. He also demonstrated that the thermal stability of 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI)-based polyurethanes is inferior to the ones derived from 4,4'-diphenyl-methane diisocyanate (MDI)-derived polymers.

Increase in crosslink density, type of crosslinking and introduction of isocyanurate ring structures in the polymer chain backbone also has a strong beneficial effect on the thermal stability of polyurethanes. The selection of the diisocyanate also has a distinct influence on the thermal stability of the polyurethanes. Some of the parameters to be considered if attempting to prepare polyurethanes with optimum thermoresistance can be listed as follows:

1. Choice of diisocyanate
2. Choice of hydroxyl component
 - a) polyester
 - b) polyether
 - c) chain extender

3. Type and density of crosslinks
4. Introduction of thermally stable (non-urethane) linkages.

The isocyanate derivatives most frequently encountered in urethane polymers can be arranged in the following order of decreasing thermo-stability:



Maximum thermal stability—Decreasing→ Minimum thermal stability

1C.3.1 Effect of Hard Segment

It was recognised previously that the retention of properties at elevated temperatures was aided by chemical crosslinking, by intermolecular attractions and the presence of hard segments in the chain¹⁹.

While the crosslinks could be in either the hard or soft segments of the block copolymers, the intermolecular attraction and hard segments would be operative primarily in the hard block. Thus, whereas the soft segment would control low temperature flexibility to a large extent, the structure of the hard segment would be expected to exert a strong influence on the high temperature properties.

The hard segments may be designed to form crystallites, especially when the polymer is elongated, serving as physical crosslinks. The strength

of the crystallite (i.e. its melting point and resistance to stress) will be expected to increase with increased length, symmetry and "fit" of the hard segments, as well as the intermolecular attractions between segments. Thus symmetrical diisocyanates and unbranched glycols may be preferred for this segment. In research directed largely towards spandex type urethane elastomers, but applicable to many others, Britain investigated the symmetry of an aromatic polyurethane hard segment, and its effect on temperature resistance⁹⁸. Data in Table 1C.1 clearly show the improvement of temperature resistance as the symmetry of the hard segment is improved by increasing the isomeric purity of MDI.

TABLE 1C.1: The effect of hard segment symmetry on the temperature resistance of polyester-MDI-butanediol elastomers

2,4' isomer in MDI, %	Heat Distortion Temp, °C
15	126
10.8	131
5.4	139
0	148

As mentioned before, one of the main factors determining the thermal stability of polyurethanes is the nature of the starting materials. Table 1C.2 can be used as a guide to show the effect of chemical structure of some starting material on urethane thermal stability⁶.

Aliphatic isocyanates, give urethanes with higher thermal stability. Accordingly the dissociation temperatures of bisphenylcarbamates of the three commercially important diisocyanates 2,4-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI) and hexamethylene diisocyanate (HDI) increase in the order⁹⁵:

(lowest thermal stability) TDI < MDI < HDI (highest thermal stability)

TABLE 1C.2: The influence of the type of urethane group on heat stability

Type of Urethane Group	Approximate maximum temperature of stability (°C)
n-Alkyl-NH-COO-n-Alkyl	250
Aryl -NH-COO-n-Alkyl	200
n-Alkyl-NH-COO- Aryl	180
Aryl -NH-COO- Aryl	120

By DTA study of thermal stability of model urethane compounds in argon, (Table 1C.3), it is shown that thermal decomposition does not take place below 166°C. The influence of alicyclic isocyanate structure and aliphatic chain extender can also be notified⁹⁵.

As a general rule, the stability of N-substituted carbamates increases with decreasing reactivity of the parent isocyanate. Thus urethanes (A) in the following series were found to be increasingly thermostable⁹⁹:

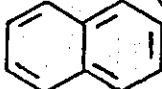
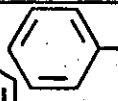
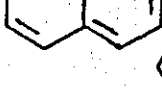
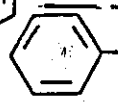

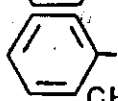

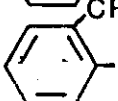

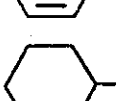
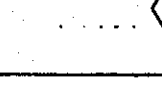
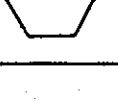


(lowest thermal stability) R = chlorosulfonyl < p-nitrophenyl < phenyl < benzyl < n-alkyl < cyclohexyl < tertiary butyl (highest thermal stability)

The stability of urethanes (A) depends on the type of hydroxyl compound used in their preparation and generally decreases in the order:

(highest thermal stability) R' = primary alkyl > secondary alkyl > tertiary alkyl (lowest thermal stability)

TABLE 1C.3: Thermal stability of model urethanes in argon

RNHCOOR'		T(°C)*
R	R'	
 	n-but	235
 	n-but	245
 	s-but	200
 	t-but	166
 	t-but	170
 	t-but	180

*Point of first deflection of DTA trace from baseline.

Matuszak and Frisch¹⁰⁰ investigated the thermal degradation of model biscarbamates, polyurethanes and poly(urethane-ureas) by pyrolysis at atmospheric pressure. The biscarbamates were prepared from phenyl, benzyl and cyclohexyl isocyanate and ethylene glycol. The polyurethanes and poly(urethane ureas) were prepared from toluene diisocyanate (TDI), xylylene diisocyanate (XDI), and 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI) and polyoxyethylene glycol of various molecular weights. Rate constants for thermal degradation were obtained by measuring carbon dioxide evolution. The thermal degradation of all materials showed that the stability increased in the following manner:

(lowest
thermal
stability)

aromatic < aralkyl < cycloaliphatic

(highest
thermal
stability)

1C.3.2 Effect of Polyols

Polyether and polyester polyols are two of the most frequently utilised building blocks in polyurethanes. Polyesters exhibit considerably higher thermal stability than polyethers and have generally been found to be quite resistant to oxidation under relatively mild conditions¹⁰¹.

The superiority in thermooxidative stability of polyesters over poly ether is also demonstrated by the stress relaxation data obtained in air and nitrogen^{102,103}, Figure 1C.1. The flat, nearly identical intermittent stress relaxation curves obtained ^{from} polyester urethanes in air and in nitrogen indicate that any chain-breaking processes taking place under these conditions are reversible and non-oxidative. In polyethers on the other hand, the fast irreversible stress decay which occurs in air (but not in nitrogen) characterises the chain scission processes and is clearly oxidative in nature. Generally, polypropyleneoxide backbones are more easily attacked by oxygen than polyethylene oxide or poly 1,4-butylene oxide chains¹⁰⁴. Stress relaxation studies of carefully crosslinked elastomers have shown better temperature resistance in air for a polyester-based elastomer than in a polyether-based elastomer, due to the better oxidation resistance of the polyester segment¹⁰⁵. Therefore, polyesters are definitely the intermediate choice if polymers with higher thermooxidative stability are desired.

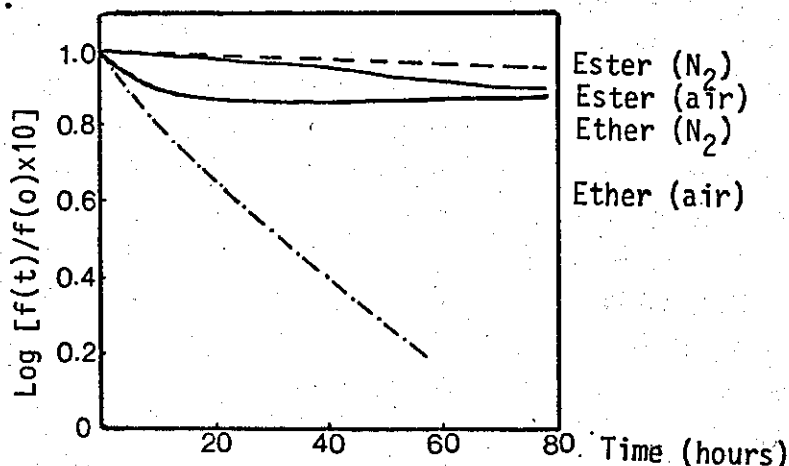


FIGURE 1C.1: Intermittent stress relaxation of polyester and polyether urethane at 130°C (95)

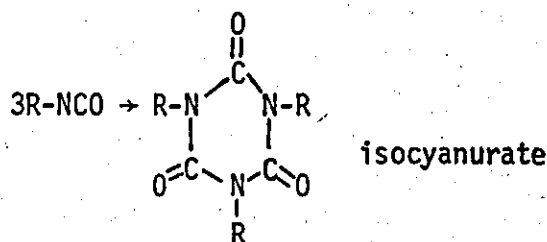
1C.3.3 Effect of Crosslinking

The methods by which crosslinking may be introduced into the polyurethane elastomers, through the use of intermediates possessing more than two functional groups per molecule, or through secondary reactions of the isocyanate group with -NH- groups in the polymer chain derived from the primary reactions of the isocyanate group, have already been described in Part B.

As in any other type of polymer increase in crosslink density of a polyurethane results in increased thermal stability simply because more bonds will have to be broken before total network breakdown occurs. However the technique has only limited use since other property requirements (elasticity, elongation, etc) normally demand the molecular weight between crosslinks to be within narrowly defined limits. There are different types of crosslinking in polyurethanes (allophanate, biuret, isocyanurate), which are produced by using excess diisocyanate; and the type of crosslinks is also of importance in thermal stability. Some biuret and allophanate structures start to free isocyanate as low as 100°C with biurets generally being slightly more stable than allophanates¹⁰⁶. Dissociation in both of these classes is ordinarily complete at 160-170°C.

1C.3.4 Effect of Isocyanurate Crosslinking

Isocyanurates are excellent structural units for high temperature resistant polyurethanes since they have high decomposition points (Table 1C.4) and can impart rigidity through an increase in the degree of crosslinking. A number of reviews describing the formation of isocyanurate structure in polyurethanes have been published^{107-110,86}. The trimerisation of isocyanates to form isocyanurates was first reported by Hofmann¹¹¹ who prepared triphenyl isocyanurate by the triethylphosphine catalysed trimerisation of phenyl isocyanate.

TABLE 1C.4: Melting point of some isocyanurate structures^{94,112}

Trimer of	Melting Point °C	TD°C
Phenyl isocyanate	285	377
Diphenylene isocyanate	374	-
1-Naphthyl isocyanate	335	-
2-Naphthyl isocyanate	344	-

The thermally most stable isocyanurate structures can be built into polyurethanes with great ease and have been used widely to prepare polymers with increased thermostability^{95,107}. Their degradation usually does not start below 270°C¹⁰⁷.

Polyurethanes with higher temperature resistance have been obtained by at least partial replacement of urethane bonds with groups of greater thermostability. Low density rigid foams made by trimerisation of a polyester-TDI prepolymer retained their dimensional stability up to 230°C¹⁰⁷. Polyisocyanurate adhesives made by the polytrimerisation of isocyanate prepolymers in the presence of organometallic catalysts retained their adhesive strength at 205°C for bonding aluminium-to-aluminium.¹⁰⁸

Sasaki et al.⁸⁶ reported the preparation of urethane elastomers containing isocyanurate rings. The catalyst system employed consisted of sodium cyanide in a solution of N,N'-dimethylformamide (DMF). A

TD°C = Decomposition temperature

comparison of mechanical properties was carried out between urethane elastomers. The isocyanurate modified urethane elastomers exhibited significantly higher tensile properties than the others, probably due to the rigid crosslinking structure of isocyanurate ring. The types of crosslinking structures are shown in Figure 1C.2.

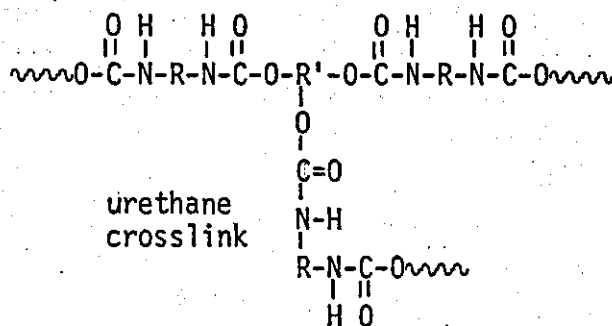
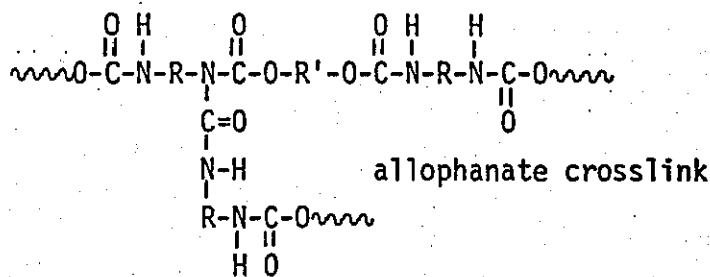
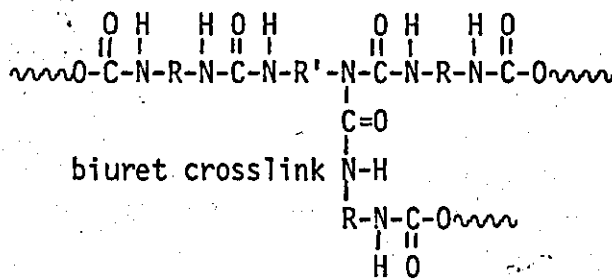
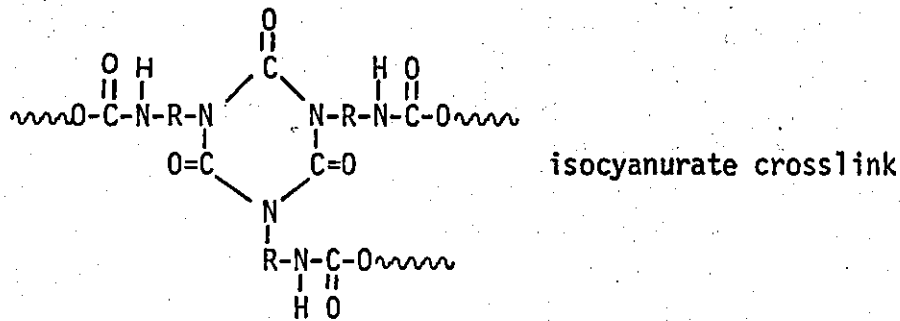


FIGURE 1C.2: Different types of polyurethane crosslink

1D OBJECTIVE OF THE RESEARCH

Polyurethane elastomers have been shown to possess excellent physical and mechanical properties, particularly at or near ambient conditions. However these advantages are considerably diminished at elevated temperatures.

The aim of the present work is to prepare thermally stable polyurethane elastomers for application as tyre materials.

The approach to this project will be to:

- a) Investigate the effect of using two new diisocyanates presently available as development products, namely p-phenylene diisocyanate (PPDI) and trans-1,4-cyclohexane diisocyanate (CHDI).
- b) Determine the optimum block ratio(s) capable of producing flexible, heat resistant polyurethane elastomers that also possess good physical and mechanical properties.
- c) Examine the effect of different diol and diamine chain extenders on thermal stability.
- d) Investigate the effect of using a large excess diisocyanate (0-50%) to produce isocyanurate crosslinking in the polymer chains.

CHAPTER 2

PREPARATION (SYNTHESIS) OF POLYURETHANES

2.1 INTRODUCTION

Polyurethane elastomers are usually prepared by bulk polymerisation techniques where the prepolymer, which can be obtained by reacting a long chain polyol with an excess of diisocyanate, and chain extender, are mixed in the molten state at elevated temperature to yield the final product. Then the product is normally cured in a mould by heating in the temperature range 50-130°C for several hours. Although this procedure has become established for many commercial elastomers, several disadvantages are apparent in the polymer preparation:

1. The choice of diisocyanate is restricted to those having a relatively low melting point.
2. Chain extenders must also be liquids or low melting point solids.
3. The reactivity of chain extender with diisocyanate must be low enough to allow efficient mixing of the chain extender with the prepolymer prior to casting the final polymer into the mould.
4. Production of uniform, homogeneous elastomeric materials depends largely on the efficient dispersion of reactants during the mixing stage.
5. Efficient dispersion of reactants is also hindered by the relatively high viscosity of the molten mixture.

6. Efficient mixing is either not possible or very difficult due to the short time available where the use of reactive chain extender leads to a short pot life.

Despite these difficulties bulk polymerisation is preferred to the solution polymerisation because several disadvantages are also apparent in solution polymerisation techniques¹¹³:

1. The solvent must not contain any active hydrogen atoms.
2. The solvent must be dry to prevent water-isocyanate reactions from occurring.
3. The solvent must be pure, i.e. it must contain no monofunctional impurities which might act as chain stoppers, and no acidic or basic impurities which could promote side reactions.
4. The solvent must be a non-reactive medium, in which diisocyanate, chain extender and polyurethane product are all readily soluble.

It has been shown that under certain conditions, solvents which should be non-reactive towards the isocyanate group can apparently react with diisocyanate to a certain extent. Reaction of N,N-dialkyl amides with the highly reactive p-toluene-sulphonyl isocyanate to give N,N-dialkyl-N'-(p-toluene-sulphonyl) amidines, has been reported¹¹⁴. Sorenson¹¹⁵ reported a side reaction between phenyl isocyanate and dimethylsulphoxide.

2.2 EXPERIMENTAL

2.2.1 Selection of Raw Materials

For this research various polyurethane systems were initially assessed in a preliminary investigation to obtain information on the best

synthesis method and some limited information on the high temperature stability of the resulting polyurethane elastomers.

Diols of aliphatic and cycloaliphatic molecular structures were used as possible chain extension agents in two basic prepolymer systems namely the polycaprolactone/CHDI and polycaprolactone/PPDI based systems. Diamines were found unsuitable as chain extenders in CHDI and more especially in PPDI based polymer systems due to their high reactivity in the bulk polymerisation technique with resulting short pot lives. Diols and diamines of bulky aromatic molecular structure were also found unsuitable as chain extenders due to their possessing high melting points and hence being unable to be dispersed. Solution polymerisation technique was used to overcome these restrictions but the polymers prepared by the method were found to have poor physical properties and hence it was not pursued.

In a further investigation it was found that some of the high melting point chain extenders could be used by means of a special semi-prepolymer (quasi) method in which the high melting point chain extenders were dissolved in polyol before mixing with diisocyanate. Therefore using this technique it was found possible to carry out a bulk polymerisation at the normal PU reaction temperature range of 100-130°C. A brief and general description of the polymerisation techniques which are normally used for PUs and some of which are employed in this study is given in Part A, Chapter 1 and a more detailed account comes later in this chapter.

Depending on the melting range of the chain extenders, an acceptable chain extension reaction temperature range was found to be 100-130°C. It was also found that with higher temperatures the rate of the reaction between chain extender and prepolymer was so fast that there was insufficient time for casting the final polymer into the mould to be satisfactorily completed. To overcome this problem, the use of a

delayed reaction catalyst was adopted. By using this type of catalyst the chain extension (pot life) time was short enough for satisfactory casting of the polymer especially if the lower end of the reaction temperature range was used.

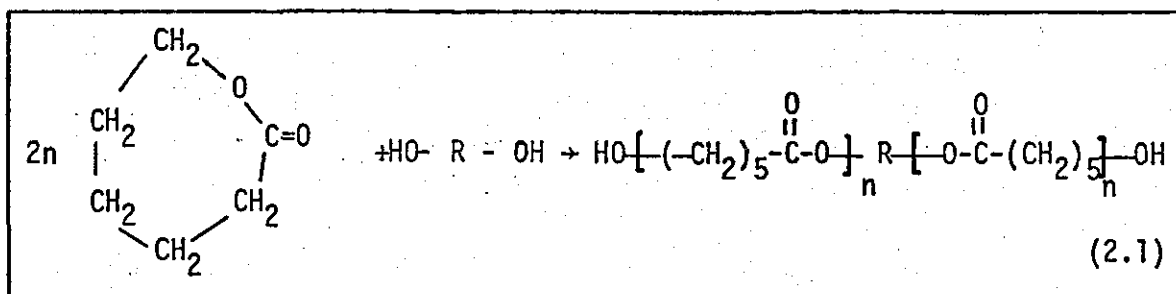
Because of health hazards associated with diisocyanates and diamines reagents were used only in a well ventilated area (fume cupboard). Face masks and plastic disposable gloves were also worn when handling these materials.

The polymers chosen for detailed study were based on polycaprolactone diol, trans-1,4-cyclohexane diisocyanate (CHDI), p-phenylene diisocyanate (PPDI) and different diols and diamines as chain extenders. Examination of the polymers based on TDI, MDI, H₁₂MDI and mixed diisocyanate was also made for comparison purposes and the results cited where appropriate.

The raw materials employed in the present research are given in Appendix 1 with their relevant technical information.

2.2.1.1 Polyol

The polyols were caprolactone derived hydroxyl terminated polyols with 2000 molecular weight e.g. (CAPA 225). The CAPA diols are polyester based diols and are white waxy solids with melting points around 60°C developed by Interlox Chemicals Ltd¹¹⁶. Polycaprolactones are obtained by the polymerisation of caprolactone in the presence of a diol (equation 2.1).



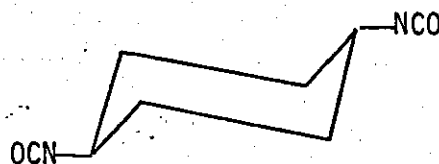
Polycaprolactones are saturated aliphatic polyesters similar in type to adipates. The polarity in CAPA due to the presence of polar C=O groups in their chemical structure backbone increases the intermolecular attractions in urethane elastomers and hence improves their physical and mechanical properties in comparison with polyether based materials.

2.2.1.2 Diisocyanates

The diisocyanates were obtained from Akzo Chemie BV¹¹⁷ and the Armac Company¹¹⁸ under the trade name of Elate 166 for CHDI and Elate 160 for PPDI with molecular weights 166 and 160 respectively. The Elate 160 and Elate 166 are two unique new diisocyanates available as development products for synthesis of polyurethane elastomers.



p-phenylene diisocyanate (PPDI)



Trans-1,4-cyclohexane diisocyanate (CHDI)

Both diisocyanates are white flaked solids of relatively high melting points, 60-64°C for CHDI and 94-95°C for PPDI. Both materials are available in a pure form, hence the calculation by weight of diisocyanate to form polyurethanes of a specific block ratio can be based on simple molecular weight stoichiometric proportionality. The basic properties of these two new diisocyanates are given in Appendix 1¹¹⁹.

Due to the close symmetry of both PPDI and CHDI molecules and their rigid, rod-like molecular shape, a very orderly structure in the build-up of the hard segments as well as the formation of a large number

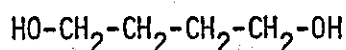
of hydrogen bonds would be expected to be promoted in the polyurethane system. It is predicted, this enables the resulting elastomers to perform better under high and low temperature conditions and achieve high modulus. Both diisocyanates have the potential economic advantage of low molecular weight and a correspondingly high NCO content.

It is known that aliphatic and cycloaliphatic diisocyanates impart superior thermal stability to polyurethanes, and the most promising of these structures (CHDI) was selected for the preparation of thermally stable materials. The p-phenylene diisocyanate (PPDI), toluene diisocyanate (TDI), 4,4'-methylene bis-phenylene diisocyanate (MDI) and 4,4'-methylene bis cyclohexyl diisocyanate (H_{12} MDI) were also included in the research programme for comparison purposes.

2.2.1.3 Chain Extenders

Various low molecular weight diols and diamines were also employed in the preparation of these experimental polyurethanes as chain extension agents. The names, formulas, melting points and suppliers of these materials are given in Appendix 1.

However, 1,4-butane diol¹²⁰, 1,4-cyclohexane dimethanol¹²¹ and mixtures of these were the most widely used in the preparation of these polyurethane elastomers.



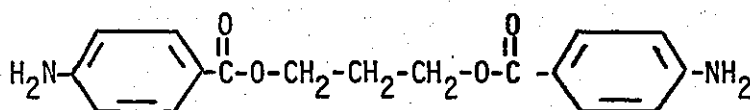
1,4-BD



1,4-CHDM

Also used was a novel diamine chain extender trimethylene glycol di-p-aminobenzoate (Polacure 740M)¹²². This was believed to be capable

of giving thermal stability due to its special chemical structure which should give polyurethanes with a mixture of both urethane and urea groups and the latter are known to possess good thermal stability.



Polacure 740M

2.2.1.4 Catalyst

To make satisfactory polyurethanes from CHDI the use of a catalyst is usually necessary and dicarbobutoxy ethyl tin dichloride* (T₂₂₀)¹¹⁴ was normally used in this series of experiments as a delayed action catalyst at the level of 0.01-0.03% by weight of the total reactants.

2.3 SYNTHESIS

The term 'block ratio' has been used in the preparation of polyurethane elastomers as a basis of indicating the stoichiometric proportions of starting materials. For example a polyurethane based on a 1:2:1 block ratio signifies the stoichiometric equivalent weight ratio by which the polyol, the diisocyanate and chain extenders are respectively reacted to give the final products. A typical example of a selected prepared polyurethane based on 1:2:1 block ratio is shown in Table 2.1.

* Trade name: T220, trivial name 'Ester Tin Dichloride'.

formula

TABLE 2.1: Typical Example of the Selection of Raw Materials for Preparation of Polyurethane Elastomers

Raw Material	Molecular Weight	Equivalent Weight	Block Ratio	Amount Used (g)
CAPA 225	2000	1000	1	100
CHDI	166	83	2	16.6
1,4-BD	90	45	1	4.5

The following synthesis method was found suitable and used as the basis of preliminary investigations.

All glassware was prepared by first placing in a muffle furnace at 600°C overnight, cooled and then carefully washed and left to dry at 100°C in a drying cabinet; silicon grease (grade M494 of ICI) was used for all quickfit cone joints. By this means all traces of organics were removed prior to a synthesis occurring.

2.3.1 Prepolymer Method

The polyol (CAPA 225) was melted and degassed at 100°C at least for one hour in a vacuum oven. The chain extender was also dried and degassed for one hour at 90-130°C depending on its melting range. The required amount of polyol and diisocyanate were placed in a round bottomed polymerisation reaction flask of 500 ml capacity and placed in an oil bath at 100-130°C while a steady flow of dry nitrogen was passed continuously through the apparatus. The flask was equipped with a dropping funnel, nitrogen inlet and variable speed constant torque stirrer motor that was connected to the flask through an anchor stirrer with close fit to side of the flask (Figure 2.1). White spot nitrogen (BOC) was used throughout and further dried by passing through silica gel guard tubes. The oil bath was a temperature controlled hot

oil bath and the temperature was also monitored by using a mercury thermometer immersed in the oil by the side of the polymerisation flask. The reaction mixture was then continuously stirred for approximately 30 minutes. Then the reaction flask was removed from the oil bath and the required amount of predried chain extender was added through the dropping funnel. Previously one or two drops of the delayed action catalyst at the concentration 0.01-0.03% by weight of the total reactants had been dissolved in the chain extender. The reaction mixture was vigorously stirred for approximately one minute, whilst maintaining the dry nitrogen blanket atmosphere.

2.3.1.1 Casting

Casting was carried out using a highly polished aluminium tray, previously coated with release agent* and heated to 120°C. The tray was levelled by using a bubble level in a hot air circulating oven at 120°C. Then the reaction mixture was carefully poured evenly over the surface of the aluminium tray, taking care not to entrap any air bubbles in the casting liquid as these would give rise to voids in the solid product. Before finally curing the polymer in a hot air oven at 120°C, the surface bubbles (if present) were removed by passing a bunsen burner's flame quickly over the cast polymer.

2.3.1.2 Curing and Post-curing

The cast polymer was left in the hot air circulating oven and cured at 120°C for 20-24 hours. These cured test sheets were then stored for one week at ambient temperature (23°C) and 60% relative humidity to condition the polyurethane elastomer and allow completion of secondary reactions.

* Ambersil's polyurethane release agent was used.

Sometimes for certain polymers only as a final step, these cured, conditions polyurethanes test sheets were post-cured for 15-24 hours at 125-130°C to complete the isocyanurate crosslinking reactions.

2.3.2 Quasi-Method of Synthesis

A quasi synthesis technique was also used where the required amount of diisocyanate was first dissolved in a part of the polyol component with the reactants being held in a round bottomed polymerisation reaction flask equipped with a dropping funnel and a stirrer and located in an oil bath at 120°C with a steady flow of dry nitrogen passing continuously over the mixture and forming a blanket of gas; this formed a quasi-prepolymer. This reaction mixture was stirred continuously for approximately 30 minutes. Next the required amount of chain extender was dissolved in the other part, or, remainder of the polyol and dried at 100°C under vacuum, and to this mixture was added one or two drops of delayed action catalyst at the concentration of 0.01-0.03% by weight of the total reactants. This polyol mixture was then added to the earlier prepared polyol/NCO quasi-prepolymer reaction mixture through a dropping funnel and the completed mixture was stirred vigorously for 2-3 minutes and cast into a pre-warmed aluminium tray. For curing and post-curing the same procedure was used as discussed in prepolymer synthesis technique.

2.4 CROSSLINKING

Chemically crosslinked polyurethanes were prepared by the use of:

1. Crosslinkers in the form of triols of different molecular weight i.e. trimethylol propane (TMP) and polycaprolactone triol (Capa 305) of molecular weight 134 and 540 respectively.
2. Use of a stoichiometric excess of diisocyanate in the prepolymer which was expected to give isocyanurate crosslinks in the chain backbone in addition to urethane linkages.

2.5 HAZARDS

Although the usual hazards apply to the handling of diisocyanates, it is particularly important in the preparation of CHDI and PPDI containing polyurethanes that no NCO vapour is released into the atmosphere as it attacks the cornea of the eye. Hence, the recommended method advised follows the unusual step of making a physical dispersion of the CHDI and PPDI flakes in polyol and then obtaining solution by slow heating with stirring. In this way the active NCO groups of the diisocyanates react in solution with the polyol before they can be volatilised and cause a hazard. More details of the hazards associated with these raw materials are given in Appendix 2.

2.6 SUMMARY OF POLYURETHANE MATERIALS PREPARED

All the polyurethanes prepared in the present investigations are given in Tables 2.3 and 2.4 with their chemical composition and designation. Chain extension reactions with some of the diols and diamines chain extension agents were found to be extremely difficult with prepolymer, due to their high melting points. Another problem was also found with some diols and especially diamine chain extenders where reaction rates went out of control due to their high reactivity producing a gelled product in the flask and therefore no useful materials were yielded in these stages.

TABLE 2.2: List of Raw Materials Abbreviations

Materials	Abbreviation
<u>Polyols:</u>	
Polycaprolactone diol MW = 2000	CAPA 225
Polycaprolactone diol MW = 2000	CAPA 720
Polycaprolactone diol MW = 3000	CAPA 231
Polycaprolactone diol MW = 4000	CAPA 240
Polycaprolactone triol MW = 540	CAPA 305
<u>Diisocyanates:</u>	
1,4-cyclohexane diisocyanate	CHDI
p-phenylene diisocyanate	PPDI
4,4'-diphenylmethane diisocyanate	MDI
4,4'-dicyclohexylmethane diisocyanate	H ₁₂ MDI
Toluene diisocyanate (2,4- and 2,6-)	TDI
<u>Chain Extenders:</u>	
<u>A. Diols:</u>	
1,4-Butane diol	1,4-BD
1,6-Hexane diol	1,6-HD
1,4-Cyclohexane diol	1,4-CHD
1,4-Cyclohexane dimethanol	1,4-CHDM
Trimethylol propane	TMP
[1,1'-isopropylidene-bis-(p-phenylene-oxy)-di- β -ethanol]	Dianol 22
[1,1'-isopropylidene-bis-(p-phenylene-oxy)-di- α -propanol-2]	Dianol 33
Hydroquinone-bis-hydroxyethyl ether	HQEE
Quinol	Quinol
Catechol	Catechol
1,5-Dihydroxy naphthalene	1,5-ND
2,3-Dihydroxy naphthalene	2,3-ND
2,6-Dihydroxy anthraquinone	Antraflavic acid
2,4- Dihydroxy benzophenone	2,4-DB
Di(4-hydroxyphenyl) sulphone	DHS
2,2-Di(4-hydroxyphenyl) propane	Bisphenol A
p,p'-Biphenol	p,p'-Biphenol
<u>B. Diamines</u>	
Trimethylene glycol di-p-aminobenzoate	Polacure 740M
4,4'-diamino diphenylmethane	MDA
2,6-diamino anthraquinone	2,6-DA
4,4'-methylene bis o-chloroaniline	MOCA
p-phenylene diamine	p-PDA
<u>Catalyst:</u>	
Dicarbobutoxy ethyl tin dichloride	T ₂₂₀

TABLE 2.3.1: List of prepared polyurethane elastomers (stoichiometry is shown by the block ratio)

Sample	Polyol	Diisocyanate	Chain Extender	Block Ratio	Hardness (Shore)		Comments
					A	D	
Capa 17,1	Capa 225	CHDI (a)	1,4-BD	1:2:1	81	27	(a) Tough and ^{more} thermally stable than other diisocyanate based polymers. (a) Good recovery and transparent (b) Very good recovery (c) Soft
B118	"	PPDI	"	"	92	42	
B26	"	H ₁₂ MDI (a)	"	"	71	23	
B5	"	CHDI+H ₁₂ MDI	"	"	80	27	
B37	"	CHDI+TDI	"	"	80	27	
B13	"	CHDI+H ₁₂ MDI	1,4-BD+1,4-CHDM	"	72	24	
B32	"	PPDI+H ₁₂ MDI	1,6-HD	"	72	25	
A3	"	CHDI	1,4-CHDM	"	87	33	
A1	"	CHDI	1,6-HD	"	89	33	
A5	"	CHDI (b)	Dianol 22	"	81	32	
	"	CHDI (c)	Dianol 33	"	79	27	
M5	"	CHDI	Polacure	"	83	30	
M7	"	CHDI	HQEE	"	86	28	
B23	"	CHDI	1,6-HD+1,4-CHDM	"	87	35	
-	"	CHDI	1,4-BD+1,4-CHDM	"	87	35	
M4	"	CHDI	1,4-BD+1,6-HD	"	87	31	
O1	"	CHDI	1,4-BD+Dianol 22	"	84	34	
O3	"	CHDI	1,4-BD+Dianol 33	"	82	30	
A4	"	CHDI	1,4-CHDM+Dianol 22	"	86	31	
B39	"	CHDI	1,4-CHD	"	79	30	
B44	"	CHDI	TMP	"	70	25	
B40	"	CHDI	1,4-BD+1,4-CHD	"	86	35	
B52	"	CHDI	1,4-CHD+1,4-CHDM	"	83	33	
B43	"	CHDI	1,4-BD+TMP	"	83	32	
B46	"	CHDI	Dianol 22 + TMP	"	70	23	
B58	"	CHDI	Quinol	"	85	31	
B67	"	CHDI	Catechol	"	82	25	

/Continued

TABLE 2.3.1: continued

Sample	Polyol	Diisocyanate	Chain Extender	Block Ratio	Hardness (Shore)		Comments
					A	D	
B57	Capa 225	CHDI	1,5-ND	1:2:1	72	22	(d) By solution polymerisation technique
B68	"	CHDI	2,3-ND	"	78	27	
B70	"	CHDI	Antraflavic acid	"	84	35	
B69	"	CHDI	2,4-BD	"	81	28	
-	"	CHDI (d)	MDA	"	93	30	
B73	"	CHDI (d)	2,6-DA	"	87	38	
-	"	CHDI	P,P'-biphenol	"	85	29	
-	"	CHDI	Bisphenol A	"	74	21	
B71	"	CHDI	MOCA	"	84	30	
M10	"	CHDI	Dianol (22+33)	"	79	29	
B4	"	CHDI	Dianol 33+TMP	"	60	17	
-	"	CHDI	DHS	"	82	29	
B11	"	CHDI	1,6-HD+TMP	"	85	30	
X3	"	CHDI (e)	Polacure + TMP	"	70	25	(e) Good recovery
X5	"	CHDI	1,4-BD+Polacure	"	83	30	
B42	"	CHDI	1,4-CHDM+TMP	"	83	27	
M16	"	PPDI	1,6-HD	"	92	40	
M9	"	PPDI (f)	Dianol 22	"	40	10	(f) Very soft and tacky
M12	"	PPDI (f)	Dianol 33	"	38	9	
A9	"	PPDI	Polacure	"	92	37	
-	"	PPDI	HQEE	"	94	50	
M13	"	PPDI	1,4-BD+1,4-CHDM	"	82	33	(g) Verv soft
B15	"	PPDI	1,4-BD+1,6-HD	"	87	37	
B19	"	PPDI	1,4-BD+Dianol 22	"	90	41	
B16	"	PPDI	1,4-BD+Dianol 33	"	80	28	
-	"	PPDI (g)	Dianol (22+33)	"	40	10	
B29	"	H ₁₂ MDI	1,4-BD+1,4-CHDM	"	65	18	

TABLE 2.3.2: List of prepared polyurethane elastomers (stoichiometry is shown by the block ratio)

Sample	Polyol	Diisocyanate	Chain Extender	Block Ratio	Hardness (Shore)		Comments
					A	D	
B45	Capa 225	CHDI	Dianol 22	1:3:2	94	42	more (a) Thermally stable than diol series (b) Tough
B1	"	CHDI	1,4-BD	"	90	38	
B142	"	CHDI (a)	Polacure	"	91	43	
A2	"	CHDI (b)	1,4-BD+1,4-CHDM	"	92	42	
M3	"	CHDI	1,4-BD+1,6-HD	"	85	33	
O1	"	CHDI	1,4-BD+Dianol 22	"	83	32	
B115	"	CHDI	Dianol 22	"	92	42	
M2	"	CHDI	1,4-BD+Dianol 33	"	85	31	
B51	"	CHDI	1,4-CHD	"	90	41	
B41	"	CHDI	1,4-BD+1,4-CHD	"	91	41	
B53	"	CHDI	1,4-CHD+1,4-CHDM	"	91	42	(c) Good recovery (d) Very soft & tacky (e) Good recovery (f) Very flexible (g) Flexible & good recovery (h) Good recovery (i) Good recovery (j) Flexible & good recovery, transparent
B47	"	CHDI	Dianol 22 + TMP	"	77	30	
B9	"	CHDI (c)	Dianol (22+33)	"	89	40	
B24	"	CHDI	1,6-HD+1,4-CHDM	"	91	43	
-	"	PPDI (d)	Dianol 33	"	55	14	
M15	"	PPDI	1,4-BD+1,4-CHDM	"	92	43	
B17	"	PPDI	1,4-BD+1,6-HD	"	92	45	
B19	"	PPDI (e)	1,4-BD+Dianol 22	"	89	40	
B18	"	PPDI	1,4-BD+Dianol 33	"	82	27	
-	"	PPDI (f)	Dianol (22+33)	"	52	16	
B27	"	H ₁₂ MDI	1,4-BD	"	81	35	
B30	"	H ₁₂ MDI	1,4-BD+1,4-CHDM	"	72	26	
B35	"	TDI (g)	1,4-BD+1,4-CHDM	"	56	15	
B14	"	CHDI+H ₁₂ MDI (h)	1,4-BD+1,4-CHDM	"	85	34	
B12	"	CHDI+H ₁₂ MDI	1,4-BD	"	86	37	
B38	"	CHDI+TDI (i)	1,4-BD	"	87	37	
B36	"	CHDI+TDI (i)	1,4-BD+1,4-CHDM	"	83	33	
B33	"	PPDI+H ₁₂ MDI (j)	1,4-BD+1,4-CHDM	"	71	26	

TABLE 2.4: List of prepared polyurethane elastomers (using excess amount of diisocyanate)

Sample	Polyol	Diisocyanate	% Excess	Chain Extender	Block Ratio	Hardness (Shore)		Comments
						A	D	
B59	Capa 225	CHDI (a)	5	1,4-BD	1:2.1:1	85	35	(a) Tough, thermal stability improves with the higher % excess diisocyanate
B60	"	"	10	"	1:2.2:1	86	37	
B61	"	"	15	"	1:2.3:1	87	38	
B62	"	"	20	"	1:2.4:1	88	39	
B56	"	"	25	"	1:2.5:1	88	40	
B63	"	"	30	"	1:2.6:1	89	41	
B64	"	"	35	"	1:2.7:1	90	42	
B65	"	"	40	"	1:2.8:1	90	43	
B66	"	"	45	"	1:2.9:1	91	44	
A6	"	"	50	"	1:3:1	91	44	
-	Capa 225	CHDI	5	Dianol 22	1:2.1:1	82	34	
-	"	"	10	"	1:2.2:1	84	36	
-	"	"	25	"	1:2.5:1	88	40	
B48	"	"	50	1,4-CHDM	1:3:1	92	43	
B54	"	"	50	1,4-CHD	1:3:1	88	42	
B56(1%)	"	"	25	1,4-BD+glass fibre (1%)	1:2.5:1	92	43	
B56(5%)	"	"	25	1,4-BD+glass fibre (5%)	1:2.5:1	92	44	
B75 (1%)	"	"	10	1,4-BD+1,4-CHDM +1% glass fibre	1:3.3:2	92	46	
-	Capa 225	CHDI	30	1,4-BD+ZnO (5%)	1:2.6:1	88	41	
B88	"	" (b)	30	HQEE	1:2.6:1	93	44	(b) Thermally stable
B91	"	"	30	MOCA	1:2.6:1	84	31	(c) Thermally stable
B92	"	" (c)	30	P,P'-biphenol	1:2.6:1	92	39	
B93	"	"	30	Quinol	1:2.6:1	90	38	

/Continued...

TABLE 2.4 (continued)

Sample	Polyol	Diisocyanate	% Excess	Chain Extender	Block Ratio	Hardness (Shore)		Comments
						A	D	
B94	Capa 225	CHDI	30	DHS	1:2.6:1	89	37	more (d) Thermally stable than diol series
B95	"	"	30	Bisphenol A	1:2.6:1	84	29	
B96	"	"	30	1,5-ND	1:2.5:1	87	33	
P20	"	" (d)	20	Polacure	1:2.4:1	89	39	
P25	"	"	25	Polacure	1:2.5:1	90	40	
P30	"	"	30	Polacure	1:2.6:1	91	40	
P35	"	"	35	Polacure	1:2.7:1	93	42	
B120	Capa 225	PPDI	5	1,4-BD	1:2.1:1	89	41	
B121	"	"	10	1,4-BD	1:2.2:1	90	42	
B122	"	"	15	1,4-BD	1:2.3:1	89	41	
B123	"	"	20	1,4-BD	1:2.4:1	89	42	
B124	"	"	25	1,4-BD	1:2.5:1	90	42	
B125	"	"	30	1,4-BD	1:2.6:1	90	42	
B126	"	"	35	1,4-BD	1:2.7:1	90	42	
B74	Capa 225	CHDI (e)	5	1,4-BD+1,4-CHDM	1:3.15:2	92	44	
B75	"	"	10	1,4-BD+1,4-CHDM	1:3.3:2	92	45	
B76	"	"	15	1,4-BD+1,4-CHDM	1:3.45:2	92	45	
B77	"	"	20	1,4-BD+1,4-CHDM	1:3.6:2	93	46	(e) Increasing thermal stability with excess diisocyanate
B78	"	"	25	1,4-BD+1,4-CHDM	1:3.75:2	94	47	
B79	"	"	30	1,4-BD+1,4-CHDM	1:3.9:2	94	48	
B80	"	"	35	1,4-BD+1,4-CHDM	1:4.05:2	94	51	
B81	"	"	40	1,4-BD+1,4-CHDM	1:4.2:2	95	52	
B82	"	"	45	1,4-BD+1,4-CHDM	1:4.35:2	95	53	
B83	"	"	50	1,4-BD+1,4-CHDM	1:4.5:2	96	53	

/Continued...

TABLE 2.4: continued

Sample	Polyol	Diisocyanate	% Excess	Chain Extender	Block Ratio	Hardness (Shore)		Comments
						A	D	
B84	Capa 225	CHDI	5	1,4-BD	1:3.15:2	92	43	more (f) Thermally stable than diol homologous, thermal stability increases with increasing NCO content
B85	"	"	10	"	1:3.3:2	92	44	
B86	"	"	25	"	1:3.75:2	96	49	
B87	"	"	30	"	1:3.9:2	96	49	
B143	Capa 225	CHDI (f)	5	Polacure	1:3.15:2	93	43	
B144	"	"	10	"	1:3.3:2	94	48	
B145	"	"	15	"	1:3.45:2	95	50	
B146	"	"	20	"	1:3.6:2	95	51	
B147	"	"	25	"	1:3.75:2	95	52	
B148	"	"	30	"	1:3.9:2	95	53	
B97	Capa 225	CHDI	30	1,4-CHD	1:3.9:2	95	48	(g) Soft polymer
B89	"	"	30	HQEE	1:3.9:2	98	56	
-	"	"	30	P,P' biphenol	1:3.9:2	98	52	
-	"	"	30	Quinol	1:3.9:2	95	48	
-	"	"	30	DHS	1:3.9:2	94	48	
B99	"	"	30	1,4-CHD+HQEE	1:3.9:2	95	52	
B100	"	"	30	HQEE+Polacure	1:3.9:2	97	52	
B100	"	"	30	1,4-CHD+Polacure	1:3.9:2	95	52	
B133	"	"	30	TMP	1:3.9:2	80	39	
B151	"	"	30	Polacure + benzoflex (10%)	1:3.9:2	92	57	
B149	"	" (g)	30	Capa 305	1:3.9:2	77	27	(g) Soft polymer
B79 (0.1%)	"	"	30	1,4-BD+1,4-CHDM (0.1% irganox)	1:3.9:2	94	46	

/Continued..

TABLE 2.4: continued

Sample	Polyol	Diisocyanate	% Excess	Chain Extender	Block Ratio	Hardness (Shore)		Comments
						A	D	
B79 (0.5%)	Capa 225	CHDI	30	1,4-BD+1,4-CHDM (0.5% irganox)	1:3.9:2	93	46	
B156	Capa 240	CHDI (h)	30	Capa 305	1:3.9:2	70	29	(h) Crystallizable
-	"	"	30	TMP	1:3.9:2	81	30	
B112	Capa 225	PPDI	30	Quinol	1:2.6:1	82	31	
B111	"	"	30	1,5-ND	1:2.6:1	83	35	
B103	"	" (i)	30	Dianol (22+33)	1:3.9:2	62	21	(i) Soft
B108	"	"	30	TMP	1:3.9:2	75	26	"
B106	"	"	30	Dianol (22+33) +TMP	1:3.9:2	66	24	"
B116	"	"	30	TMP+Dianol 33	1:3.9:2	66	25	"
B130	"	"	30	TMP	2:5.2:2	64	21	"
B132	"	"	30	TMP+Benzoflex(10%)	2:5.2:2	60	18	"
B109	"	"	30	TMP	1:2.6:1	64	21	"
-	Capa 240	PPDI	30	HQEE	1:2.6:1	95	52	
B102	"	" (j)	30	Dianol (22+33)	1:3.9:2	94	46	(j) Crystallizable
B107	"	"	30	TMP	1:3.9:2	90	33	"
B110	"	"	30	TMP+Benzoflex(10%)	1:3.9:2	93	35	"
B131	Capa(240+305)	PPDI	30	TMP	1:3.9:2	70	26	Soft
B104	Capa 240	CHDI (k)	30	TMP	1:2.6:1	95	49	(k) Crystallizable
B105	"	"	30	TMP+Benzoflex(10%)	1:2.6:1	93	28	"
B117	Capa 225	CHDI	30	Dianol 33 + TMP	1:2.6:1	80	29	

/Continued...

TABLE 2.4: continued

Sample	Polyol	Diisocyanate	% Excess	Chain Extender	Block Ratio	Hardness (Shore)		Comments
						A	D	
B114	Capa 240	H ₁₂ MDI	30	TMP+Benzoflex (10%)	1:3.9:2	88	38	(1) Good recovery
B137	"	"	30	TMP	1:3.9:2	89	36	
B134	"	"	30	1,4-BD	1:2.6:1	68	23	
B135	Capa 225	TDI	30	1,4-BD	1:2.6:1	62	17	
B136	"	TDI	30	TMP	1:3.9:2	71	23	
B153	"	MDI	30	Polacure	1:3.9:2	93	46	
B138	"	MDI (1)	30	1,4-BD	1:2.6:1	65	23	
B141	"	"	30	TMP	1:3.9:2	77	30	
B140	"	"	30	Dianol (22+33)	1:3.9:2	75	30	
B155	Capa 231	CHDI (m)	30	Capa 305	1:3.9:2	72	22	(m) Soft
B158	"	"	30	Polacure	1:3.9:2	85	42	
B154	Capa 225	"	30	Polacure	2:5.2:2	92	43	
B159	Capa 720	PPDI	30	TMP	1:3.9:2	78	35	
B150	"	CHDI	30	Polacure	1:3.9:2	93	54	

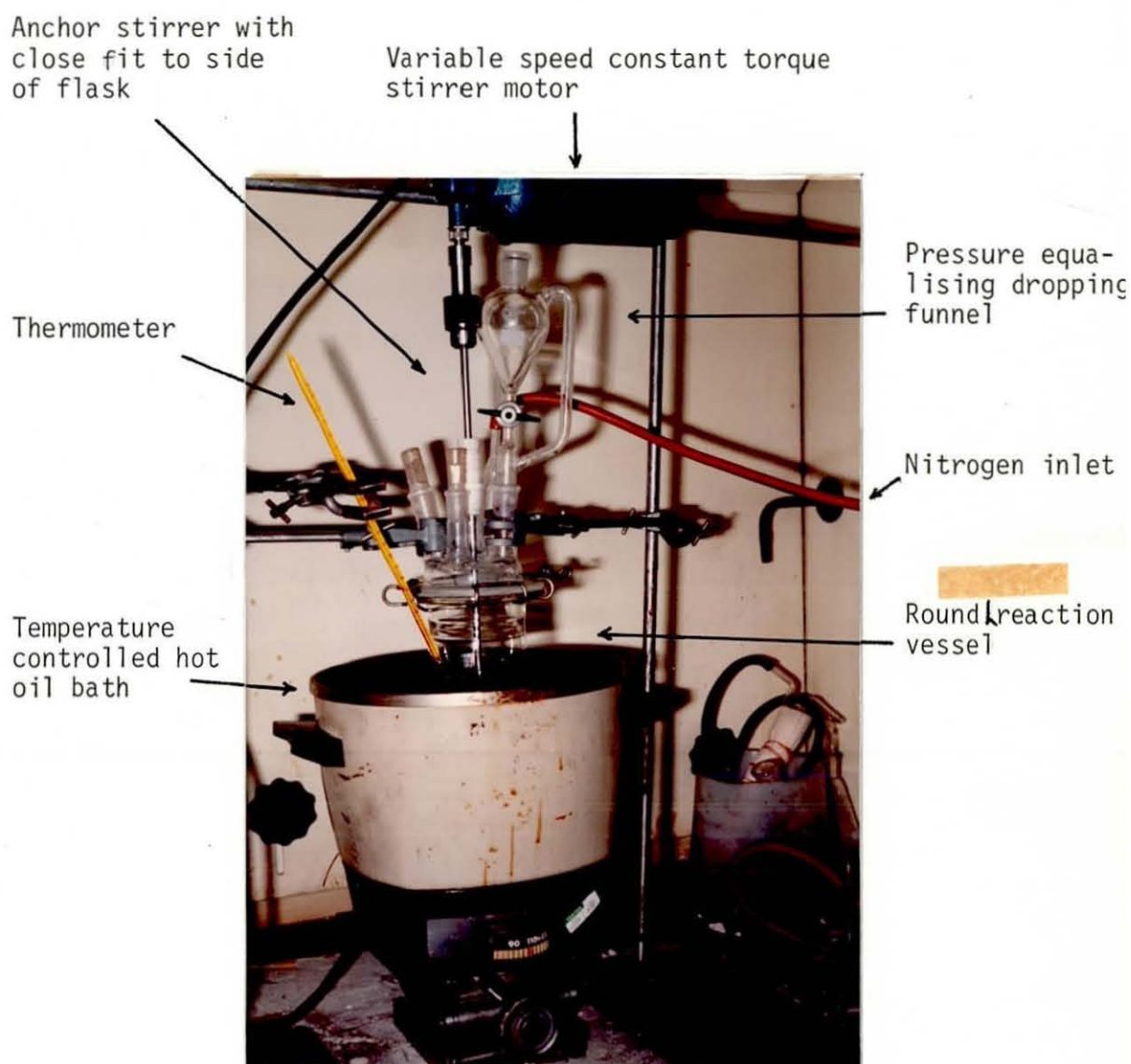


FIGURE 2.1: Typical laboratory apparatus for the preparation of a polyurethane elastomer

CHAPTER 3
CHARACTERISATION AND PROPERTIES
OF POLYURETHANES

3.1 CHARACTERISATION

A number of analytical techniques are used in the study of polymer morphology and their solid state structure property relationship. These include dynamic mechanical analysis, thermal analysis, infra-red spectroscopy, X-ray diffraction and scanning electron microscopy. Since these techniques have been employed in the present investigation on thermally stable polyurethane elastomer, they will be briefly reviewed.

3.1.1 Dynamic Mechanical Analysis

The dynamic mechanical methods have been employed to understand polymer morphology and microphase separation. Huh and Cooper¹²³ studied the dynamic mechanical properties of polyester and polyether urethane block polymers at different frequencies in the temperature range of -150 to 200°C. The existence of a two phase structure was demonstrated by the observation of two major transition regions, the glass transition temperature (T_g) of the ester or ether soft segments and the softening temperature of the aromatic-urethane hard segments. They also showed that all relaxation phenomena were greatly influenced by the molecular weight of the prepolymer, weight percent of the hard segments and thermal history. An increase in the molecular weight of the prepolymer above 1000 at constant hard segment content resulted in a semi-crystalline material, which possessed a lower T_g for the macroglycol segments.

Illinger and co-workers¹²⁴ studied the low temperature dynamic mechanical properties of polyether based urethanes as a function of composition, temperature and frequency. The T_g of the soft segment was

found to be approximately the same as that of a homopolymer up to a minimum diisocyanate level. However, when this level exceeded the soft segment T_g was significantly raised. This was explained by restrictions in soft segment mobility due to termination of soft segments by urethane groups and also because of participation of the urethane block in the domain structure. Seefried et al.⁷⁵ investigated both the soft and hard segment variation effects in thermoplastic polyurethanes based on polycaprolactone diol/MDI/1,4-BD systems by using dynamic mechanical techniques. They found the glass transition temperature of these materials progressively shifted to lower temperatures as the chain length of the soft segment was increased. A similar technique was used to study the variation of hard segment concentrations in two different molecular weight polyester diols with soft segments of 830 \overline{M}_n and 2100 \overline{M}_n respectively. The urethane polymers based on an 830 \overline{M}_n polycaprolactone diol exhibited a progressive increase in glass transition temperature at increased level of hard segments. In contrast, the urethane polymers prepared with a 2100 \overline{M}_n polycaprolactone diol as the soft segment maintained a relatively constant glass transition temperature. These differences are attributed to the relative degree of phase separation between the constitutive blocks of the copolymer.

Non-hydrogen bonded PUs: Brunette et al.¹²⁵ investigated the effect of hard segment content variation on a series of segmented polyurethanes based on a Hydroxy II terminated polybutadiene soft segment (HTPBD). These materials are linear and amorphous and have no potential for hydrogen bonding between the hard and soft segments. The existence of two-phase morphology was deduced from dynamic mechanical behaviour, and thermal analysis. Both techniques showed a soft segment glass transition temperature, (T_g) at -56°C and hard segment transitions between 20 and 100°C , depending on the urethane content. The value of T_g in these polyurethanes as compared to a value of -64°C for the pure HTPBD and its invariance with increasing urethane content indicate that phase segregation is very nearly complete. Since TDI/BD form amorphous hard segment regions, the driving force for phase

segregation must come from the extreme incompatibility of the apolar soft segment and the strongly polar hard segment units. In addition there is no hydrogen bonding contribution to increase the compatibility between the two phases.

3.1.2 Thermal Analysis

Thermoanalytical techniques have been used in the study of the morphology and intermolecular bonding in polyurethane elastomers. These techniques include differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermomechanical analysis (TMA) and thermogravimetry (TG)¹²⁶. Three characteristic transitions common to samples of varying composition are normally seen by DSC, namely the major glass transition and two higher transitions were attributed by several earlier workers^{40,54} to the disruption of different types of hydrogen bonding. Miller and Saunders⁹⁴ demonstrated therefore, that all thermal transitions can be attributed to either the soft segment, the hard segment or interactions of the two. The following effects were suggested as being possible in segmented polyurethane materials:

- a) Transition of the soft segment may be unaffected by copolymerisation;
- b) Interference by the hard segments may lead to a reduction of soft segment transition behaviour;
- c) The soft segment transition may be increased by the hydrogen bonding with the hard segment;
- d) The hard segment transition may fall due to interaction with soft segments;
- e) The hard segment transition may be low due to short segment length;

- f) Hard segments of sufficient length may form ordered zones (truly crystalline) giving transitions comparable to those in the pure polyurethane.

The differential scanning calorimetry (DSC) studies of urethane block polymers that have no capability of hydrogen bonding confirm that the DSC endotherms do not result from disruption of specific secondary bond interaction. Ng et al⁷⁸ investigated thermal transition behaviour by DSC in polyurethane based on polyoxytetramethylene/piperazine/1,4-BD. These materials possess a well defined segment molecular weight and molecular weight distribution and no possibility of intermolecular hydrogen bonding as there are no NH groups available. It rather appears that all three endotherms are morphological in origin. A transition at approximately -70°C was associated with the glass transition temperature of the soft segment and a poorly defined transition around 40°C was associated with the glass transition temperature of amorphous hard segment. The highest temperature peak may be assigned to relatively well ordered microcrystalline polyurethane segments, the numbers and perfection of which are determined by segment length and thermal history. DSC curves of annealed samples indicate that domain morphology may be affected by thermal treatment. The lower temperature endotherms represent disordering of hard segments with relatively short-range order that may be improved in a continuous manner by annealing. Annealing followed by rapid cooling of a segmented copolymer was studied by Hesketh et al⁹⁶. DSC measurements taken immediately after the quench show that the soft segment T_g is higher than that of the control, suggesting that the applied thermal history promoted increased mixing of hard and soft segments. The T_g then decreases back to its original value at a rate dependent on the driving force for phase segregation and the viscosity of the material. If the material has highly ordered hard segment domains or is semi-crystalline, this effect is significantly reduced or even absent.

Comparison of the transition behaviour of the materials prepared by Ng et al⁷⁸ with the hydrogen bonded polyurethanes of Huh et al¹²³ demonstrates the increased soft segment T_g value in the hydrogen bonded systems associated with hard/soft segment hydrogen bonded interactions. Increased hard segment content in the piperazine elastomers was found to give higher soft segment glass transition temperatures. This was explained in terms of interaction of hard segment domains with the soft matrix, i.e. the domains act as filler particles in the systems. A poorly defined DSC endotherm at approximately 60°C was found to move to higher temperatures and finally merge with the higher temperature transition on annealing the sample. Similar behaviour has been reported in hydrogen bonded systems by Seymour and Cooper^{56,127}.

Schneider et al¹²⁸⁻¹²⁹ studied structural organisation and thermal transition behaviour of polyurethanes based on toluene diisocyanate. Thermal transition behaviour was observed by DSC. Three major transitions were observed and designated T₁, T₂ and T₃. The T₁ transition, associated with the soft segment glass transition temperature was found to increase with increasing urethane concentration in the 2,4-TDI samples. T_g for 2,6-TDI samples was generally independent of urethane concentration. In 2,4-TDI materials a T₂ transition around 60°C was observed although no similar transition was found for 2,6-TDI samples. They suggested that the T₂ transition which occurs in the 2,4-TDI polyurethanes is indicative of weak domain structure and that the increase in T_g with urethane concentration is due to extensive hard segment mixing with the soft segment phase. The absence of a T₂ transition in 2,6-TDI is taken to indicate that all domain structure which occurs is highly ordered and therefore that hard segment-soft segment mixing is minimal. All 2,6-TDI polyurethanes displayed a repeatable transition (T₃) in the range 120-160°C whereas only 2,4-TDI samples with highest urethane content showed a T₃ transition above 150°C.

Paik Sung et al.¹³⁰ studied the polyether poly(urethane ureas) and polyester poly(urethane ureas) based on 2,4-TDI/ethylene diamine/poly(tetramethylene oxide) or poly(butylene adipate), to find out the effect of urea linkage in the hard segment on the extent of phase segregation, domain structure and polymer properties. They reported that in both series, the hard segment domains are amorphous with a very high T_g (165-190°C) even in low urea content compositions.

3.1.3 Infrared Spectroscopy

It is well known that interchain interaction forces, including hydrogen bonding (H-bonding) affect many physical properties of urethane elastomers to a considerable extent¹⁹. The extent and possible forms of hydrogen bonding is dependent on many factors including the electron donating ability, relative proportion and spatial arrangement of the proton-acceptor groups in the polymer chains. Functional groups of a molecule possess characteristic vibrational frequencies and by observing these absorption frequencies, information on the overall molecular structure can be obtained. Infrared spectroscopic techniques have been used to determine the groups involved in hydrogen bonding in polyurethane materials. While the majority of hydrogen bonding occurs between hard segments, it appears that a significant proportion also occurs between NH groups of the polyurea or polyurethane hard segment and the ether oxygen of the polyether or ester carbonyl oxygen of the polyester soft segment.

Several investigations into the nature and extent of hydrogen bonding in segmented polyurethane elastomer systems have been reported^{52,131-134}. Paik Sung and Schneider⁴⁹ investigated hydrogen bonding in two series of toluene diisocyanate polyurethanes based on the individual 2,4- and 2,6-TDI isomers, a polyether soft segment and butane diol. Three major absorption regions were investigated:

1. NH stretching band in the region of $3460-3300\text{ cm}^{-1}$.
2. Carbonyl (C=O) stretching band in the region of $1740-1700\text{ cm}^{-1}$.
3. Ether (C-O-C) stretching band in the region of $1300-1000\text{ cm}^{-1}$.

The major NH bond at near 3300 cm^{-1} is attributed to the hydrogen bonded NH groups, while a shoulder on the high frequency side (near 3460 cm^{-1}) is assigned to the non-bonded NH groups. Their results indicated that 95% of all NH groups are hydrogen bonded in the solid state at room temperature.

The regions that are mentioned above, ~~together with the CH_2 stretch~~ absorptions region ($3000-2700\text{ cm}^{-1}$) are important in polyurethane analysis. Participation in hydrogen bonding decreases the frequency of the NH and C=O vibrations and increases their intensity, making these absorptions very useful in the study of hydrogen bonding effects. Changes in hydrogen bonding can thus be followed, in principle, by frequency or intensity measurements.

Absorption of the carbonyl groups are also of potential use in hydrogen bond studies. Splitting of the carbonyl ~~band~~ ($1740-1700\text{ cm}^{-1}$) due to hydrogen bonding has been reported by Seymour et al¹³⁵ for a polyether/MDI based polyurethane elastomer. They interpreted a band at 1703 cm^{-1} as caused by hydrogen bonded carbonyl while a band at 1733 cm^{-1} was attributed to the free carbonyl groups. Similarly, Paik Sung and Schneider⁴⁹ reported splitting of the carbonyl band for polyether/TDI based polyurethanes. 2,4-TDI based polymers showed splitting of the absorption band into two peaks, one at 1740 cm^{-1} that was attributed to the free carbonyl group, and the other at 1720 cm^{-1} that was assigned to the hydrogen bonded carbonyl group. Spectra of 2,6-TDI based polymers showed two peaks at 1740 cm^{-1} and 1700 cm^{-1} assigned to free and hydrogen bonded carbonyl groups respectively.

Seymour and Cooper⁵⁶ investigated the thermal behaviour of hydrogen bonds in polyurethane elastomers by studying the temperature dependence of infrared absorption for the NH vibration. Virtually all of the NH groups were hydrogen bonded at 25°C giving a single peak at 3320 cm^{-1} . As the temperature was raised, a high frequency shoulder developed and the overall intensity diminished. Non-hydrogen bonded NH groups are known to absorb at a higher frequency and with much lower intensity, so that the latter effect can be used to monitor hydrogen bond disruption.

The dependence of the segment size on hydrogen bonding was considered by Tanaka et al¹³⁶. They showed that in polyether based polyurethane materials, the increase in hydrogen bonding between NH and ether groups **is accompanied by** the increase in soft segment size. Further evidence of this effect is provided by the result of Nakayama et al¹³⁴ on polyether/MDI/ethylene diamine based materials.

Paik Sung and co-workers¹³⁷ investigated hydrogen bonding in two series of polyether poly(urethane ureas) based on 2,4-toluene diisocyanate, ethylene diamine and either 1000 and 2000 molecular weight poly tetramethylene oxide. They concluded that three dimensional hydrogen bonding may exist within their hard segment domains, where one urea carbonyl is hydrogen bonded to two NH groups. As suggested by IR studies, this type of three dimensional hydrogen bond formation may provide the driving force for much improved phase segregation, even at low urea content. It was noted that this type of three dimensional hydrogen bonding has not been detected in polyurethanes extended with diol. IR studies also indicated that the interface between the hard segment domain and the soft polyether matrix is quite sharp, since most of the urethane carbonyl is free from bonding.

The presence of the isocyanurate structure absorption band at 1412 cm^{-1} was suggested by Schollenberger and Stewart¹⁶¹. This absorption band has also been reported by Filip¹⁶³ at the same frequency. The isocyanurate carbonyl band is also reported to appear in the region of 1703-1694 cm^{-1} .¹⁶⁴

3.1.4 X-Ray Diffraction

X-ray scattering ~~is a~~^{as it} technique which is appropriate to determine the geometry of the regularly repeating unit cell and polymer segments in block copolymers. ~~is~~^{as it} is one of the effective techniques for investigating the ordered arrangements of atoms and molecules present in a solid substance.

Bonart and co-worker in a series of publications^{58,138,139,140}, reported the investigation of structure in polyurethane elastomers by using X-ray diffraction techniques. A polyurethane based on poly(oxytetramethylene)/MDI and extended with hydrazine was investigated¹³⁸ by wide-angle X-ray (WAXS) and small angle X-ray scattering (SAXS) techniques. They observed in relaxed samples a broad amorphous halo at 4.5 \AA and a weak interference ring at 12 \AA in the (WAXS) photographs indicating the absence of crystallinity. However, at 500% elongation the samples showed clear fibre type diagrams having highly oriented crystal reflexes. This was considered due to the crystallisation of soft segment polyol on extension. Polyether soft segments tended to stress crystallise whereas polyester soft segments showed only paracrystalline behaviour.

A small angle X-ray scattering (SAXS) study¹⁴⁰ of aliphatic diol (e.g. 1,4-BD) and aliphatic diamine (e.g. hydrazine) chain extended polyurethanes showed a retention of phase segregation at lower hard segment sizes in the diamine materials and a loss of phase segregation in the diol materials. This effect was thought to be due to the excess NH groups present in the diamine extended material resulting in the interaction of carbonyl (C=O) groups with at least two NH groups through hydrogen bonding in different directions.

The domain structure in both polyether and polyester derived polyurethanes was studied by Clough et al.^{40,41}. By means of light scattering and small angle X-ray scattering (SAXS), they concluded that phase

separation into a domain structure occurs in both types of elastomers, but to a higher degree in the polyether-based polymers than in the polyester-based polymers, possibly due to restrictions in the latter imposed by interaction of the ester and urethane groups.

Samuels and Wilkes⁶⁰ investigated the structure of non-hydrogen bonded piperazine polyurethane using wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) techniques to gain more knowledge about the detailed nature of the spherulitic texture in the polymers. The presence of a well defined small angle diffraction corresponding to a Bragg spacing of approximately 10 nm was thought to indicate domain structure. The wide angle diffraction patterns of the polymers showed an increase in sharp crystalline reflexes with increasing hard segment length. This was suggested to be due to the formation of larger crystalline components.

Wilkes and Yusek¹⁴¹ investigated diol extended polyether and polyester derived polyurethanes by wide angle and small angle X-ray diffraction to gain some understanding of the extent of domain formation in polyurethanes of varying urethane content. They found that the domains are generally lamellar in shape with an average centre-to-centre separation of 10 to 25 nm. It was suggested that these domains serve as crosslinks which prevent rapid relaxation of the chains, so that when the polymers are stretched, the rubbery polyester or polyether can stress-crystallise and give a high tensile strength.

Chang and Wilkes⁶¹ reported X-ray studies on a series of segmented polyether urethanes with polyethylene oxide, polypropylene oxide or both soft segments. Hard segments were composed of H₁₂MDI (Hylene W) and diamines of varying structures. A series of polyether/H₁₂MDI/diamine materials of varying soft segment/hard segment relative sizes were investigated. Only samples with high molecular weight soft segments gave crystalline reflexes. All other samples showed no evidence of crystallinity.

Schneider et al¹²⁸ found that wide angle X-ray diffraction patterns of the polyurethanes based on asymmetrical toluene diisocyanate (2,4-TDI) showed only a broad amorphous ring and gave no indication of crystallinity. The more symmetrical 2,6-TDI based polyurethanes of highest urethane content exhibited crystalline diffraction.

Minoura et al¹⁴² investigated the wide angle X-ray diffraction intensity of urethane elastomers with varying molar ratio in the hydroxylterminated polybutadiene/HDI/1,6-HD system. They found an increase in the diffraction intensity of the elastomers with increase in molar ratio. The effect of changing diisocyanates structure on X-ray diffraction intensity was also investigated by using TDI, MDI and HDI cured elastomers. The diffraction intensity of the TDI-cured system was weaker than those of the MDI and HDI cured systems. This was thought to be due to the spatial order of polymer segments in TDI cured systems which is restricted sterically, but in the MDI and HDI systems crystallinity is easily induced because of facility in the orientation of the polymer segments. These series of investigations were carried out by using aromatic diols as chain extenders. In the wide angle X-ray diffractions on the elastomers derived from catechol, resorcinol and quinol, the diffraction intensity was shown to decrease as follows:

Para isomer > meta isomer > ortho isomer

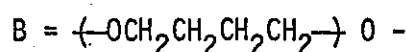
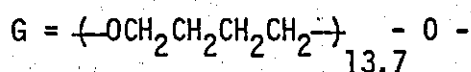
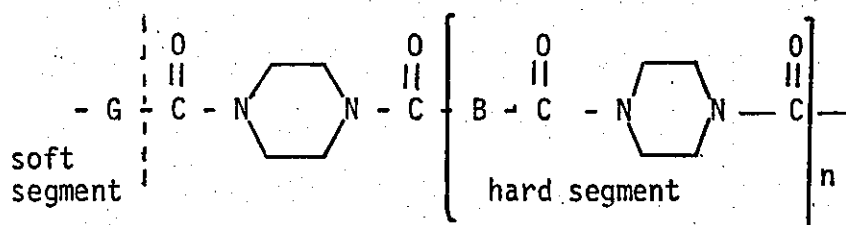
—————→
decreasing order

3.1.5 Electron Microscopy

Electron microscopy has proved to be a successful technique for studying the complex morphology of block polymers. The direct observation of sample surfaces can be provided by scanning electron microscopy techniques. Under favourable conditions, such as when the domains are crystalline, transmission electron microscopy can provide direct information on the domain structure in polyurethanes.

Koutsky et al¹⁴³ studied the evidence of a domain structure in polyether and polyester segmented polyurethanes by using transmission electron microscopy. Domain structures were observed for both systems and hard domains were found to vary from 3 to 10 nm in width. The relative size of the domains varies depending on sample preparation.

Wilkes et al¹⁴⁴ studied scanning (SEM) and transmission (TEM) electron microscopy of a model series of four segmented polyurethanes (Figure 3.1). They found that well-structured spherulitic morphologies could be induced in the homopolymer systems and their mixtures, and the control over the textures could be maintained by solution casting conditions. The domains were observable via TEM, and the general orientation of this structure within the spherulites was also noted.



$$n = 1, 2, 3, 4$$

FIGURE 3.1: The Model Series of Segmented Urethanes Used in Electron Microscopic Study by Wilkes et al

3.2 EXPERIMENTAL

3.2.1 Dynamic Mechanical Thermal Analysis (DMTA)

3.2.1.1 Introduction

In order to understand polymer morphology and microphase separation, the development of short time screening tests has therefore been undertaken in recent years resulting in one particular technique which is now increasingly used to predict suitability for service in the engineering field. This is the Dynamic Mechanical Thermal Analyser (DMTA) test method which measures both the stiffness and energy absorption properties of a material in dynamic modes by subjecting a small strip of the polymer to constant cyclic deformation and measuring the resulting storage modulus (E') and energy absorption ($\tan \delta$). Dynamic Mechanical Thermal Analysis (DMTA) senses any change in molecular mobility in the sample as the temperature is raised or lowered. Generally the applied force and the resulting deformation are varied sinusoidally with time. The time scale required for the molecular motion to manifest itself is determined by the frequency, f , of the impressed sinusoidal stress.

A knowledge of the viscoelastic behaviour of polymers, and its relation to molecular structure is essential to understanding of both processing and other related properties. Polymers are termed viscoelastic because some fraction of the energy required to cause recoverable deformation is dissipated within the material. There are three moduli which are used to describe the viscoelastic behaviour of polymers.

Storage modulus (E')

Storage modulus (E') which is usually plotted against temperature or frequency with logarithmic scale, is a measure of the energy stored and recovered per cycle when different systems are compared at the same strain amplitude.

Loss modulus (E'')

Loss modulus (E'') is a measure of the energy dissipated or lost per cycle of sinusoidal deformation when different systems are compared at the same strain amplitude.

Loss tangent ($\tan \delta$)

Loss tangent is a measure of the ratio of energy lost to energy stored in a cyclic deformation. It is dimensionless parameter, $\tan \delta = \frac{E''}{E'}$.

DMTA characterises the rubber and glassy state modulus levels.

Dynamic properties (storage modulus and $\tan \delta$) are dependent on both frequency and temperature and it is possible to approximately relate the two effects quantitatively. The general form of the effect of temperature on storage modulus (E') and $\tan \delta$ is shown in Figure 3.2.

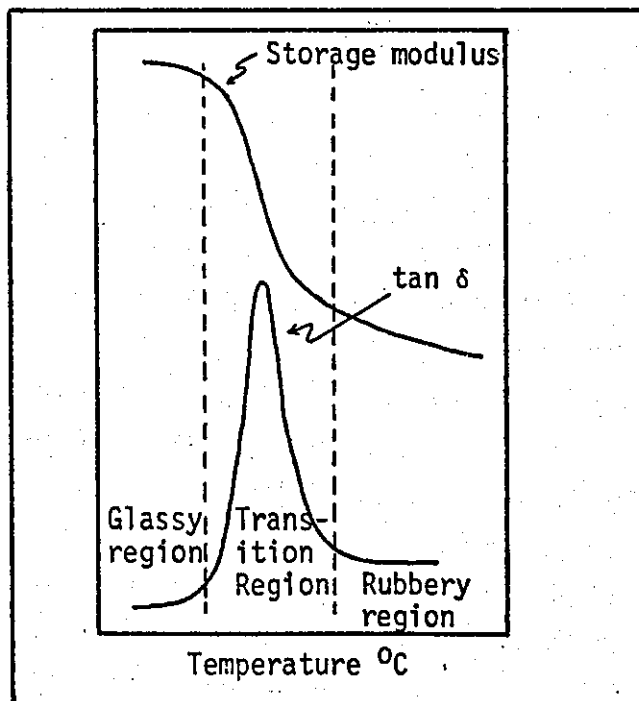


FIGURE 3.2: General form of the effect of temperature on storage modulus and $\tan \delta$

The effect of increasing or decreasing frequency is to shift the curves to the right or left respectively along the temperature axis, Figure 3.3.

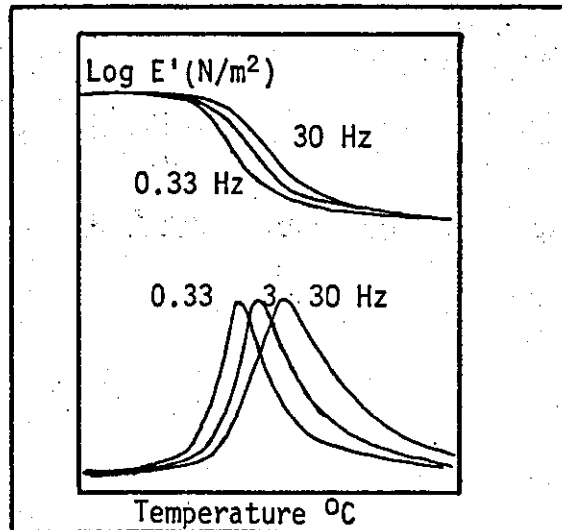


FIGURE 3.3

DMTA has been considered as one of the most effective tools in the investigation of poly-blend and block copolymer systems. Just as phase separation is demonstrated by separate T_g relaxation processes in copolymers (i.e. SBR which shows clearly two T_g), so a reliable and most sensitive method for assessing compatibility is the observation of one conjoint relaxation process (i.e. blend of PS and PPO). Fig 3.4 & 3.5

In the present work DMTA was used to measure thermal stability and strength retention to predict suitability for service in the engineering field by observing the changes in modulus which occurred with rise in temperature. In addition the morphology and hard/soft segment mixing was also examined.

SBR = Styrene Butadiene Rubber
 PS = Polystyrene
 PPO = Polypropylene oxide

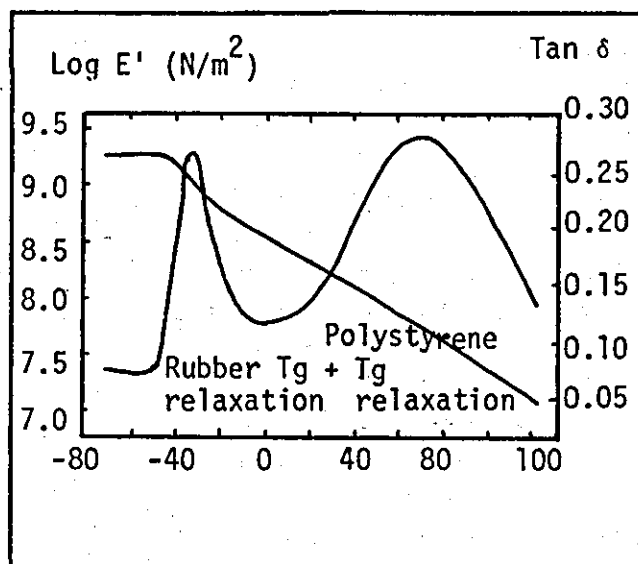


FIGURE 3.4: Styrene-butadiene block copolymer. Phase separated

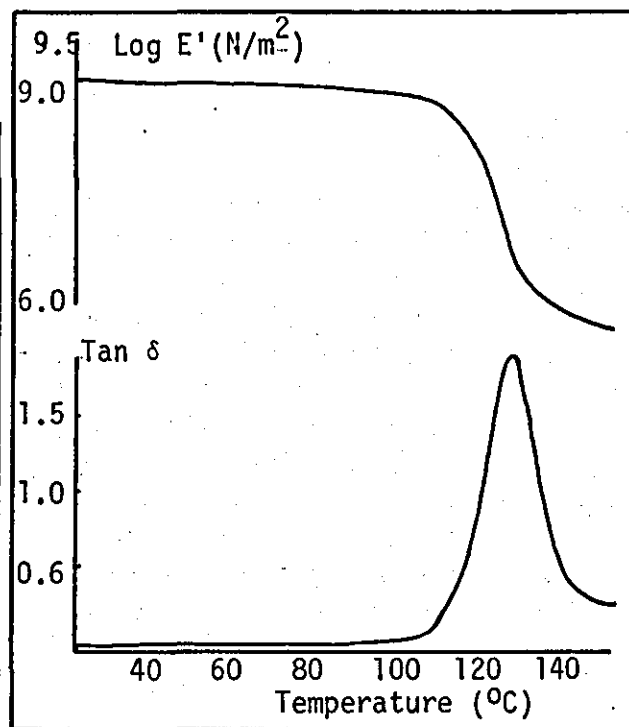


FIGURE 3.5: Compatible blend exhibiting one Tg relaxation

3.2.1.2 Experimental Procedure

The properties of the prepared polyurethane elastomers were measured by using the Polymer Laboratory's Dynamic Mechanical Thermal Analyser (PL-DMTA)*. A small rectangular strip test specimen of dimensions (40 x 10 x 2 mm) was used. The test specimens were subjected to constant cyclic deformation of the type shown in Figure 3.24. over a constantly changing temperature and the storage modulus (E') and $\tan \delta$ were ~~recovered~~ and used. Analysis was carried out at 1 Hz frequency over the temperature range -140°C to $+300^{\circ}\text{C}$ maximum, whenever possible; heating rate was $4^{\circ}\text{C}/\text{minute}$. The temperature at which $\log E'$ reached a value of 5.5 N/m^2 was taken as an arbitrary indication of the loss of mechanical integrity and melting of the hard segments and then the test was stopped. The $\log E'$ and $\tan \delta$ were plotted on an X-Y recorder (PL 2500 JJ).

* Polymer Laboratories Ltd, Loughborough, Leicestershire, UK.

3.2.1.3 Results and Discussion

The DMTA results determined over the temperature range -140°C to $+300^{\circ}\text{C}$ are presented in Figures 3.6 to 3.22 and Tables 3.2 to 3.20. Figure 3.6 shows a typical DMTA ~~scan~~ of a prepared polyurethane elastomer which exhibits a constant $\log E'$ value of 9 N/m^2 in its glassy region (below T_g), see Part A of Figure 3.6.

A sharp decrease in modulus ~~occurs~~ (approximately two orders of magnitude) as the temperature is increased through the glass transition region over a narrow temperature range of approximately 20°C , which is the rubbery region (above T_g), where no further decrease in modulus is observed to occur with temperature rise. Finally at the elevated temperature of 160°C and above, a general softening and lowering of modulus occurs and all specimen clamping forces are lost. All the PU polymer samples prepared showed a similar trend of relaxation.

More than one transition will normally be encountered in the temperature plane. The main transition which is designated as the α -relaxation and enables T_g to be derived is considered to represent the soft segment (polyol) transition in the polyurethane molecule. It is considered due to the onset of micro-Brownian motion of the main chains about T_g ¹⁴⁷.

At low temperatures a secondary relaxation peak is observed at about -80°C and designated as a β peak. The β damping peak may be attributed to the motion of NH- or carbonyl (C=O) groups¹⁴⁵ of the esters and urethanes to which water molecules are associated by hydrogen bonding. This secondary peak is also ascribed to the motion of water molecules in polyamide and polyurethane systems¹⁴⁶. Another secondary loss peak observed at about -120°C (1 Hz) is designated as the γ peak. The γ relaxation may be assigned to a local motion of the methylene sequences^{148,149} including polycaprolactone polyester soft segment.

Determination of the relaxation spectra of polymers is useful not only for understanding the molecular motions in the structure, but also for practical applications. The α dispersion is associated with the glass transition temperature and is accompanied by the greatest change in the stiffness of materials.

Influence of the diisocyanates structure on thermal stability

In this research the effect of the chemical structure of various diisocyanates on the thermal stability of their polyurethane elastomers is found by comparing five different types of diisocyanate based PU polymers in which the variable was the diisocyanate. The basic formulation was based on CAPA 225/diisocyanate/1,4-BD of molar ratio 1/2.6/1 respectively. The results are given in Table 3.2 and Figure 3.7. The temperature at which the value of $\log E'$ changes significantly is considered to indicate the limit of thermal stability of the polyurethanes. Table 3.2 gives the temperature for each system at which the storage modulus starts to significantly decrease. It is seen that the CHDI based polyurethane demonstrated relatively higher temperature stability than other diisocyanate based polymers. As seen in Table 3.2, the storage modulus of the CHDI based PU started to decrease at +181°C while the storage modulus of the H₁₂MDI based PU starts to decrease at 100°C*. The other diisocyanate based PU's fall in between these two temperatures. From the results obtained from Figure 3.7 the contribution to thermal stability of the various diisocyanates falls into the following order:



—————→
Decreasing thermal stability

It is important to note that the H₁₂MDI based polyurethane does not

* The limit of thermal stability was determined by taking the point of inflexion.

show constant dynamic storage modulus in the rubbery region. It is also important to note that an unusual property possessed by the CHDI based PU's is the apparently constant dynamic storage modulus (E') possessed over the relatively large temperature range of $+20^{\circ}\text{C}$ to $+180^{\circ}\text{C}$ or above depending on types of formulation; by comparison the other diisocyanate based polyurethanes show a continual, though often gradual, reduction in modulus as temperature increases.

Figure 3.8 compares the loss tangents ($\tan \delta$) of different diisocyanate based polyurethanes. Three relaxation peaks are observed in the low temperature range and designated as the α , β , and γ peaks. The overall effects of the diisocyanate structures are significant with the major phase changes occurring at about -15 to -33°C (Table 3.3). However the CHDI based PU's show better low temperature properties (lower T_g), than other diisocyanate studied. It is noted that the magnitude of the β and γ -peaks are small in comparison with the α -peak (Table 3.3).

Influence of the mixed diisocyanate structure on thermal stability

DMTA data of Figure 3.9 and Table 3.4 enable information to be derived concerning the effect of mixed diisocyanates on temperature stability. Figure 3.9 represents the temperature dependence of the storage modulus and loss tangent ($\tan \delta$) of two series of polyurethanes based on CAPA 225/CHDI+TDI/1,4-BD and CAPA 225/CHDI+H₁₂MDI/1,4-BD. The mixed CHDI+TDI based PU shows higher thermal stability than mixed CHDI+H₁₂MDI. On the other hand from the information resulting from the Tables 3.2 and 3.4 it is clearly shown that the thermal stability can be improved by using CHDI as a co-diisocyanate in both series of CAPA 225/TDI/1,4-BD and CAPA 225/H₁₂MDI/1,4-BD based polymers. This shows that the effect of adding CHDI to a PU is to generally promote thermal stability.

Influence of block ratio on the thermal stability of PU elastomers

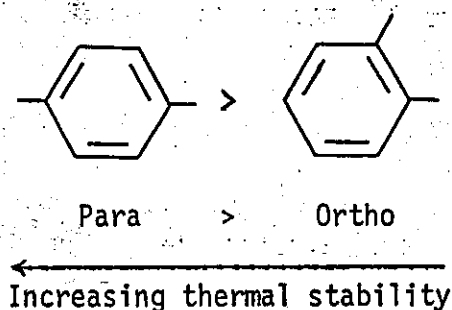
Figure 3.10 compares the dynamic mechanical behaviour (storage modulus and $\tan \delta$) of two series of CAPA 225/CHDI/1,4-BD based polyurethanes in which the variable is block ratio. It is clearly shown that the thermal stability increases with increasing block ratio. The maximum temperature to which storage modulus ($\log E'$) values will remain constant are also given in Table 3.5. The temperature resistance has been increased by 20°C through the use of the higher block ratio. Higher thermal stability of the 1/3/2 PU over its 1/2/1 analogue is considered as primarily due to its higher CHDI content. Molar ratios higher than 1/3/2 were not used because of the increasing hardness and decreasing flexibility of the resulting PU elastomer. It was also found that the magnitude of the $\tan \delta$ decreases with increasing block ratio.

Influence of the diol structure on thermal stability of the PU elastomer

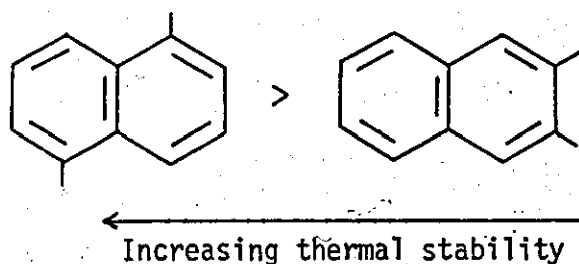
Figure 3.11 shows the dynamic mechanical property of a series of polyurethane elastomer based on CAPA 225/CHDI and extended with several different diol chain extenders with a block ratio of 1/2/1, so the variable is the chain extender. From this figure the following maximum thermal stability values are implied:

- i) P,P'-biphenol based PU starts to lose stability at 175°C;
- ii) Quinol (1,4-benzene diol) based PU starts to lose stability at 170°C;
- iii) Catechol (1,2-benzene diol) based PU starts to lose stability at 125°C;
- iv) 1,5-naphthalene diol based PU starts to lose stability at 165°C;
- v) 2,3-naphthalene diol based PU starts to lose stability at 100°C;
- vi) Di(4-hydroxyphenyl) sulphone based PU starts to lose stability at 150°C.

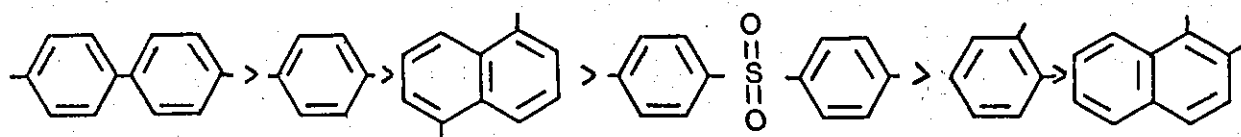
These results clearly show that para isomer of benzene diol chain extender gives higher thermally stable polyurethane than its ortho isomer.



A similar result is obtained by comparison between the thermal stability of 1,5-naphthalene diol and 2,3-naphthalene diol chain extender based polyurethane elastomers:



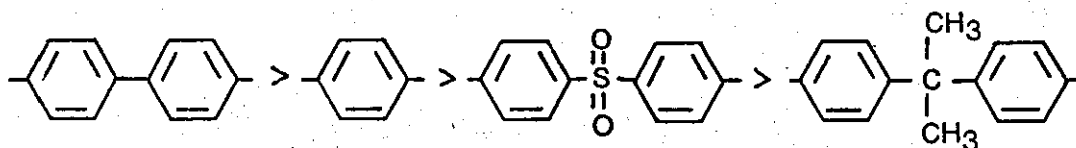
Finally the effect of chemical structure of chain extenders on thermal stability can be obtained from Table 3.6. Through Table 3.6 the following order of decreasing thermal stability is observed:



Order of decreasing thermal stability →

Figure 3.12 represents the temperature dependence of the loss tangent ($\tan \delta$) for the various chain extender containing polyurethanes. All series display three relaxations, labelled α , β and γ . The major relaxations are characterised by a decrease in modulus over a narrow temperature range. The relaxation temperature and magnitude of $\tan \delta$ are shown in Table 3.7. The α -relaxation that occurs at -32 to -37 is associated with the glass transition temperature of the soft (polycaprolactone) segment.

The influence of the diol chain extender structure on thermal stability of PU elastomers was also studied in a series of CAPA 225/CHDI/chain extender based polymers by using four different diols as a chain extender with molar ratio of 1/2.6/1. Figure 3.13 compares the storage modulus and $\tan \delta$ as a means of observing the dependence of temperature stability on a chain extender's structure. The maximum temperature to which storage modulus ($\log E'$) values of the PU elastomers remain constant is given in Table 3.8. From the data obtaining from this table, the following order of decreasing thermal stability can be presented:



Order of decreasing thermal stability \longrightarrow

The glass transition temperature of these systems is also given in Table 3.9 accompanied by β and γ transition temperature and related $\tan \delta$.

Influence of the diamine structure on thermal stability in comparison with diols

Figure 3.14 compares the dependence of temperature stability on diol and diamine chain extended polyurethane elastomers based on CAPA 225/CHDI/chain extender with molar ratio 1/3/2. The diamine which is selected in this study was Polacure and the diols were 1,4-BD, 1,4-BD + 1,4-CHDM and 1,4-CHD. The maximum temperature to which storage modulus ($\log E'$) values of PU will remain constant is given in Table 3.10. From the figures the following maximum thermal stability values are implied:

- i) 1,4-BD + 1,4-CHDM based PU's start to lose stability at 175°C;
- ii) 1,4-BD based PU start to lose stability at 185°C;
- iii) 1,4-CHD based PU start to lose stability at 200°C;
- iv) Polacure based PU start to lose stability at 230°C.

As the results show the temperature stability is higher in the case of using the diamine chain extension agent. The higher thermal stability of the Polacure based PU is considered as primarily due to its special structure and hence its higher hydrogen bonding capacity over the diol chain extenders.

Influence of excess diisocyanate on the thermal stability of the PU elastomer

Figures 3.15 to 3.18 show the dependence of temperature stability on excess diisocyanate crosslinking in a PU elastomer.. It is obvious from the data that as the amount of excess diisocyanate increases from 5% to 45% the thermal stability of each PU is enhanced; for example in the case of the 1/2/1 block ratio (1,4-BD system) from a position of complete thermal equilibrium up to 155°C $\log E'$ has lost 0.1 Nm^{-2} by 170°C when crosslinked with 5% excess diisocyanate whereas the same PU crosslinked with a 45% excess of diisocyanate has enhanced temperature resistance remaining in equilibrium to 190°C and loses the

same amount of modulus (0.1 Nm^{-2}) at 205°C , hence its temperature resistance has been increased by 35°C through the use of isocyanate crosslinking.

Tables 3.12 to 3.15 and Figures 3.15 to 3.18 give the temperature for each crosslinked PU at which the storage modulus starts to significantly decrease. It can be seen by inspection that an approximately linear relationship applies between the quantity of crosslinking in a PU and its thermal stability. Very generally, for every 5% increase in the amount of excess diisocyanate left in the cast PU, the temperature at which the PU remains stable increases by 5°C .

The higher thermal stability of the 1/3/2 PU is considered as primarily due to its higher CHDI content over the 1/2/1 analogue.

The DMTA data of Figures 3.15 to 3.18 enable information to be derived concerning the effect of crosslink density on low temperature stiffening and glass transition temperature (T_g). In brief the overall effects of the large crosslink density changes are small with the major phase changes occurring at about -35°C and -80°C . Their presence, as discussed before, is ascribed to the micro-Brownian motion of the amorphous polyol segments. The main transition at about -35°C is designated as the α -relaxation and enables T_g to be derived, it is considered to represent the soft segment (polyol) transition in the PU molecule.

Influence of chain extender structure coupled with crosslink density on thermal stability

Figure 3.19 compares the DMTA property of a series of polyurethane elastomers based on CAPA 225/CHDI and extended with several different diols and diamine chain extenders with a block ratio of 1/3.9/2. So the variable is chain extender. The polymers also contain 30% excess

CHDI which acts as crosslinking agent into PU elastomer. The results show clearly that using excess CHDI together with chain extender structure can give higher temperature stability. For example in the case of the Polacure based PU, this when crosslinked with a 30% excess of CHDI has enhanced temperature resistance remaining in equilibrium up to 260°C. The maximum temperature to which storage modulus ($\log E'$) values of the PU elastomer remain constant are given in Table 3.16. It can be seen by inspection that the thermal stability of PU elastomers are improved by the effect of the chain extender structure together with isocyanurate crosslinking. Through this results the following order of decreasing thermal stability can be observed:

Polacure > P,P'-biphenol > 1,4-CHD > HQEE > 1,4-BDO > Quinol > DHS

Influence of crosslinking on thermal stability by using excess diisocyanate and TMP as a crosslinking agent

Figure 3.20 shows the effect of using trimethylol propane (TMP), a trifunctional chain extender and as a crosslinking agent in comparison with the mixed Dianol (22+33) chain extender in the soft polymer series. Table 3.17 gives the maximum temperature to which storage modulus ($\log E'$) values of the PU elastomer will remain constant. As the results show the thermal stability increases by using TMP as a chain extension agent. Increasing thermal stability is believed to be due to increasing crosslinking density in the TMP based polymer, so as in most polymers increasing crosslinking density increases thermal stability on the basis that more bonds need to be broken before serious network breakage becomes apparent.

Table 3.18 gives the temperature dependence of the loss tangent ($\tan \delta$) for these soft polymer series. By comparison between these results (see Figure 3.20) with the results obtaining from hard polymer series (see Figures 3.12 to 3.19) it can be seen that the main α -transition

temperature has shifted to a higher temperature range. This effect is thought to be due to more phase mixing occurring in the soft polymer series than in the hard series which hence results in a higher glass transition temperature. To overcome this undesirability the copolymer of polycaprolactone (CAPA 720*) was employed instead of CAPA 225. The results which are given in Table 3.19, show that the glass transition temperature will be about 9°C lower in the case of using CAPA 720. Table 3.20 also shows the effect of CAPA 720 on glass transition temperature (T_g) of the hard polymer series to be about 14°C lower than that of the equivalent CAPA 225 series.

Figures 3.21 and 3.22 also represent the effect of CAPA 720 polyol on low temperature properties of the polyurethane elastomer.

* Interlox Chemicals Ltd

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TABLE 3.2: Maximum temperature to which storage modulus ($\log E'$) values of polyurethane elastomer will remain constant*

Sample No	Type of Diisocyanate	Log E' (N/m^2)	$T^\circ C$
B63	CHDI	7.4	181
B125	PPDI	7.1	155
B138	MDI	6.4	150
B135	TDI	6.1	135
B134	H_{12} MDI	6.2	100

* The polymers are based on Capa 225/diisocyanate/1,4-BD with block ratios 1/2.6/1

TABLE 3.3: α and β transition temperatures of polyurethane elastomers based on different diisocyanates

Sample No	Type of Diisocyanate	β Transition		α Transition	
		$\tan \delta$	$T^\circ C$	$\tan \delta$	$T^\circ C$
B63	CHDI	0.032	-78	0.285	-33
B125	PPDI	0.031	-78	0.375	-30
B138	MDI	0.027	-78	1.1	-15
B135	TDI	0.032	-78	1.0	-21
B134	H_{12} MDI	0.03	-78	0.575	-22

TABLE 3.4: Maximum temperature to which storage modulus ($\log E'$) values of polyurethane elastomer will remain constant*

Sample No	Type of Diisocyanate	$\log E'$ (N/m^2)	$T^{\circ}C$
B38	CHDI + TDI	7.4	155
B12	CHDI + H_{12} MDI	7.0	130



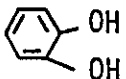
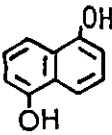
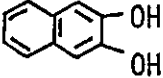
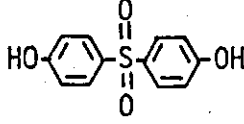
* The polymers are based on Capa 225/diisocyanate/1,4-BD with block ratios 1/3 (1.5 + 1.5)/2

TABLE 3.5: Maximum temperature to which storage modulus ($\log E'$) values of polyurethane elastomer will remain constant in the case of using different block ratios

Molar Ratio	$\log E'$ (N/m^2)	$T^{\circ}C$
1/2/1	7.2	160
1/3/2	7.6	180

* The polymers are based on Capa 225/CHDI/1,4-BD

TABLE 3.6: Maximum temperature to which storage modulus ($\log E'$) values will remain constant in the case of using different chain extenders*

Sample No	Type of Chain Extender	$\log E'$ (N/m ²)	T°C	Structure of Chain Extender
-	P,P'-biphenol	7.1	175	
B58	Quinol	6.8	170	
B67	Catechol	6.8	125	
B57	1,5-ND	6.6	165	
B68	2,3-ND	6.8	100	
-	DHS	7.1	150	

* The polymers are based on Capa 225/CHDI/chain extender with molar ratio 1/2/1

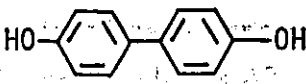

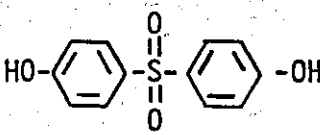
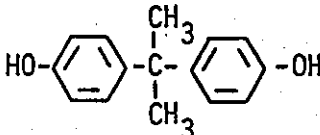
TABLE 3.7: α , β and γ transition temperature of polyurethanes in the case of using different diol chain extenders*

Sample No	Type of Chain Extender	γ Transition		β Transition		α Transition	
		$\tan \delta$	T°C	$\tan \delta$	T°C	$\tan \delta$	T°C
-	P,P'-biphenol	0.042	-110	0.033	-75	0.41	-32
B58	Quinol	**	**	0.03	-80	0.4	-37
B67	Catechol	0.027	-117	0.028	-80	0.42	-37
B57	1,5-ND	0.037	-114	0.034	-75	0.45	-33
B68	2,3-ND	0.035	-113	0.031	-78	0.46	-34
-	DHS	0.035	-113	0.028	-79	0.37	-33

* As Table 3.6

** Not measured

TABLE 3.8: Maximum temperature to which storage modulus ($\log E'$) values of polyurethane elastomer* will remain constant in the case of using different chain extenders

Sample No	Type of Chain Extender	$\log E'$ (N/m^2)	$T^\circ C$	Structure of Chain Extender
B92	P,P'-biphenol	7.3	205	
B93	Quinol	7.3	190	
B94	DHS	7.3	171	
B95	Bisphenol A	7.0	140	

*The polymers are based on Capa 225/CHDI/chain extender with molar ratio 1/2.6/1

TABLE 3.9: α , β and γ transition temperature of polyurethanes in the case of using different diol chain extenders

Sample No	Type of Chain Extender	γ Transition		β Transition		α Transition	
		$\tan \delta$	$T^\circ C$	$\tan \delta$	$T^\circ C$	$\tan \delta$	$T^\circ C$
B92	P,P'-biphenol	0.037	-121	0.034	-79	0.26	-35
B93	Quinol	-**	**	0.029	-80	0.23	-37
B94	DHS	0.037	-118	0.028	-79	0.27	-38
B95	Bisphenol A	0.037	-116	0.031	-83	0.46	-38

* As Table 3.8

** Not measured

TABLE 3.10: Maximum temperature to which storage modulus ($\log E'$) values of polyurethane elastomers will remain constant in the case of using diols and diamine chain extenders

Type of Chain Extender	$\log E'$ (N/m^2)	$T^{\circ}C$
1,4-BD	7.4	185
1,4-BD +1,4CHDM	7.4	175
1,4-CHD	7.4	200
Polacure	7.4	230

* The polymers are based on Capa 225/CHDI/chain extender with molar ratio 1/3/2

TABLE 3.11: α and β transition temperatures of polyurethane elastomers based on various chain extenders*

Type of Chain Extender	β Transition		α Transition	
	$\tan \delta$	$T^{\circ}C$	$\tan \delta$	$T^{\circ}C$
1,4-BD	0.027	-77	0.17	-30
1,4BD +1,4CHDM	0.028	-77	0.19	-30
1,4-CHD	0.023	-80	0.18	-33
Polacure	0.021	-80	0.21	-32

* As Table 3.10

TABLE 3.12: Maximum temperatures to which storage modulus ($\log E'$) values of the crosslinked polyurethane elastomers* will remain constant

Block Ratio	% Excess CHDI	Log E' (N/m^2)	$T^{\circ}C$
1:2.04:1	0.2	7.2	115
1:2.1:1	5	7.2	160
1:2.2:1	10	7.3	170
1:2.3:1	15	7.3	173
1:2.4:1	20	7.3	180
1:2.5:1	25	7.4	180
1:2.6:1	30	7.4	181
1:2.7:1	35	7.5	183
1:2.8:1	40	7.5	183
1:2.9:1	45	7.5	188
1:3.0:1	50	7.5	190

*The polymers are based on Capa 225/CHDI/1,4-BD and the data is derived from the DMTA data of Figure 3.15 and from other data not shown on these graphs for clarity of presentation

TABLE 3.13: Maximum temperatures to which storage modulus ($\log E'$) values of the crosslinked polyurethane elastomers will remain constant*

Block Ratio	% Excess CHDI	$\log E'$ (N/m ²)	T°C
1:3.02:2	0.2	7.5	165
1:3.15:2	5	7.5	170
1:3.3:2	10	7.5	175
1:3.45:2	15	7.58	178
1:3.6:2	20	7.58	180
1:3.75:2	25	7.60	185
1:3.9:2	30	7.65	190
1:4.05:2	35	7.70	190
1:4.2:2	40	7.70	200
1:4.35:2	45	7.70	200
1:4.5:2	50	7.75	205

* The polymers are based on Capa 225/CHDI/1,4-BD + 1,4-CHDM and the data is derived from the DMTA data of Figure 3.16 and from other data not shown on these graphs for clarity of presentation

TABLE 3.14: Maximum temperature to which storage modulus ($\log E'$) values of the crosslinked polyurethane elastomers will remain constant*

Sample No	Block Ratio	% Excess PPDI	$\log E'$ (N/m^2)	$T^\circ C$
B118	1/2/1	0	7.2	110
B120	1/2.2/1	10	7.2	130
B123	1/2.4/1	20	7.2	145
B125	1/2.6/1	30	7.2	150

*The polymers are based on Capa 225/PPDI/1,4-BD

TABLE 3.15: Maximum temperature to which storage modulus ($\log E'$) values of crosslinked polyurethane elastomer will remain constant

Sample No	Block Ratio	% Excess CHDI	$\log E'$ (N/m^2)	$T^\circ C$
B84	1/3.15/2	5	7.6	180
B86	1/3.75/2	25	7.8	200

* The polymers are based on Capa 225/CHDI/1,4-BD

TABLE 3.16: Maximum temperature to which storage modulus ($\log E'$) values of the polyurethane elastomer will remain constant in the case of using excess CHDI and different chain extenders

Chain Extender	% Excess CHDI	$\log E'$	$T^\circ\text{C}$
Polacure	30	7.84	260
P,P-biphenol	30	7.54	230
1,4-CHD	30	7.64	220
HQEE	30	7.82	215
1,4-BD	30	7.72	212
Quinol	30	7.30	192
DHS	30	7.66	162

* The polymers are based on Capa 225/CHDI/chain extender with block ratios 1:3.9:2

TABLE 3.17: Maximum temperature to which storage modulus ($\log E'$) values of the polyurethane elastomers will remain constant in the case of using excess PPDI and different chain extenders

Chain Extender	% Excess PPDI	$\log E'$	$T^{\circ}\text{C}$
Dianol (22+33)	30	6.2	165
Dianol 22+33 + TMP (1+1)	30	6.55	200
TMP	30	6.6	210

The polymers are based on Capa 225/PPDI/chain extender with block ratio 1:3.9:2

TABLE 3.18: Temperature dependence of the α and β transition for Capa 225/PPDI type polyurethanes based on various chain extenders

Chain Extender	β Transition		α Transition	
	$\tan \delta$	$T^{\circ}\text{C}$	$\tan \delta$	$T^{\circ}\text{C}$
Dianol (22+33)	0.028	-73	0.86	+13
Dianol (22+33)+TMP	0.023	-73	0.74	+11
TMP	0.021	-73	0.053	+7

TABLE 3.19: Temperature dependence of the α -transition for the various polyol containing polyurethanes in PPDI/TMP based polymers

The Polyol/PPDI/TMP System		
Polyol	α -transition	
	$\tan \delta$	T°C
Capa 225	0.53	+7
Capa 720	0.36	-2

TABLE 3.20: Temperature dependence of the α -transition for the various polyol containing polyurethanes in CHDI/Polacure based polymers

The Polyol/CHDI/Polacure System		
Polyol	α -transition	
	$\tan \delta$	T°C
Capa 225	0.13	-35
Capa 720	0.15	-49

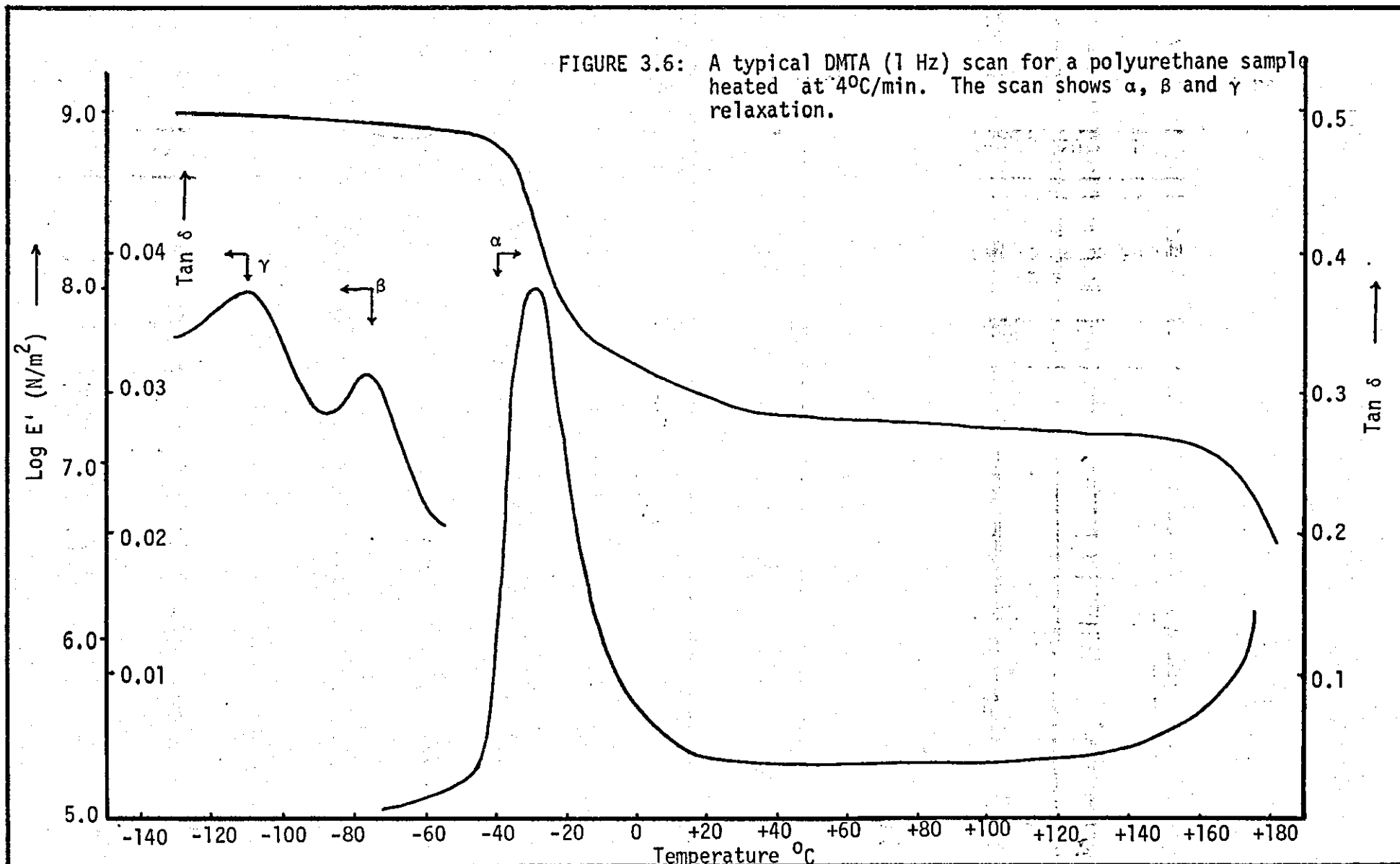


FIGURE 3.7: Storage modulus as a means of observing the dependence of temperature stability on diisocyanate structure

(PU type: Capa 225/diisocyanate/1,4-BD)
Molar ratio: 1/2.6/1

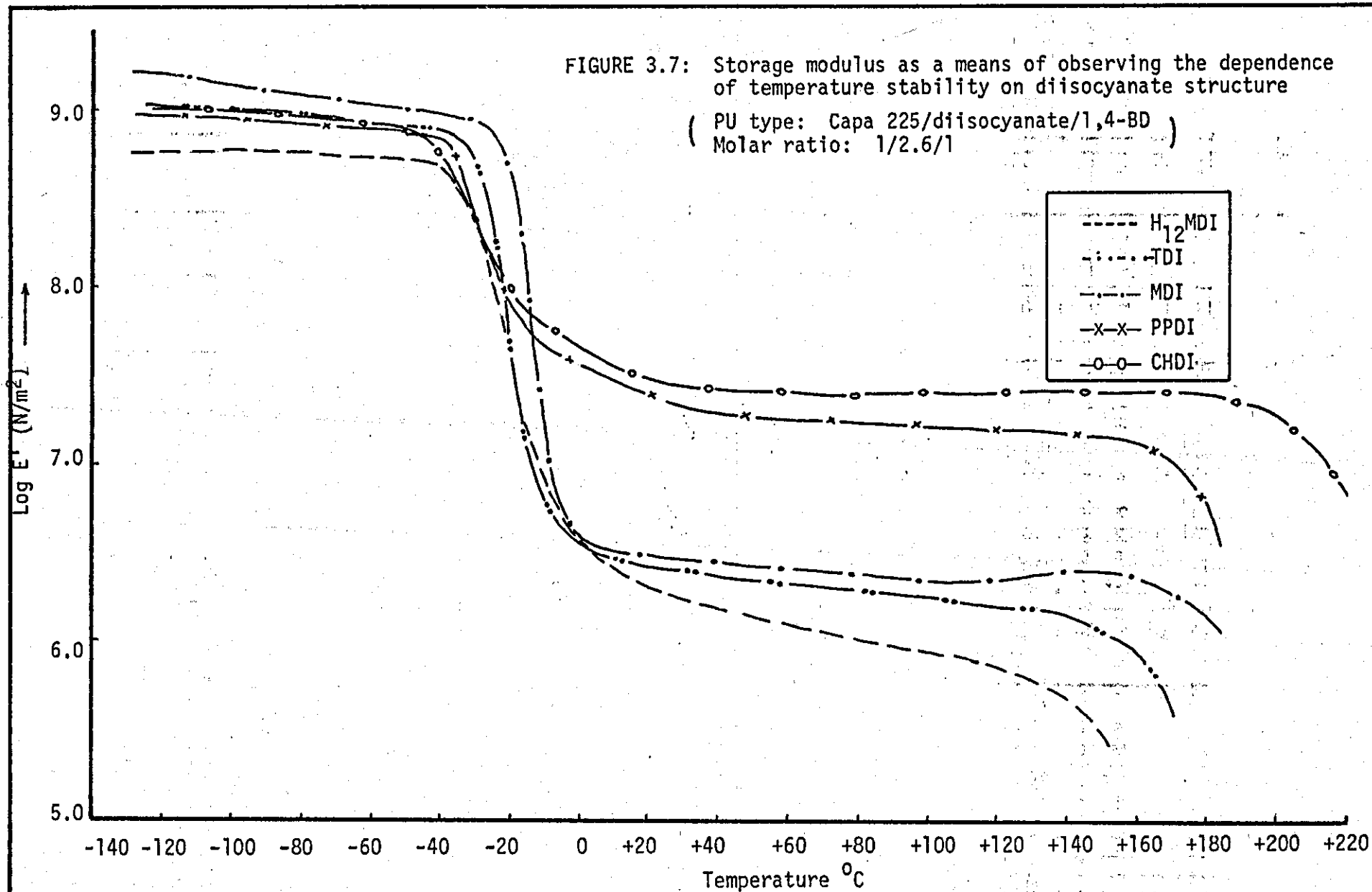


FIGURE 3.8: Temperature dependence of the loss tangent ($\tan \delta$) of different diisocyanate based polyurethanes.

(PU type: Capa 225/diisocyanate/1,4-BDO)
Molar ratio: 1/2.6/1

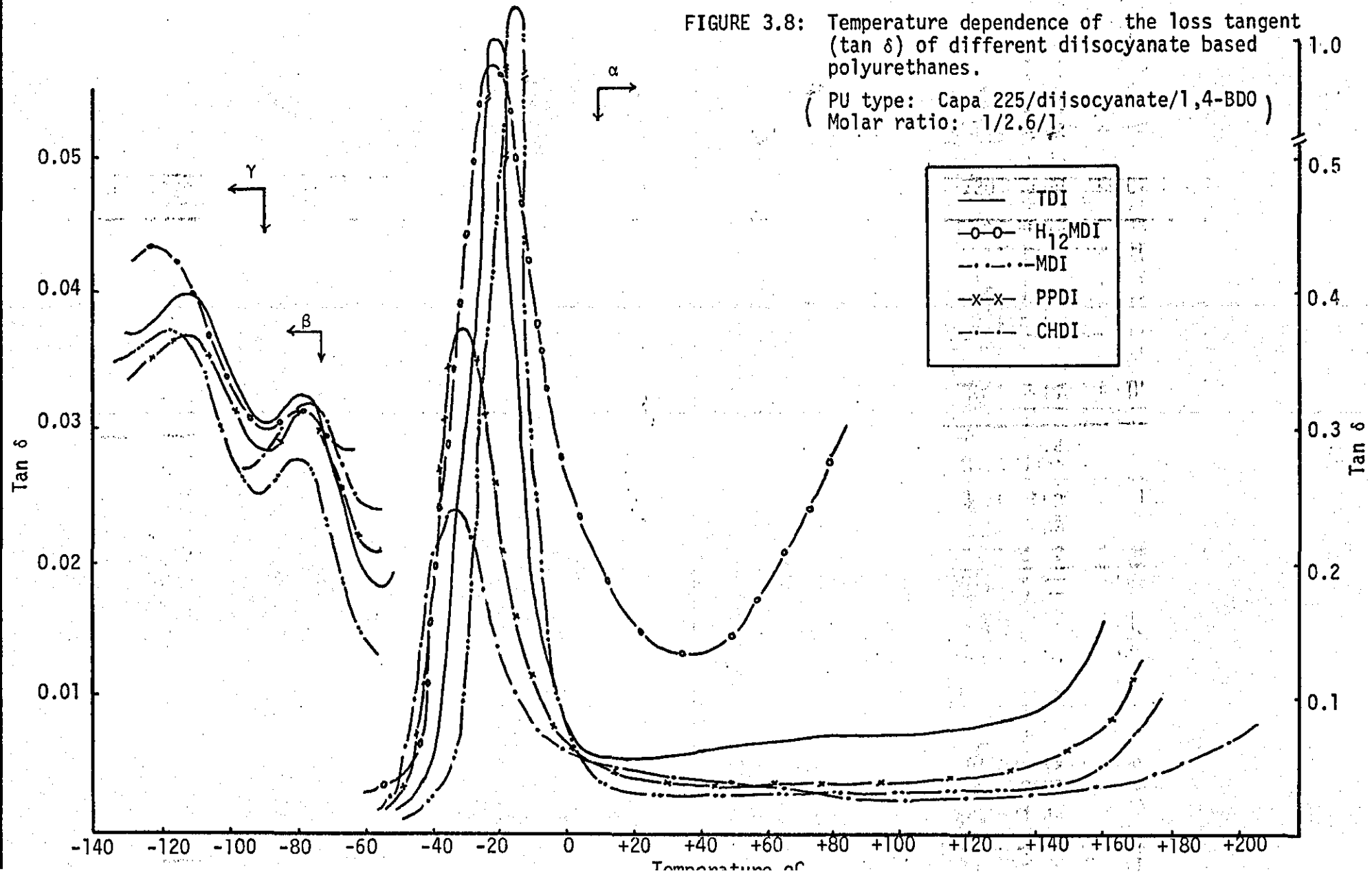


FIGURE 3.9: Storage modulus and $\tan \delta$ as a means of observing the dependence of temperature stability on mixed diisocyanate structure

(PU type: Capa 225/diisocyanate/1,4-BDO)
(Molar ratio: 1/3/2)

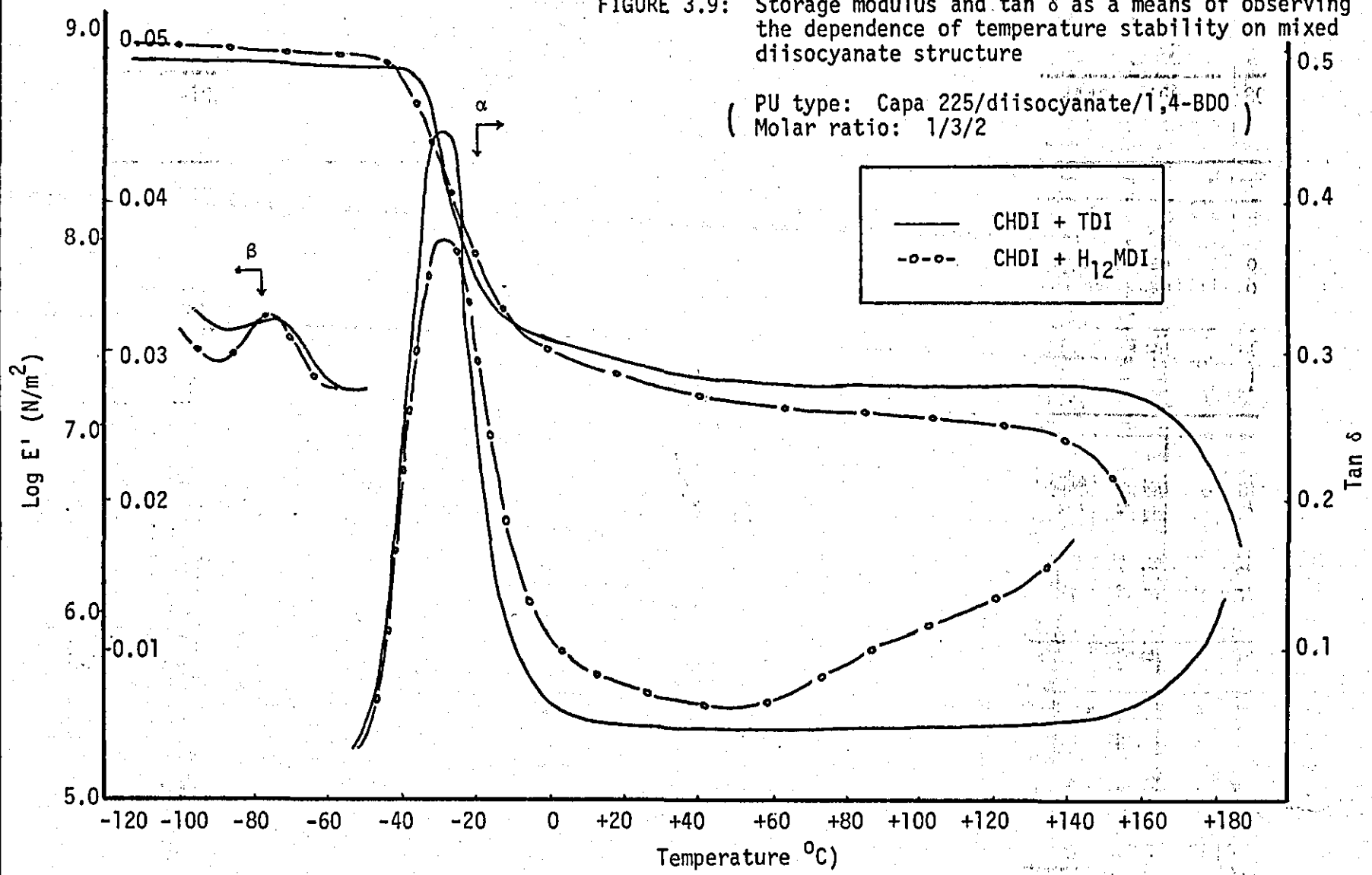


FIGURE 3.10: Storage modulus and $\tan \delta$ as a means of observing the dependence of temperature stability on molar ratios
(PU type: Capa 225/CHDI/1,4-BDO)

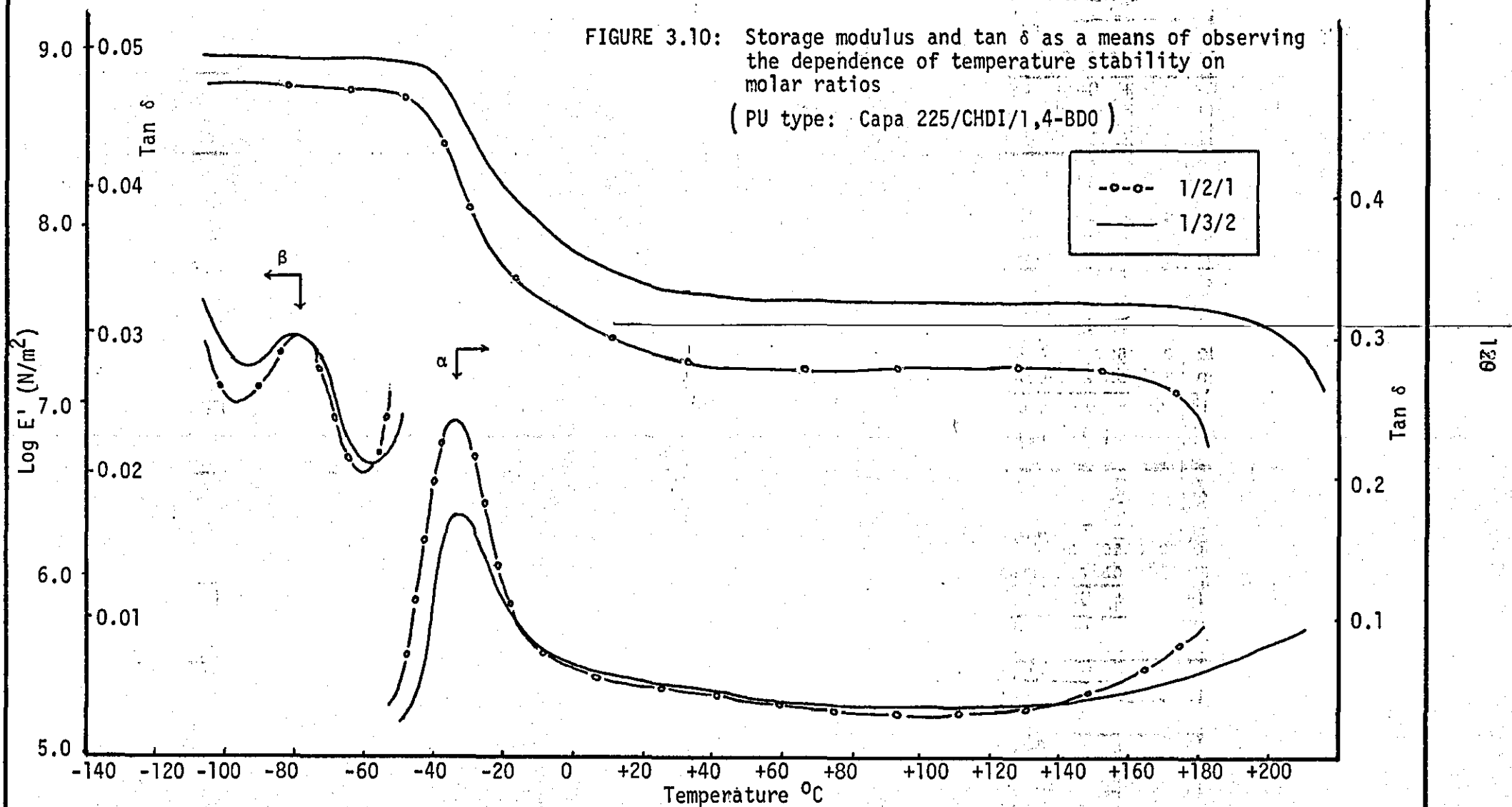
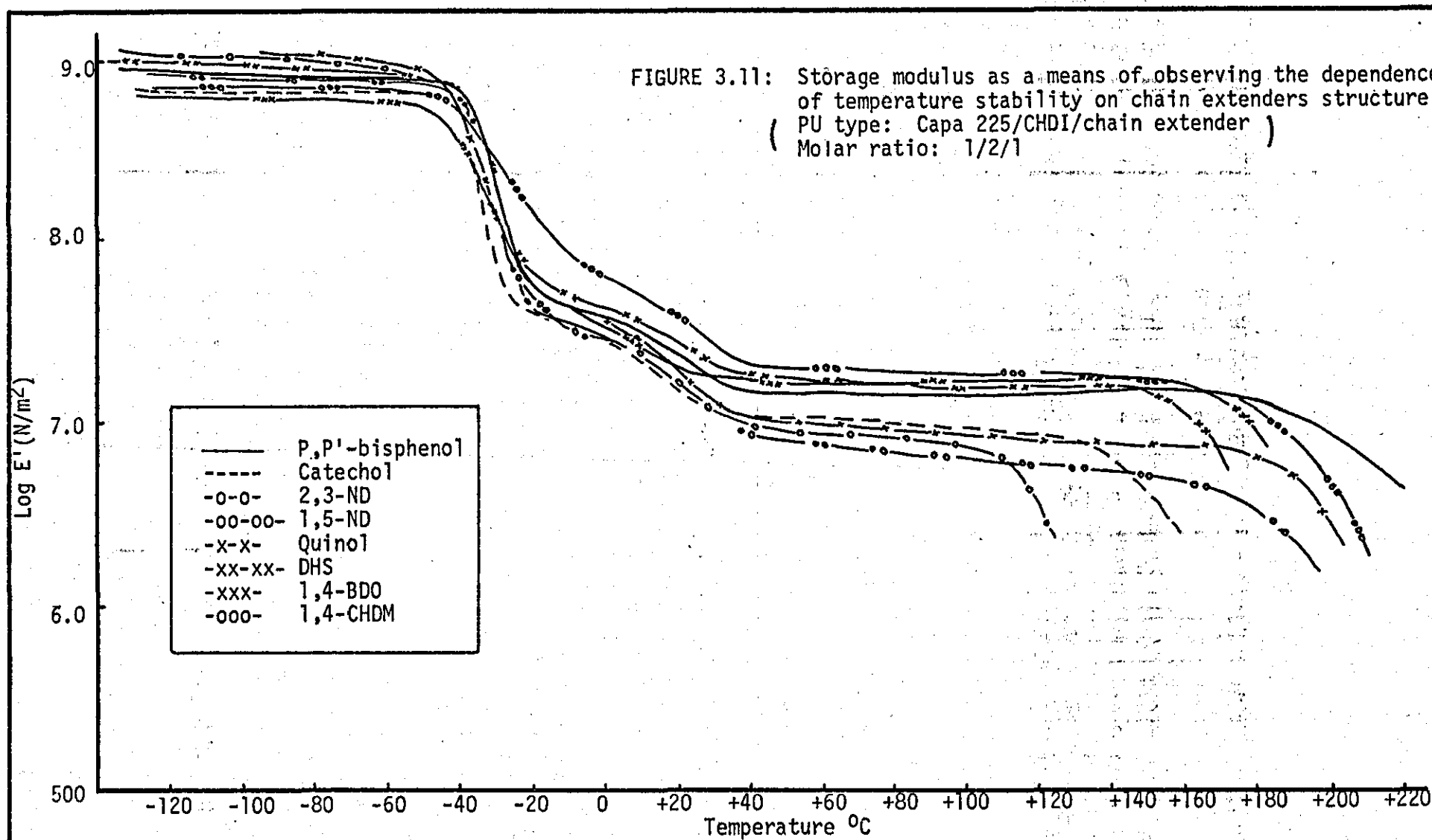
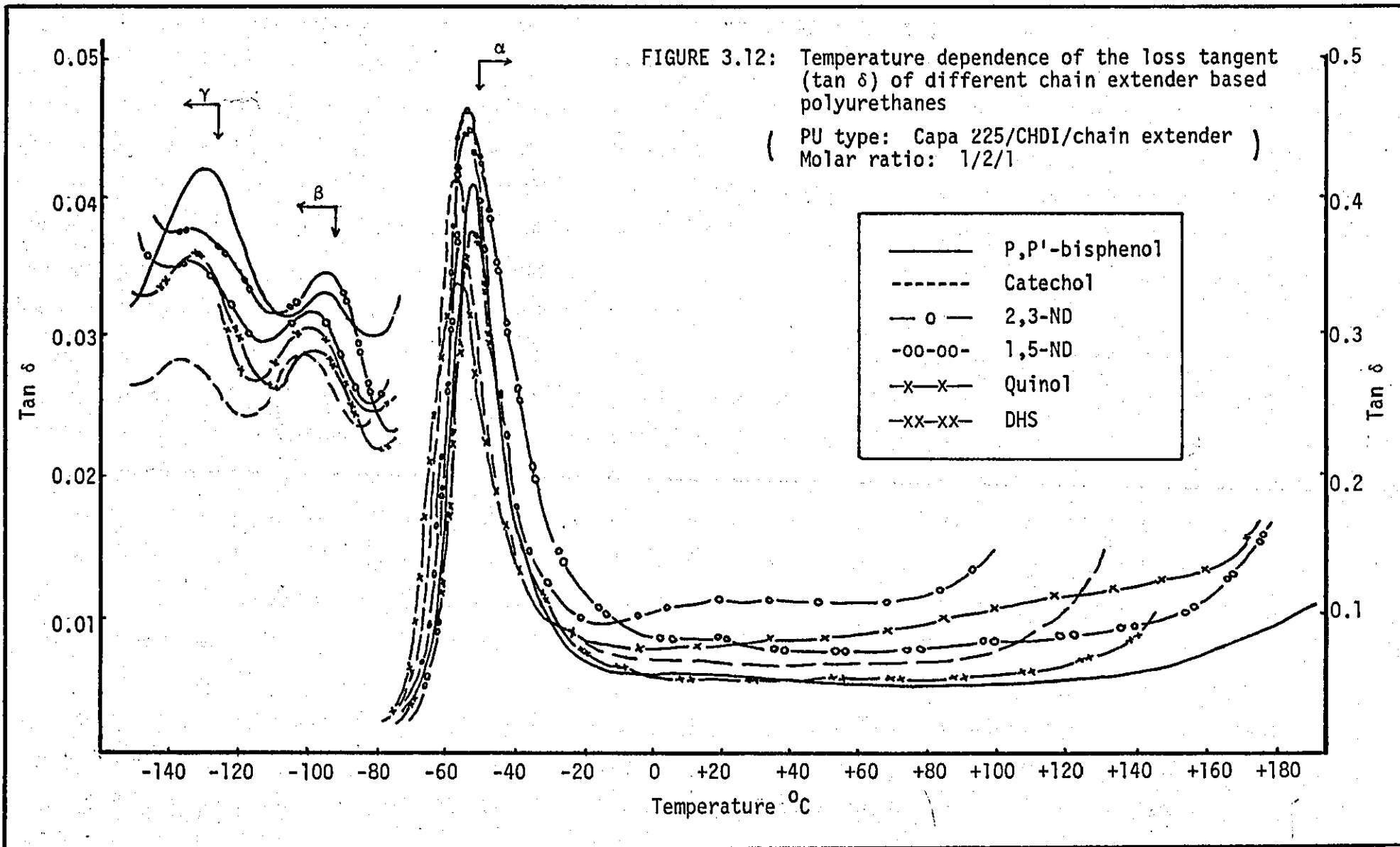
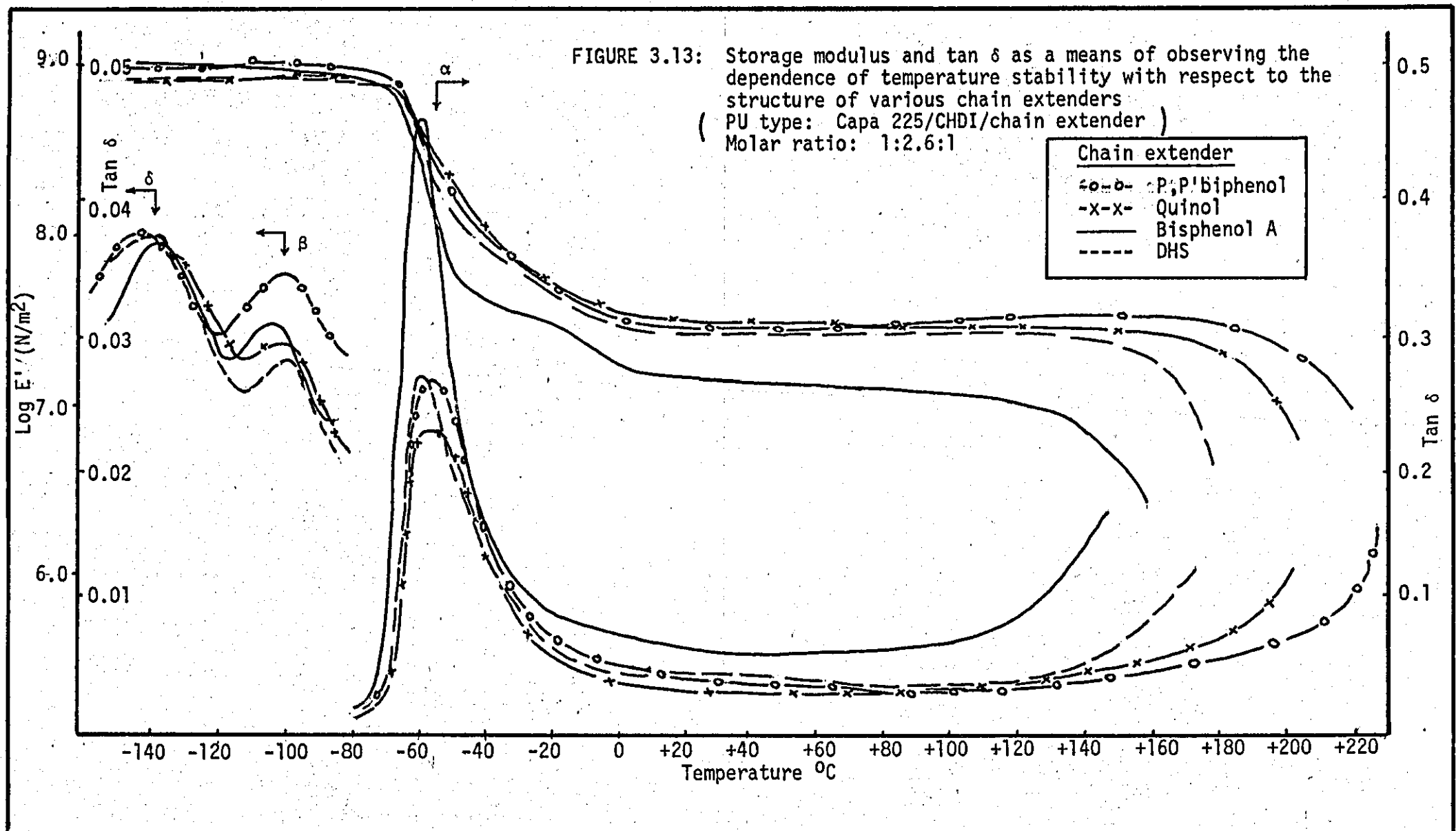
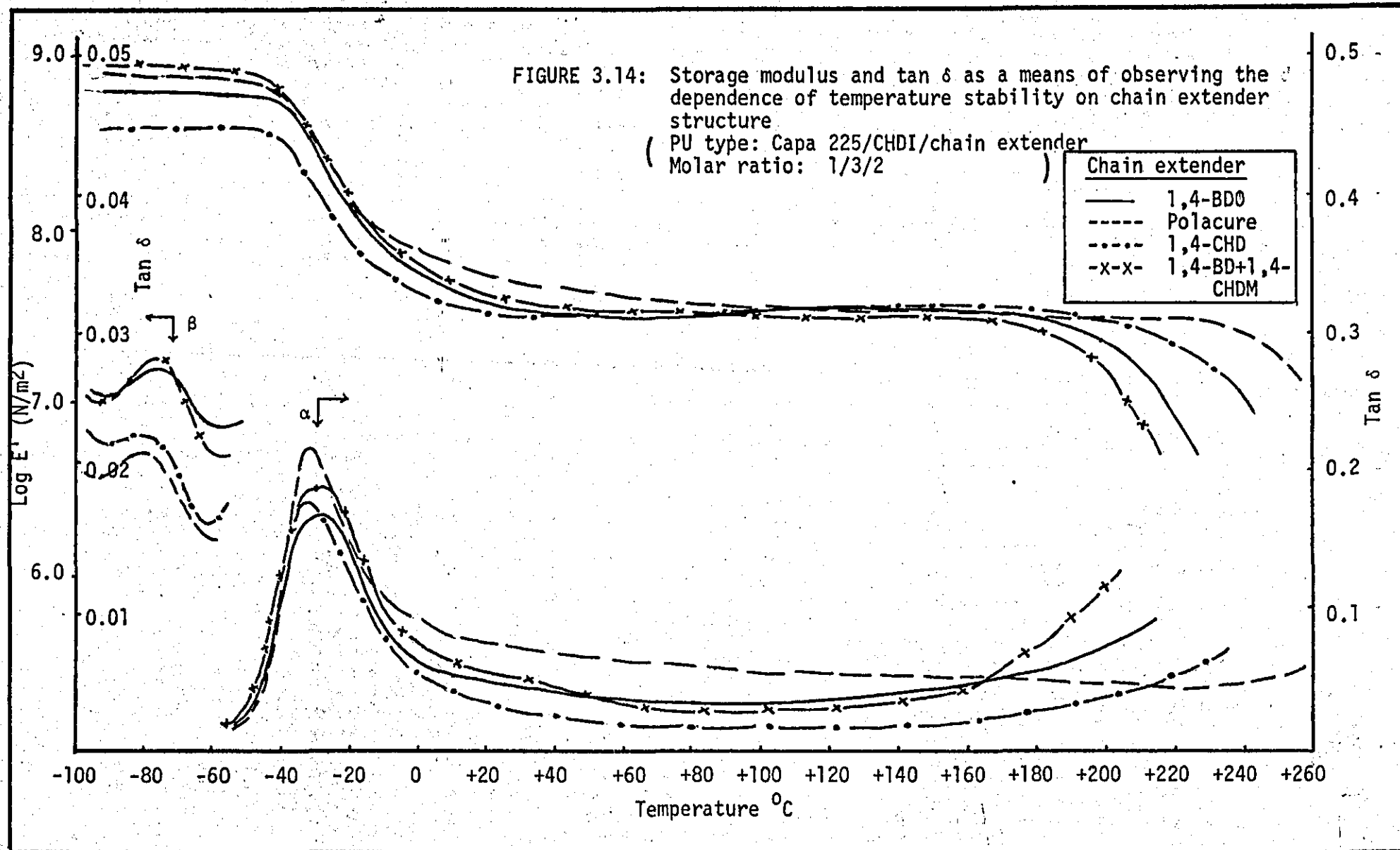


FIGURE 3.11: Storage modulus as a means of observing the dependence of temperature stability on chain extenders structure
 (PU type: Capa 225/CHDI/chain extender)
 Molar ratio: 1/2/1









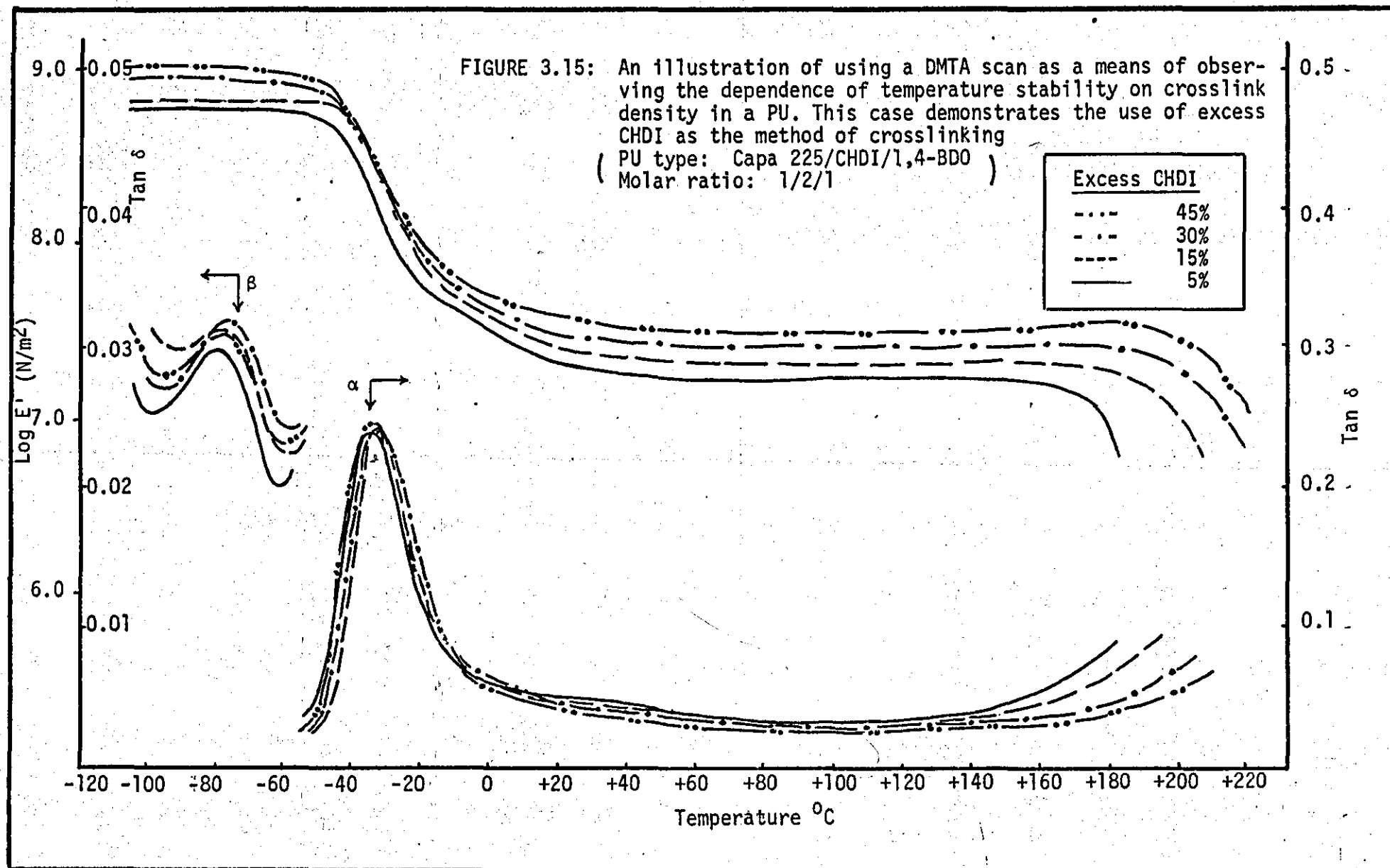
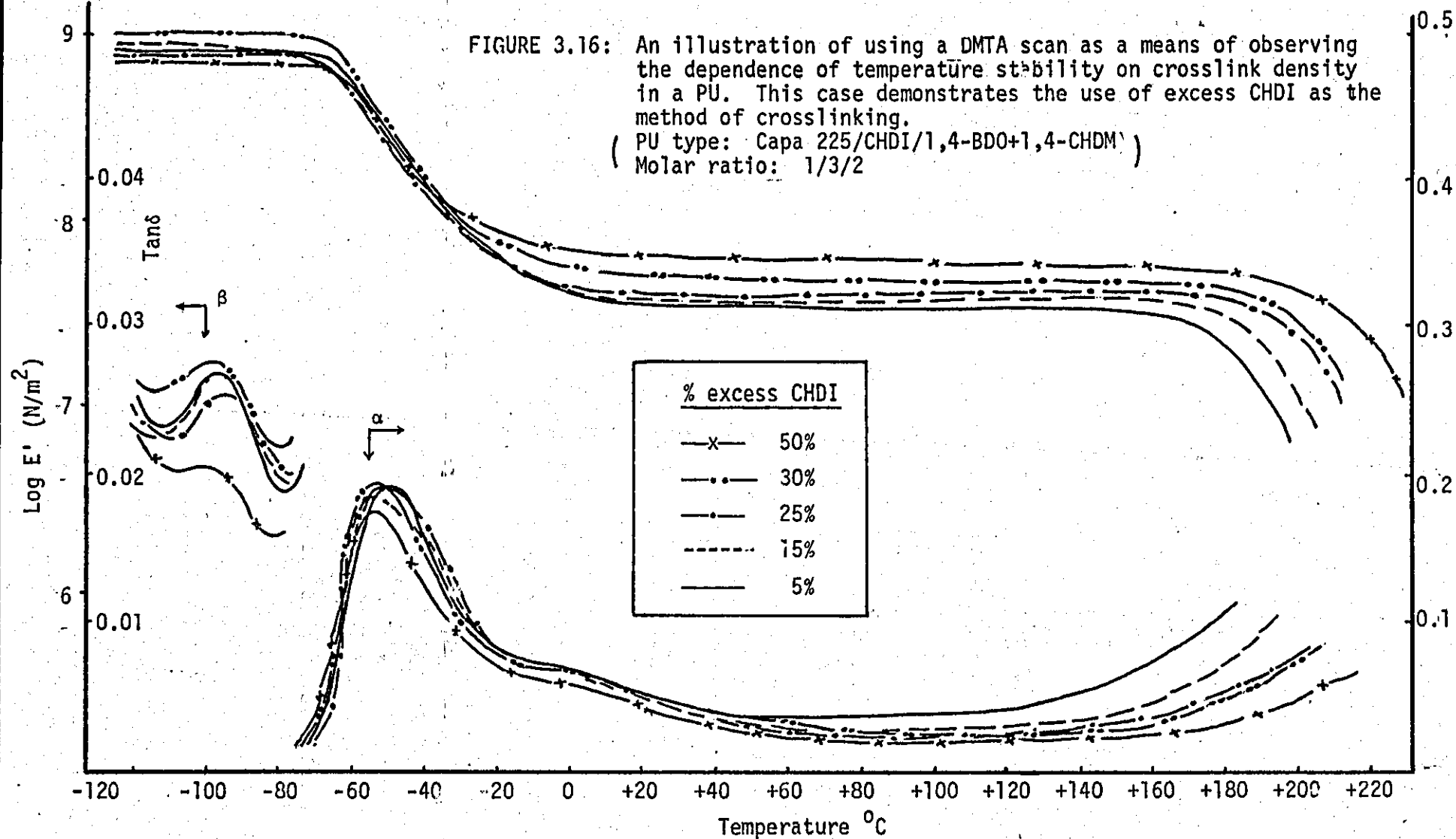
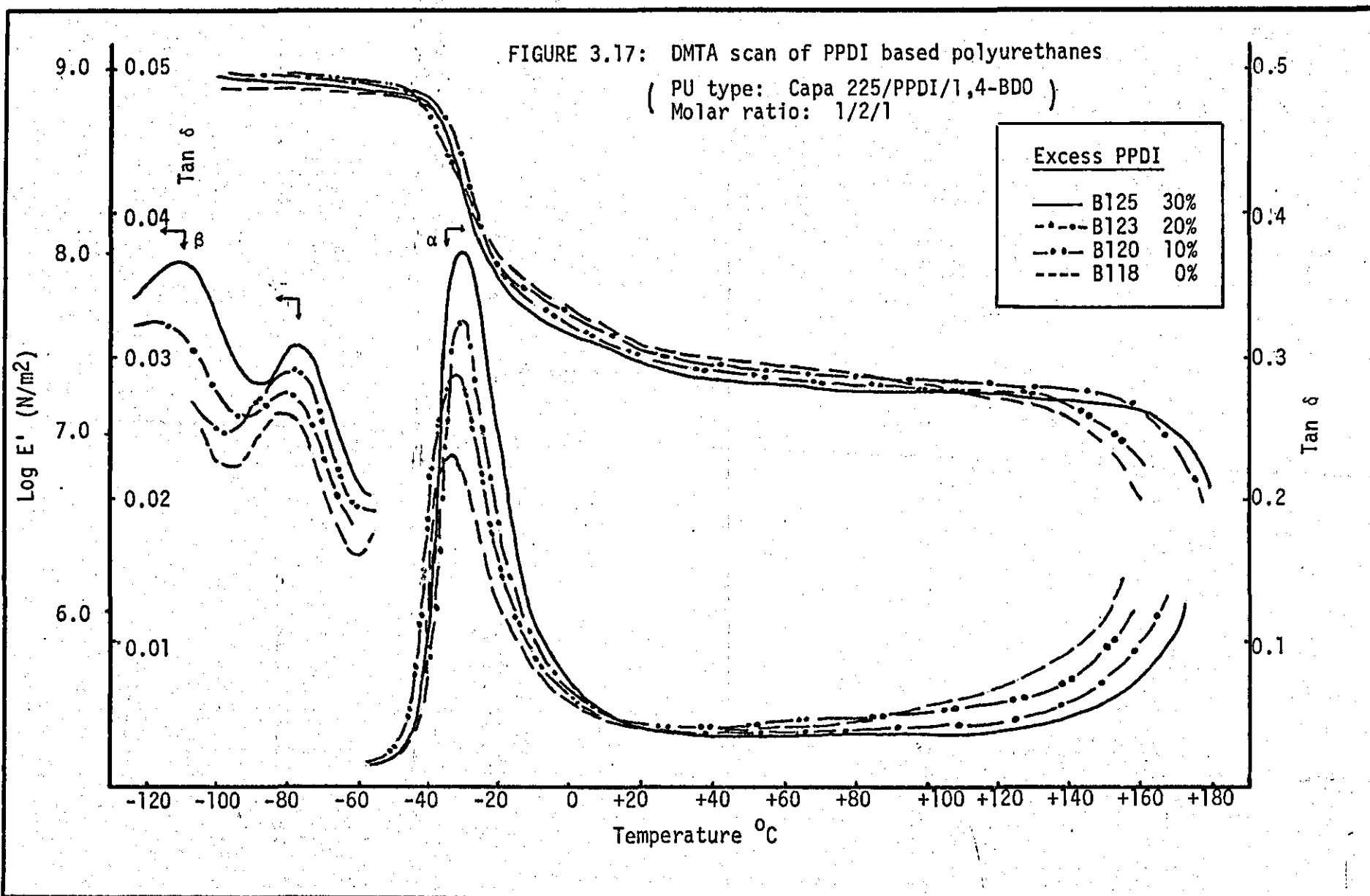


FIGURE 3.16: An illustration of using a DMTA scan as a means of observing the dependence of temperature stability on crosslink density in a PU. This case demonstrates the use of excess CHDI as the method of crosslinking.
 (PU type: Capa 225/CHDI/1,4-BDO+1,4-CHDM)
 Molar ratio: 1/3/2





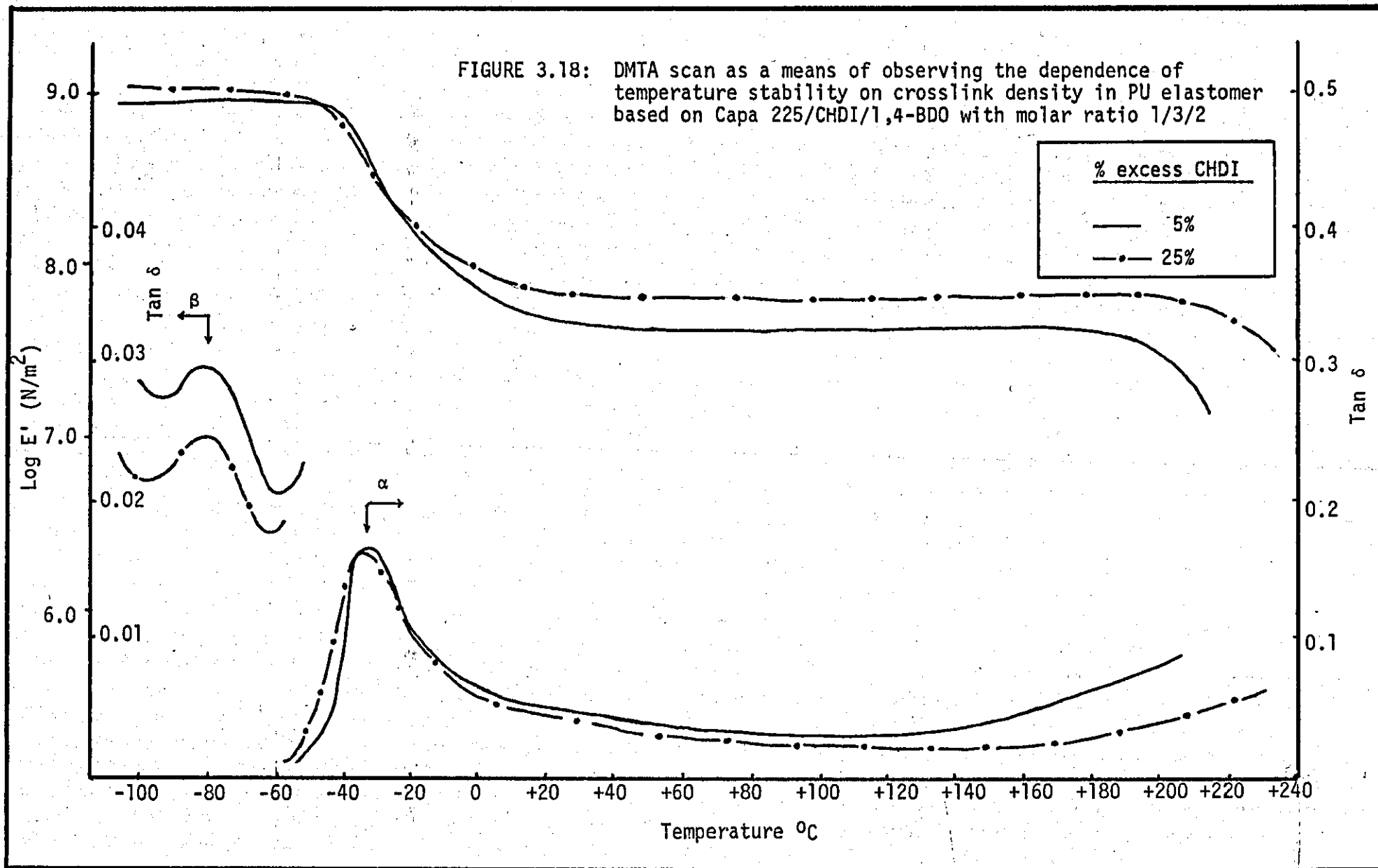
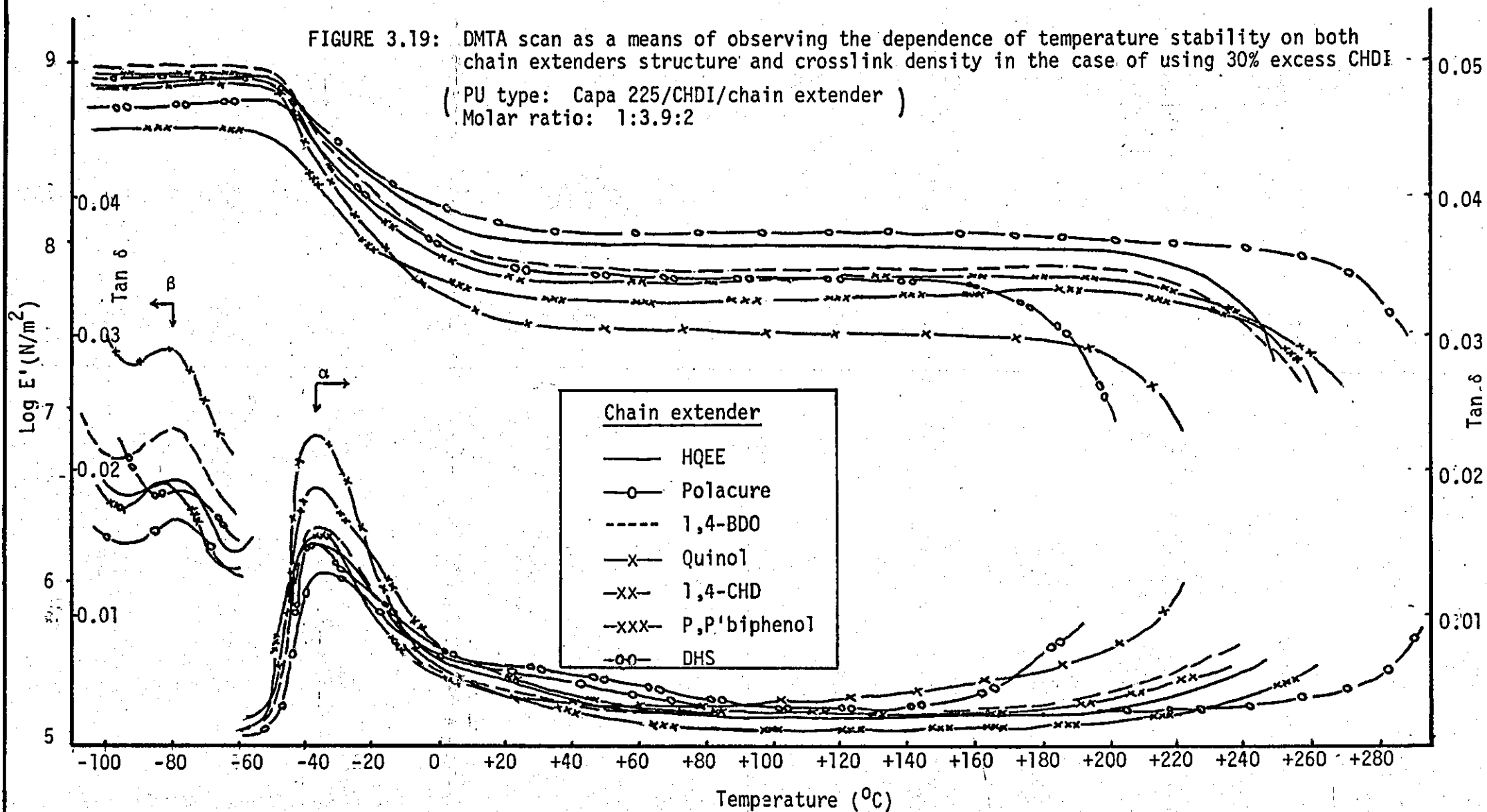
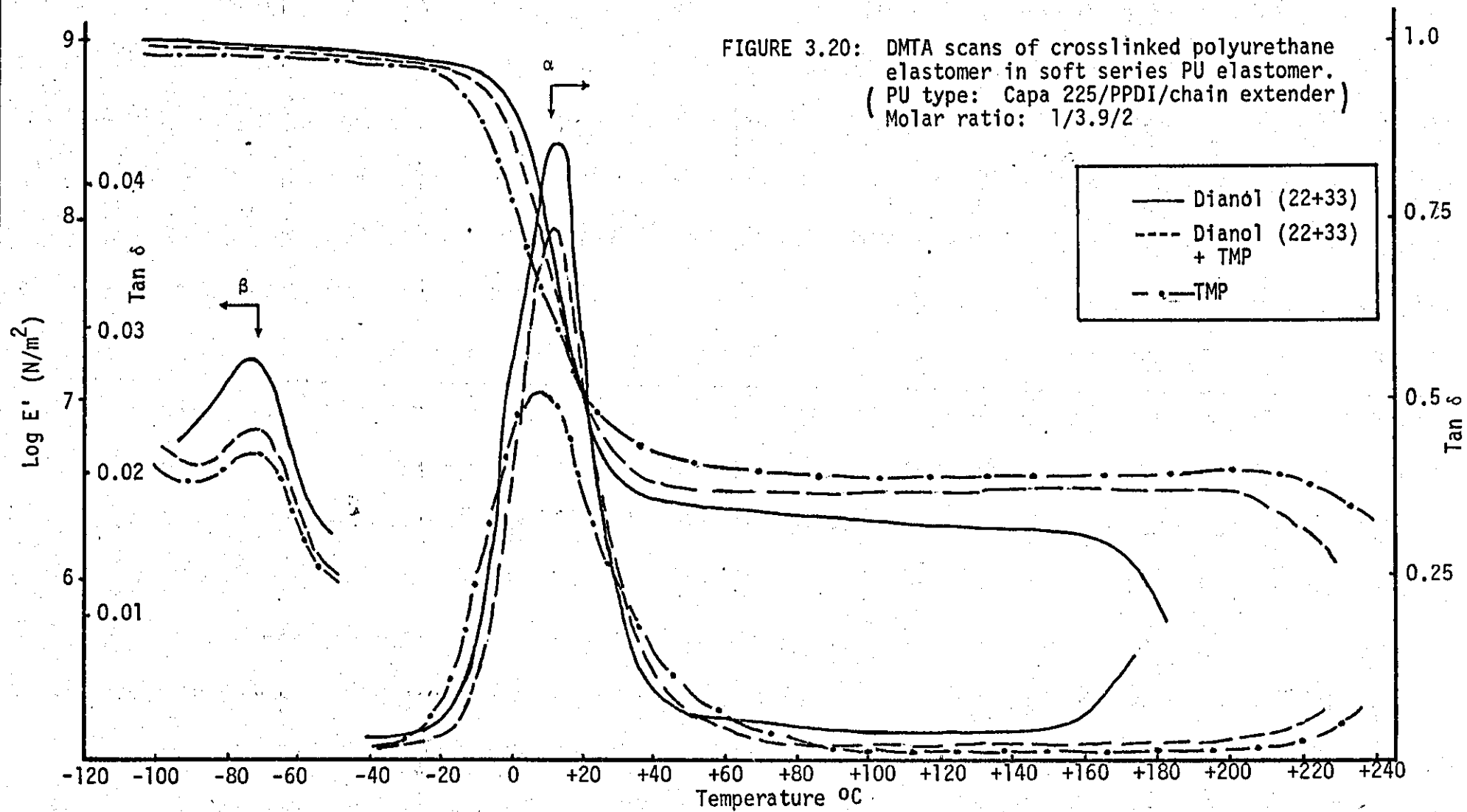


FIGURE 3.19: DMTA scan as a means of observing the dependence of temperature stability on both chain extenders structure and crosslink density in the case of using 30% excess CHDI
 (PU type: Capa 225/CHDI/chain extender)
 Molar ratio: 1:3.9:2





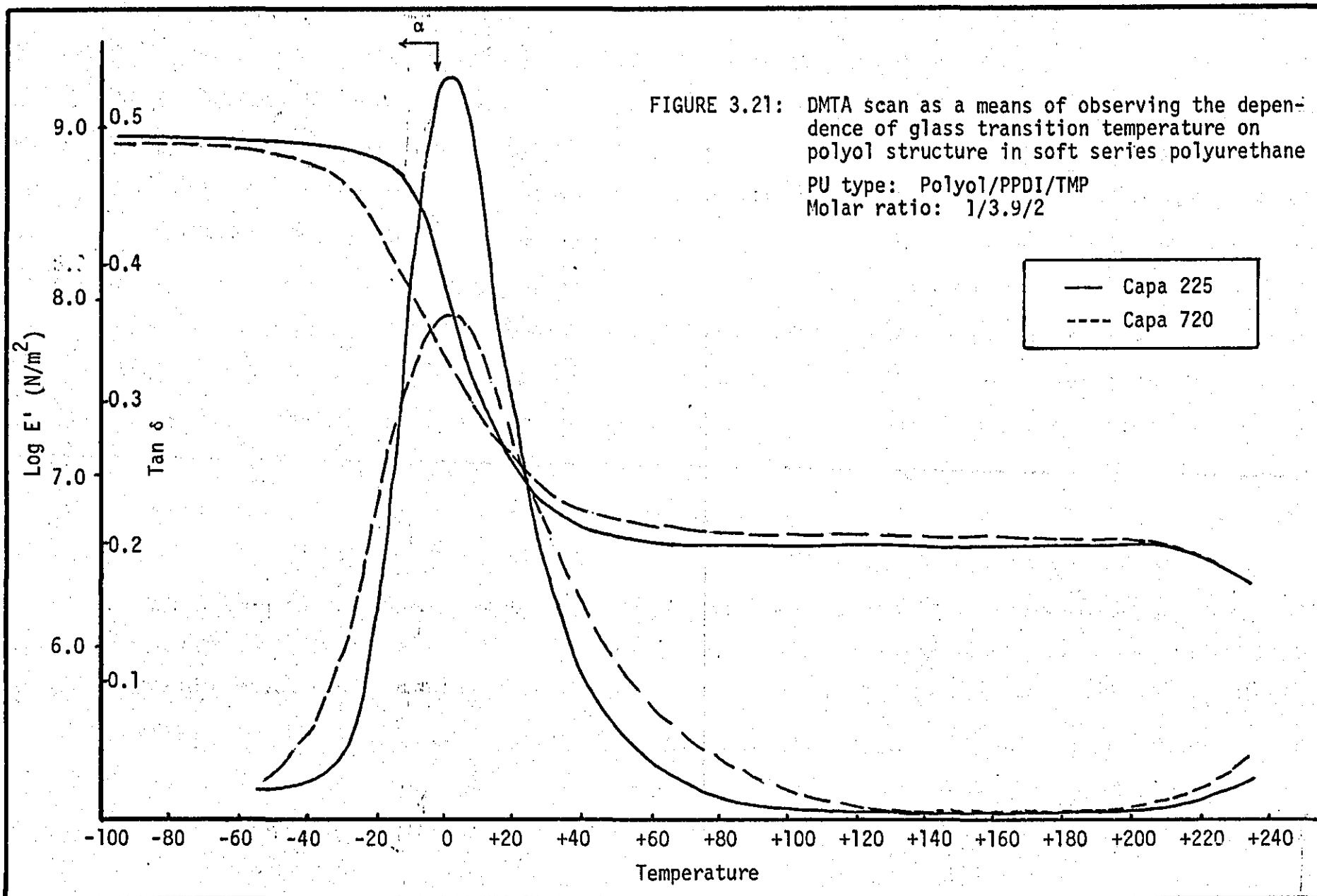
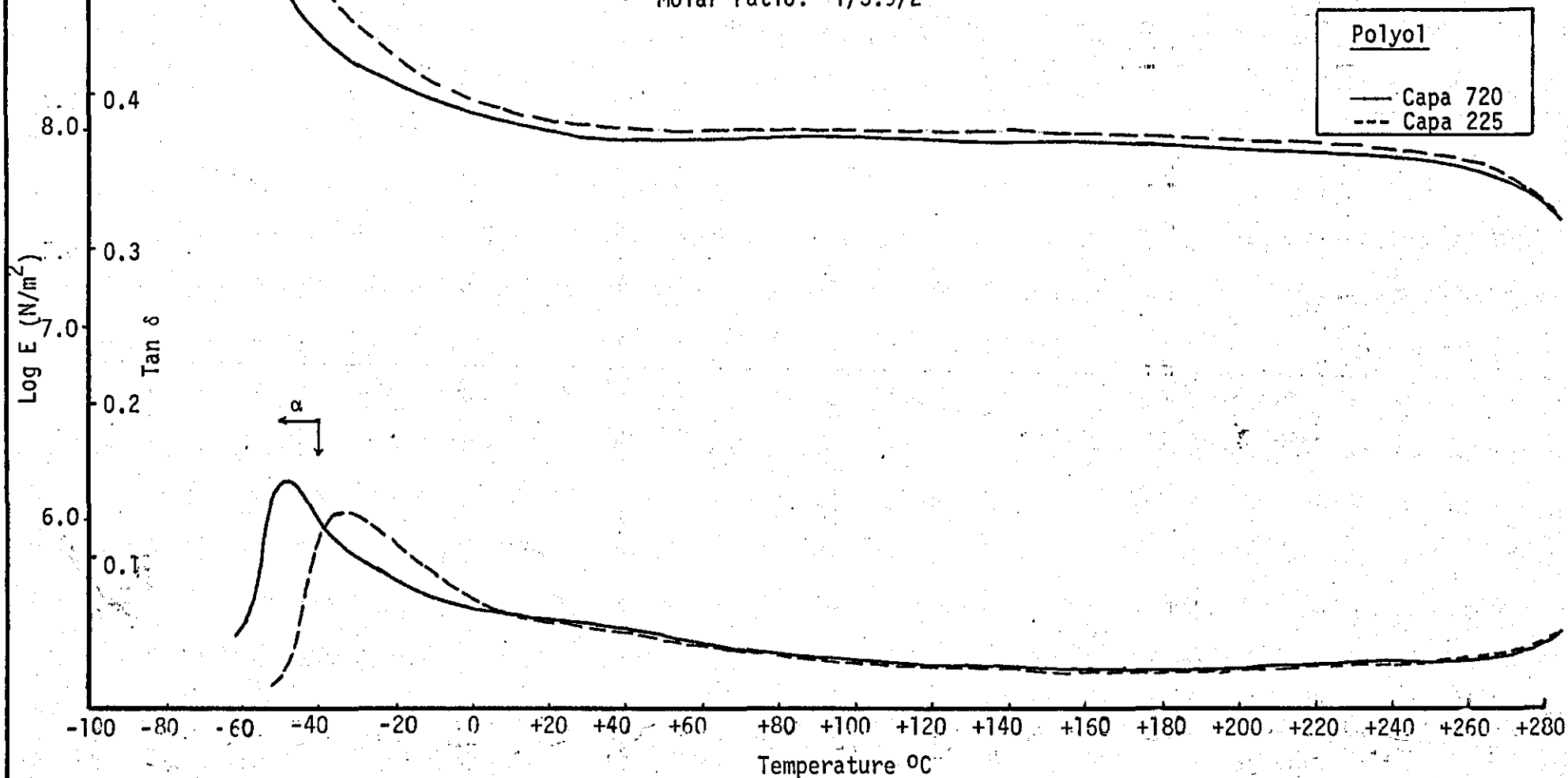


FIGURE 3.22: DMTA scan as a means of observing the dependence of glass transition temperature (T_g) on polyol structure in hard series polyurethanes

(PU type: Polyol/CHDI/Polacure)
Molar ratio: 1/3.9/2



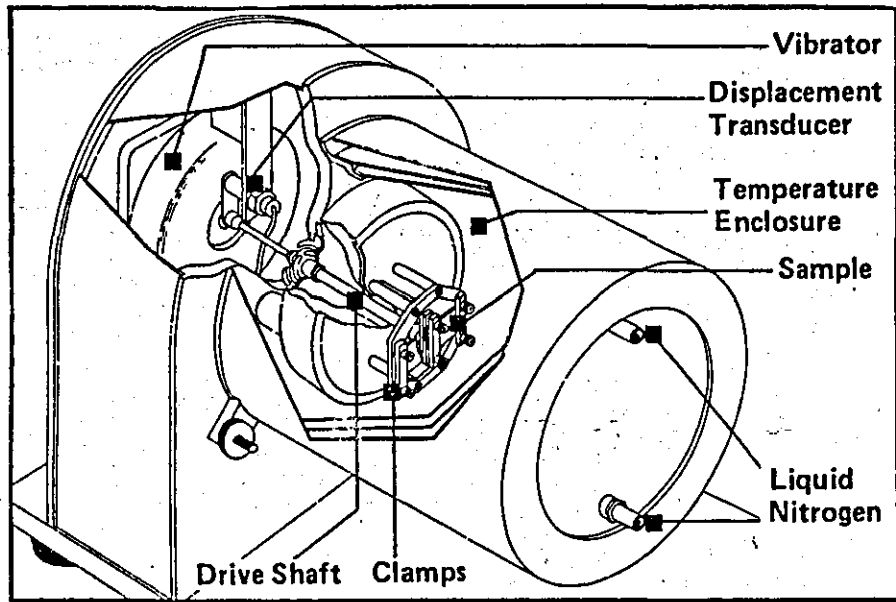


FIGURE 3.23: A Schematic View of the Mechanical Heat - cut away view

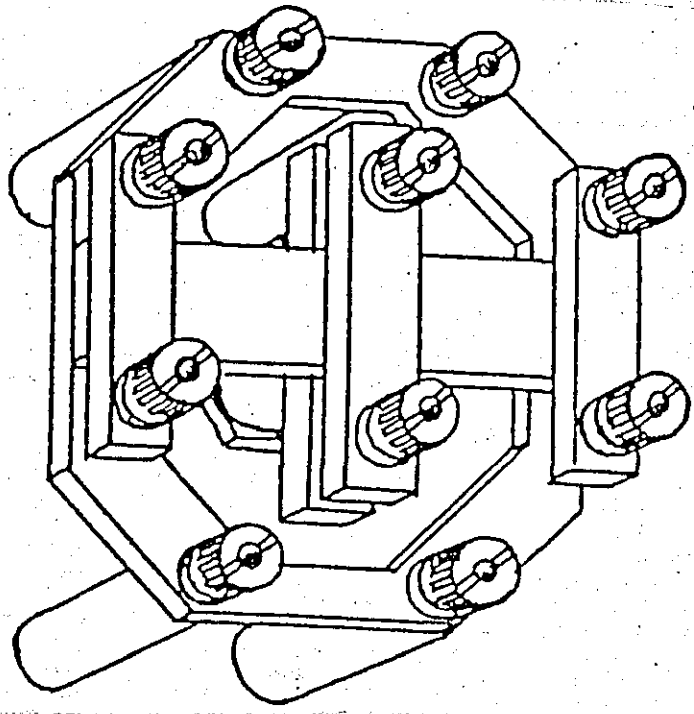


FIGURE 3.24: Urethane sample clamped in the PL-DMTA prior to measurement

3.2.2 Differential Scanning Calorimetry (DSC)

3.2.2.1 Introduction

Thermal properties of the variously prepared polyurethanes were also investigated by differential scanning calorimetry (DSC). Among all the thermal techniques available, DSC is one of the most widely used for polyurethane studies. Its usefulness as a significant analytical technique is to follow almost any physical and chemical changes that occur and produce a change in enthalpy and can therefore be followed by calorimetry¹⁵⁰. DSC is a technique which measures the heat flow into or out of a sample relative to an inert reference material when both are subjected to the same linear increase or decrease in temperature. The temperature difference between the sample and the reference is measured using twin thermocouples connected in position. When the temperature of the sample is equal to the reference, the two thermocouples produce identical voltages and therefore the net voltage equals zero. When the temperature between the two differs there is produced a net voltage which is proportional to the difference in temperature between the reference and the sample under examination. Thus net voltage is amplified and recorded on the Y-axis of an X-Y recorder. The temperature of the experimental reference material which is varied at a programmed constant rate, is monitored on the X-axis.

With regard to polyurethanes, it was believed at first that observed thermal transitions generally fell into three groups as follows:

- i) Below -30°C - associated with the T_g of the soft block;
- ii) Between $80-150^{\circ}\text{C}$ - frequently ascribed to the dissociation of soft/hard segment hydrogen bonds;
- iii) Above 160°C - associated with the thermal dissociation of hard block aggregates which may be crystalline or paracrystalline.

However further research by workers has since changed these interpretations. It is now believed that there are three transitions above room temperature to be observed making with the glass transition, a total of four altogether. The transitions above room temperature are also now thought to be the result of changes in long and short ordering and not hydrogen bond dissociations.

These transitions have been labelled by Seymour and Cooper^{56,127} as follow:

- i) $70-80^{\circ}\text{C}$, T_m of shortest average hard segment. Sometimes this reflects the melting of soft segment crystallites.
- ii) $145-170^{\circ}\text{C}$, long range order hard segment melting.
- iii) Above 185°C , relatively well ordered microcrystalline aromatic polyurethane hard segments (not seen in polyurethanes with short hard segment lengths).

A schematic representation of ordered, non-crystalline domains and a highly ordered, crystalline domain are shown in Figure 3.25⁹⁶.

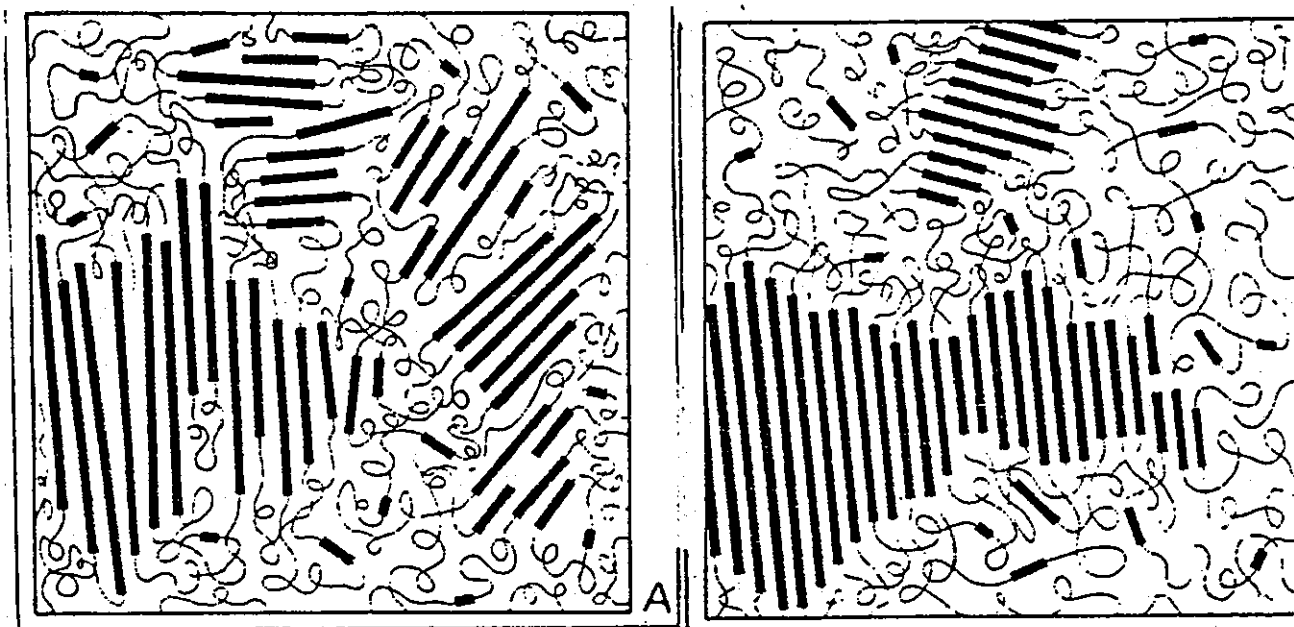


FIGURE 3.25: Schematic representation of two types of hard segment domain order (broad line - hard segment; thin line - soft segment). A-order, non crystalline hard segment domains; B-microcrystalline hard segment domains.⁹⁶

3.2.2.2 Experimental Procedure

DSC ~~thermogram~~ of prepared polyurethanes were measured on a Du Pont 990 thermal analyser in conjunction with a standard Du Pont heating cell. ~~scans~~ were recorded using urethane samples of 10-15 mg which were encapsulated in a small aluminium pan. An empty pan was used as a reference. In the case of some samples the cell was cooled to approximately -120°C by pouring liquid nitrogen into a steel jacket surround and then this is replaced by a cover. A bell jar also covers the cell and thus protects the user from any gas that might be generated and also permits cell evacuation to be possible. This cell is then

heated at a constant rate of $20^{\circ}\text{C}/\text{min}$ with a steady purge of dry nitrogen passing through. The ~~scans~~ were recorded between -100°C and 300°C or room temperature and 350°C on a two pen recorder, each pen being set at different sensitivities of 5 and 10 mV/cm. The simplified block diagram of the thermal analysis apparatus is shown in Figure 3.26.

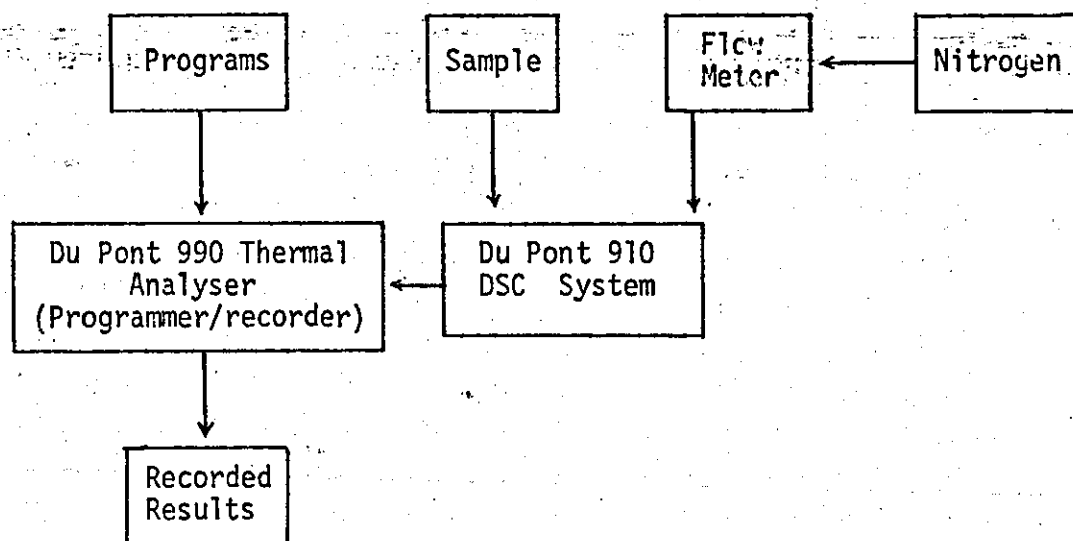


FIGURE 3.26: Block diagram of the thermal analysis apparatus

Before a thermal analysis experiment, temperature calibration of the apparatus was made with indium as a reference standard which has a crystalline melting point of 156.6°C . DSC samples were prepared from cast moulded sheets. X

3.2.2.3 Results and Discussion

The results of the DSC scans are presented in Figures 3.27 to 3.40 and Tables 3.21 to 3.32. The arrows in the figures designate the position of the transition temperatures.

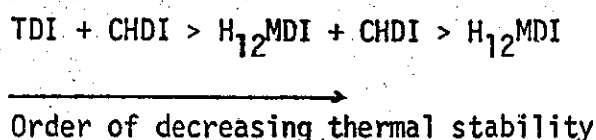
Figure 3.27 shows the DSC scans of various diisocyanate based polyurethane elastomers with the formulation of CAPA 225/diisocyanate/1,4-BD in the molar ratio of 1/2.6/1. Table 3.21 lists the position of the DSC endotherms for the first, second and third DSC traces taken for these polyurethanes. Those endotherms, which are observed to occur at above room temperature are associated with hard segment domains. The temperature at which the first transition takes place above room temperature is considered to indicate the limit of thermal stability of the PU elastomers. Table 3.21 gives the transition temperature for each system and it can be seen that the CHDI based polyurethane elastomer demonstrates relatively higher thermal stability than other diisocyanate based elastomers. As seen in Table 3.21 the first transition (above room temperature) of the CHDI based PU takes place at 249°C while the first transition of H₁₂MDI based PU happens at 80°C. This assignment was also confirmed by the DMTA results (Figure 3.7).

The first endotherm above room temperature which is denoted Transition I is believed to be the break up of short range order and the next higher series of endotherms (Transition II) is attributed to dissociation of long range ordering in the hard microphase. The highest endotherm (Transition III) is considered to correspond to microcrystalline hard segment melting. This is defined as the δ relaxation in the dynamic mechanical test procedure (DMTA).

Influence of the mixed diisocyanate structure

DSC results of Figure 3.28 and Table 3.22 enable information to be derived concerning the effect of mixed diisocyanates on transition temperature. Figure 3.28 shows the transition behaviour of three series of polyurethanes based on CAPA 225/H₁₂MDI/1,4-BD, CAPA 225/H₁₂MDI + CHDI/1,4-BD and CAPA 225/TDI + CHDI/1,4-BD with block ratios of 1/3/2. Arrows in these figures show the position of these transitions.

As seen in Table 3.22 the mixed H_{12} MDI + CHDI based PU shows higher transitions than H_{12} MDI based polyurethane. Thus it is clearly seen that the thermal stability of a polyurethane can be improved by using CHDI as a co-diisocyanate in H_{12} MDI based PU elastomer. It is also shown that the mixed TDI + CHDI based PU shows higher thermal stability than mixed H_{12} MDI + CHDI based polyurethane. Through Table 3.22 the following order of decreasing thermal stability is observed:



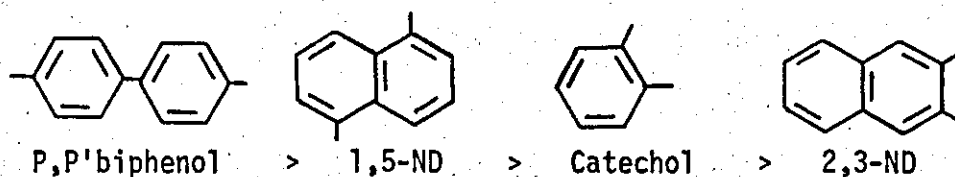
The same sequence of decreasing thermal stability with respect to diisocyanate type was observed from the DMTA results (Table 3.4).

Influence of block ratio

Figure 3.29 compares the transition temperature of the two series of PU elastomers based on CAPA 225/CHDI/1,4-BD with block ratios of 1/2/1 and 1/3/2 respectively. It is shown that the transition temperature increases with increasing block ratio. Transition temperatures of these PU elastomers are given in Table 3.23. As seen in this table, the transition temperature increases by 24°C through the use of the higher block ratio.

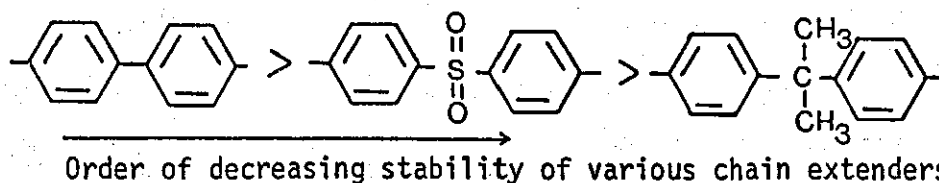
Influence of diol chain extender structure

Figure 3.30 shows the ~~thermogr~~ of a series of polyurethane elastomers based on CAPA 225/CHDI and chain extended with several different diol chain extenders with a block ratio of 1/2/1; so the variable is the chain extender. The position of each transition is designated by arrows. Table 3.24 gives the various transition temperatures of these different chain extender based PU elastomers. From Table 3.24 the following order of decreasing transition temperatures which represent the decreasing thermal stability is observed:



Order of decreasing thermal stability of various chain extenders

The influence of the diol chain extender structure on transition behaviour of PU elastomers was also studied in a series of CAPA 225/CHDI/chain extender based polymers by using different diols as chain extender with a PU of molar ratio of 1/2.6/1. Figure 3.31 compares the DSC ~~scans~~ of these different chain extender based PU elastomers. The hard segment transition temperatures of these polymers are given in Table 3.25. From the data obtained from this table, the following order of decreasing stability can be presented:



Influence of the diamine chain extender in comparison with diols

Figure 3.32 shows the DSC scans of diamine and diol extended PU elastomers based on CAPA 225/CHDI/chain extender with molar ratio of 1/3/2. The diols which are selected in this study were 1,4-BD, 1,4-BD + 1,4-CHDM, 1,4-CHD and the diamine was Polacure. Hard segment transition temperatures of these PU elastomers are given in Table 3.26. As seen in this table the Polacure based PU elastomers show a higher hard segment transition temperature and therefore, higher thermal stability by comparison with the diol based PU elastomers.

Influence of excess diisocyanate

Figure 3.33 represents the dependence of transition temperature on excess diisocyanate crosslinking in a polyurethane elastomer based on

the CAPA 225/CHDI/1,4-BD system. The data obtained from the Table 3.27 shows that as the amount of excess diisocyanate increases from 0.2% to 5%, the hard segment transition temperature increases from 205°C to 253°C; hence the temperature resistance is increased by nearly 50°C through the use of excess diisocyanate in the synthesis of the polyurethane elastomer. It can be seen that an approximately linear relationship applies between the quantity of crosslinking in a PU and its hard segment transition. Very generally for every 1% increase in the amount of excess diisocyanate left in the cast PU, the transition temperature increases by 1°C.

Figure 3.24 shows the DSC scans of the crosslinked PU elastomer based on CAPA 225/CHDI/1,4-BD + 1,4-CHDM with molar ratio of 1/3/2 to 1/4.2/2. The hard segment transition temperatures are given in Table 3.28, which shows the same trend of increasing transition temperature in the 1/2/1 series due to the increasing use of excess diisocyanate and hence resulting isocyanurate crosslinking. Figures 3.35 and 3.36 also show the DSC scans of crosslinked PU elastomers based on CAPA 225/CHDI/1,4-BD and CAPA 225/CHDI/Polacure systems respectively. Both figures represent the effect of using excess diisocyanate on transition temperature, and hence on thermal stability. The position of the transitions are shown by arrows.

Figure 3.37 shows the DSC scans of CAPA 225/CHDI/1,4-BD + 1,4-CHDM based PU elastomers which has run from -100°C to +300°C to show the soft segment T_g together with the hard segment transition temperature. Transition temperatures of these polymers are given in Table 3.29. As seen in the table the glass transition temperature is similar to the DMTA results (Figure 3.16). It is important to note that the effect of using excess diisocyanate on glass transition temperature of PU elastomers is very small, this means these PU elastomers are strongly phase separated.

DSC scans of PPDI based PU elastomers are shown in Figure 3.38 and the position of the hard segment transitions are designated by arrows. The exact transition temperature of these polymers is given in Table 3.30. As seen in this table, the hard segment transition temperature is also increased in the case of PPDI based PU elastomers due to the use of excess diisocyanate.

Influence of chain extender structure coupled with crosslinking

Figure 3.39 shows the DSC ~~scans~~ of a series of PU elastomers based on CAPA 225/CHDI and extended with several different diols and diamine chain extenders with block ratios of 1/3.9/2. The results obtained from this figure are given in Table 3.31. It can be seen by inspection that the use of excess CHDI together with an appropriate chain extender structure can give higher hard segment transition temperatures. For example, in the case of the Polacure based polyurethane, this when crosslinked with a 30% excess of CHDI, has an enhanced hard segment transition temperature occurring at 343°C. It means that the thermal stability of PU elastomers may be improved by the effect of the chain extender structure together with isocyanate crosslinking. Through the results obtained from Table 3.31 the following order of decreasing thermal stability can be concluded to apply through the use of the DSC technique and this enables conclusions similar to the DMTA results to be made.

Polacure > P,P-biphenol > 1,4-CHD > HQEE > Quinol > DHS
Order of decreasing thermal stability of various chain extenders

Figure 3.40 shows the DSC scans of the soft polymer series which is mostly based on PPDI and extended with TMP or mixed chain extenders. The transition temperatures of these polymers are given in Table 3.32. It can be seen that the transition increases by using TMP as a chain extension agent in comparison with TMP + Dianol (22+33) and Dianol (22+33).

chain extenders. This increasing transition temperature is attributed as due to increasing crosslinking density in the TMP based polymers.

Figure 3.40 also shows the DSC scan of a soft polymer based on CAPA 231/CHDI and chain extended with CAPA 305. The hard segment transition temperature of this PU elastomer is also given in Table 3.32.

TABLE 3.21: Transition Temperatures (above room temperature) of various diisocyanate based polyurethane elastomers*

Sample No	Diisocyanate	Transition Temperatures		
		I °C	II °C	III °C
B135	TDI	142	-	215
B134	H ₁₂ MDI	80	185	250
B138	MDI	130	-	250
B125	PPDI	190	221	261
B63	CHDI	-	249	-

* The polymers are based on Capa 225/diisocyanate/1,4-BD with block ratio 1/2.6/1

TABLE 3.22: Transition Temperatures of mixed diisocyanate based polyurethane elastomers*; a means of observing the effect of CHDI on thermal properties

Sample No	Diisocyanate	Transition Temperatures		
		I °C	II °C	III °C
B27	H ₁₂ MDI	62	104	152
B12	H ₁₂ MDI+CHDI	70	183	243
B38	TDI+CHDI	67	196	242

* The polymers are based on Capa 225/mixed diisocyanate/1,4-BD with block ratio 1/3/2

TABLE 3.23: Transition temperature of PU elastomers ; a means of observing the effect of block ratio on thermal properties

Sample No	Polyol	Diisocyanate	Chain Extender	Block Ratio	Transition* °C
B59	Capa 225	CHDI	1,4-BD	1/2/1	224
B84	Capa 225	CHDI	1,4-BD	1/3/2	248

* Hard segment transition

TABLE 3.24: Transition temperature of different chain extender based PU elastomers* ; a means of observing the effect of chain extender structure on thermal properties

Sample No	Chain Extender	Transition ** °C
B68	2,3-Naphthalene diol	230
B67	Catechol	250
B57	1,5-Naphthalene diol	280
-	P,P'biphenol	285

* The polymers are based on Capa 225/CHDI/chain extender with block ratio 1/2/1

** Hard segment transition

TABLE 3.25: Transition temperature of different chain extender based PU elastomers* in the case of using excess diisocyanate

Sample	Chain Extender	Transition ** °C
B95	Bisphenol A	214
B94	DHS	228
B92	P,P'biphenol	288

* The polymers are based on Capa 225/CHDI/chain extender with block ratio 1/2.6/1

** Hard segment transition

TABLE 3.26: Transition temperature of diamine and diols based PU elastomers* as a means of observing the influence of their structure on thermal properties

Sample No	Chain Extender	Transition** °C
Capa 18.6	1,4-BD + 1,4-CHDM	245
B84	1,4-BD	245
B51	1,4-CHD	264
B142	Polacure	334

* The polymers are based on Capa 225/CHDI/chain extender with block ratio 1/3/2

** Hard segment transition

TABLE 3.27: Transition temperature of crosslinked PU elastomers* ; a means of observing the influence of excess diisocyanate on thermal properties

Sample No	Capa 17.1	B59	B60	B61	B62	B63	B64	B66	A'6
% Excess CHDI	2	5	10	15	20	30	35	45	50
Transition ** °C	205	225	237	240	242	246	250	251	253

* The polymers are based on Capa 225/CHDI/1,4-BD with block ratio 1/2/1 to 1/3/1

** Hard segment transition

TABLE 3.28: Transition temperature of crosslinked PU elastomers based on Capa 225/CHDI/1,4-BD+1,4-CHDM with block ratio 1/3/2 to 1/4.2/2 ; a means of observing the influence of excess CHDI on thermal properties

Sample No	Capa 18.6	B74	B76	B78	B79	B81
% Excess CHDI	0.2	5	15	25	30	40
Transition*	246	248	254	262	265	267

* Hard segment transition

TABLE 3.29: Transition temperatures of mixed chain extender based PU elastomers* ; a means of observing soft and hard segment transitions

Sample No	% Excess CHDI	Transition Temperature	
		Tg °C ^(a)	Tg °C ^(b)
Capa 18.6	0.2	-35	246
B77	20	-35	257
B79	30	-35	265

(a) Tg of soft segment

(b) Tg of hard segment

* The polymers are based on Capa 225/CHDI/1,4-BD+1,4-CHDM with block ratio 1/3/2

TABLE 3.30: Transition temperature of PPDI based PU elastomers* ; a means of observing the influence of excess PPDI on thermal properties

Sample No	B118	B120	B123	B124	B125	B126
% Excess PPDI	0	5	20	25	30	35
Transition Temperature °C**	135	183	184	187	190	192

* The polymers are based on Capa 225/PPDI/1,4-BD with block ratio 1/2/1

** Hard segment transition

TABLE 3.31: Transition temperature of crosslinked PU elastomer based on various diols and diamine chain extenders* ; a means of observing the effect of excess CHDI and chain extender structure on thermal properties

Chain Extender	DHS	Quinol	1,4-BD	HQEE	1,4-CHD	P,P'-Bi-phenol	Polacure
% Excess CHDI	30	30	30	30	30	30	30
Transition °C**	245	268	270	285	290	305	343

* Based on Capa 225/CHDI/chain extender with block ratio 1/3.9/2

** Hard segment transition

TABLE 3.32: Transition temperature of soft polymer series PU elastomers

Sample No	Polyol	Diisocyanate	Chain Extender	Block Ratio	% Excess Diisocyanate	Transition °C
B103	Capa 225	PPDI	Dianol (22+33)	1/3.9/2	30	276
B106	Capa 225	PPDI	Dianol (22+33)+ TMP (1/1)	1/3.9/2	30	284
B108	Capa 225	PPDI	TMP	1/3.9/2	30	298
B130	Capa 225	PPDI	TMP	2/5.2/2	30	290
B131	Capa 240+ Capa 305	PPDI	TMP	1/3.9/2	30	265
B155	Capa 231	CHDI	Capa 305	1/3.9/2	30	228

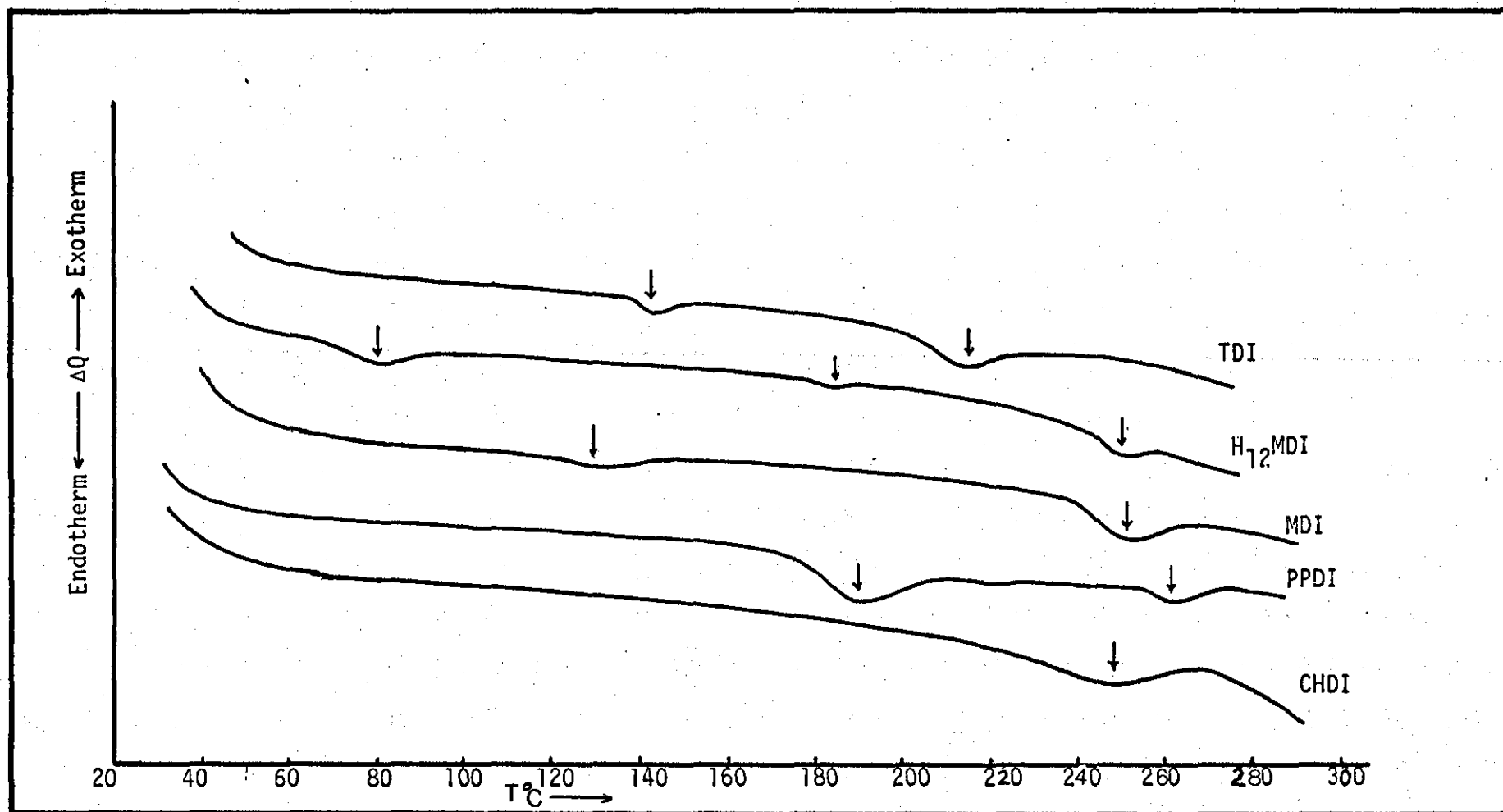


FIGURE 3.27: DSC Scans of Various Diisocyanate Based Polyurethane Elastomers (arrow designates the position of transitions).

PU type: Capa 225/diisocyanate/1,4-BD.

Molar ratio: 1/2.6/1

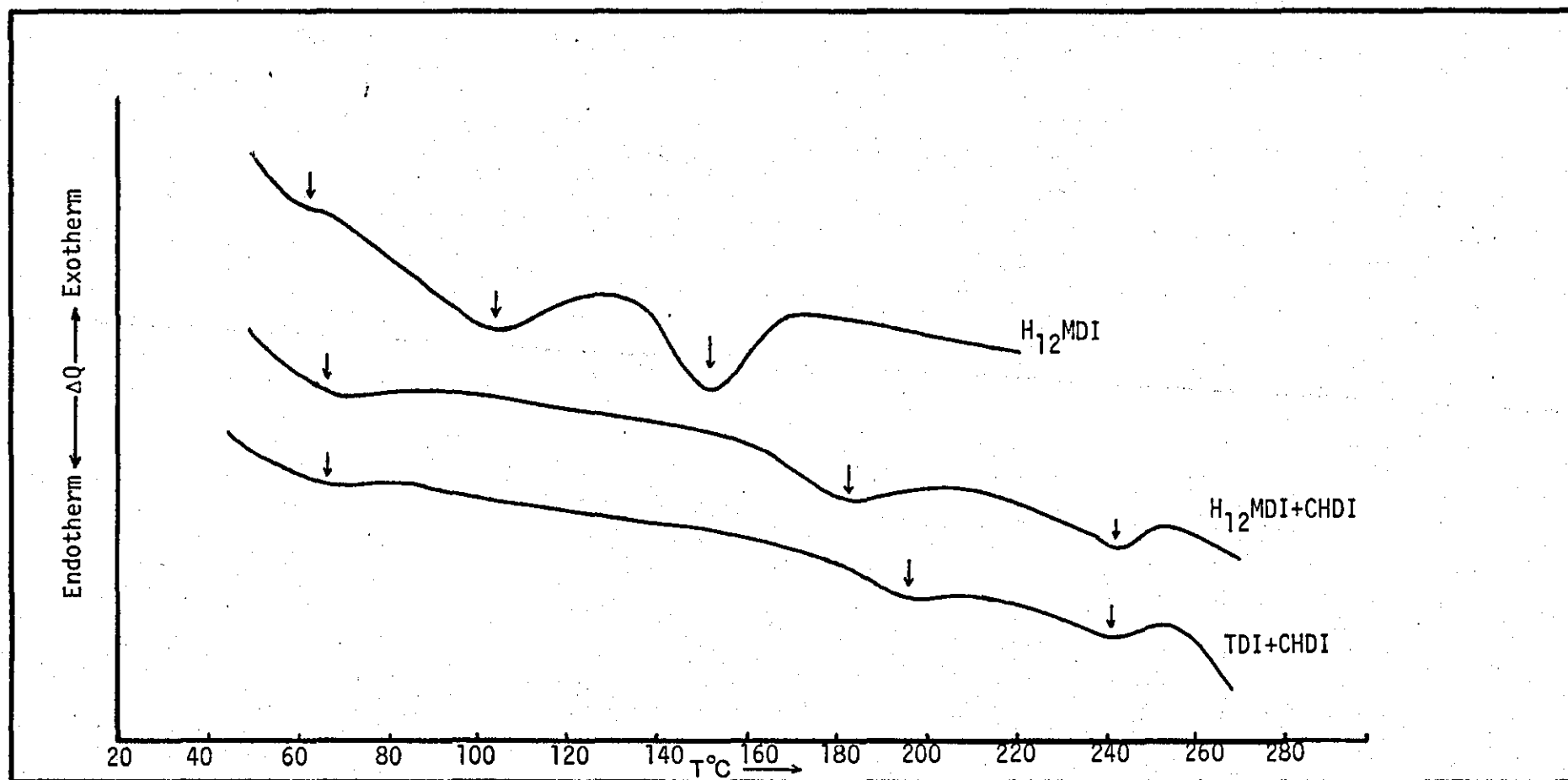


FIGURE 3.28: DSC Scans of Mixed Diisocyanate Based Polyurethane Elastomer as a means of observing the effect of CHDI on transition temperature

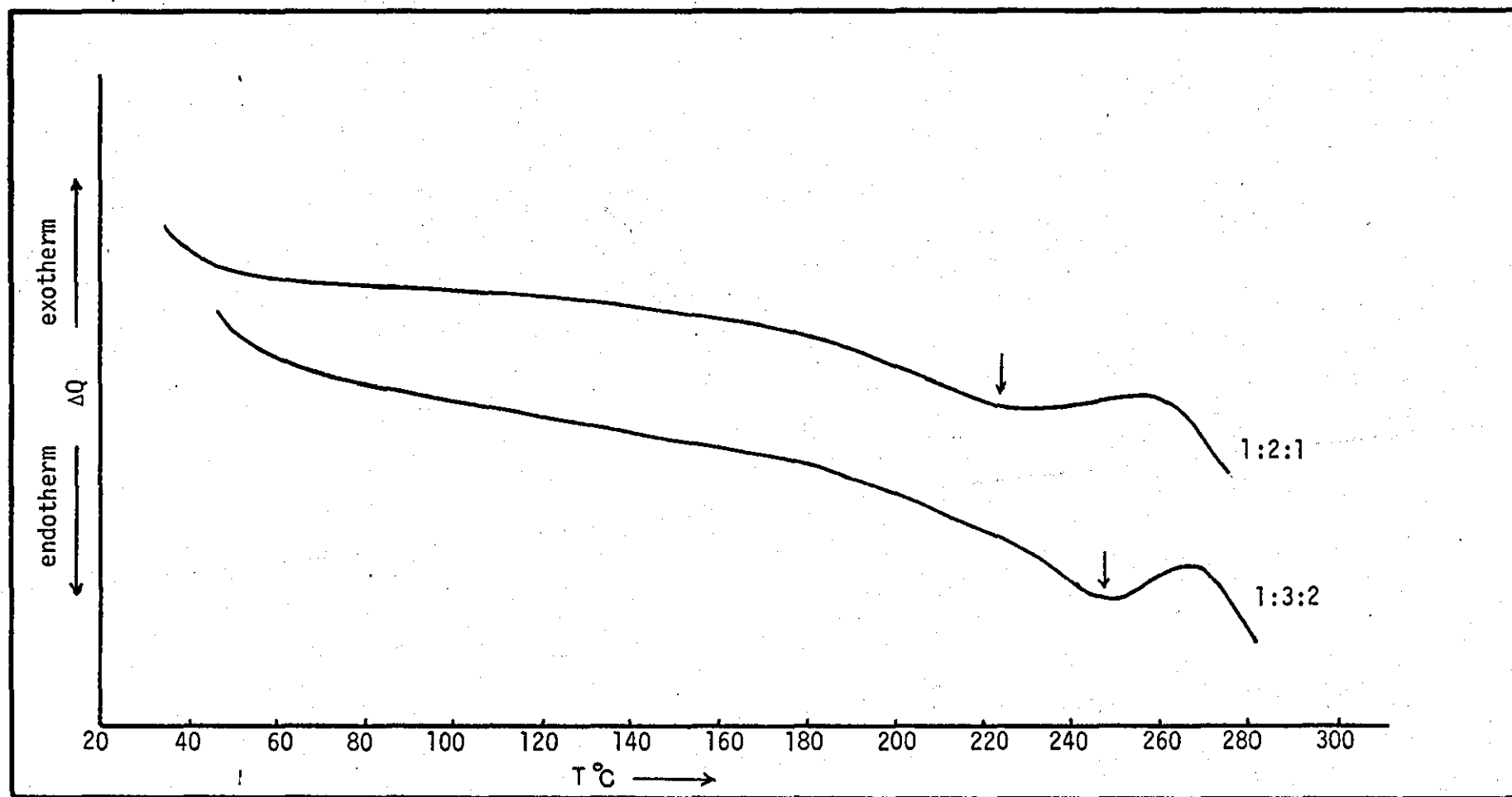


FIGURE 3.29! DSC Scans of Polyurethane Elastomer Based on Capa 225/CHDI/1,4-BD with Different Block Ratios

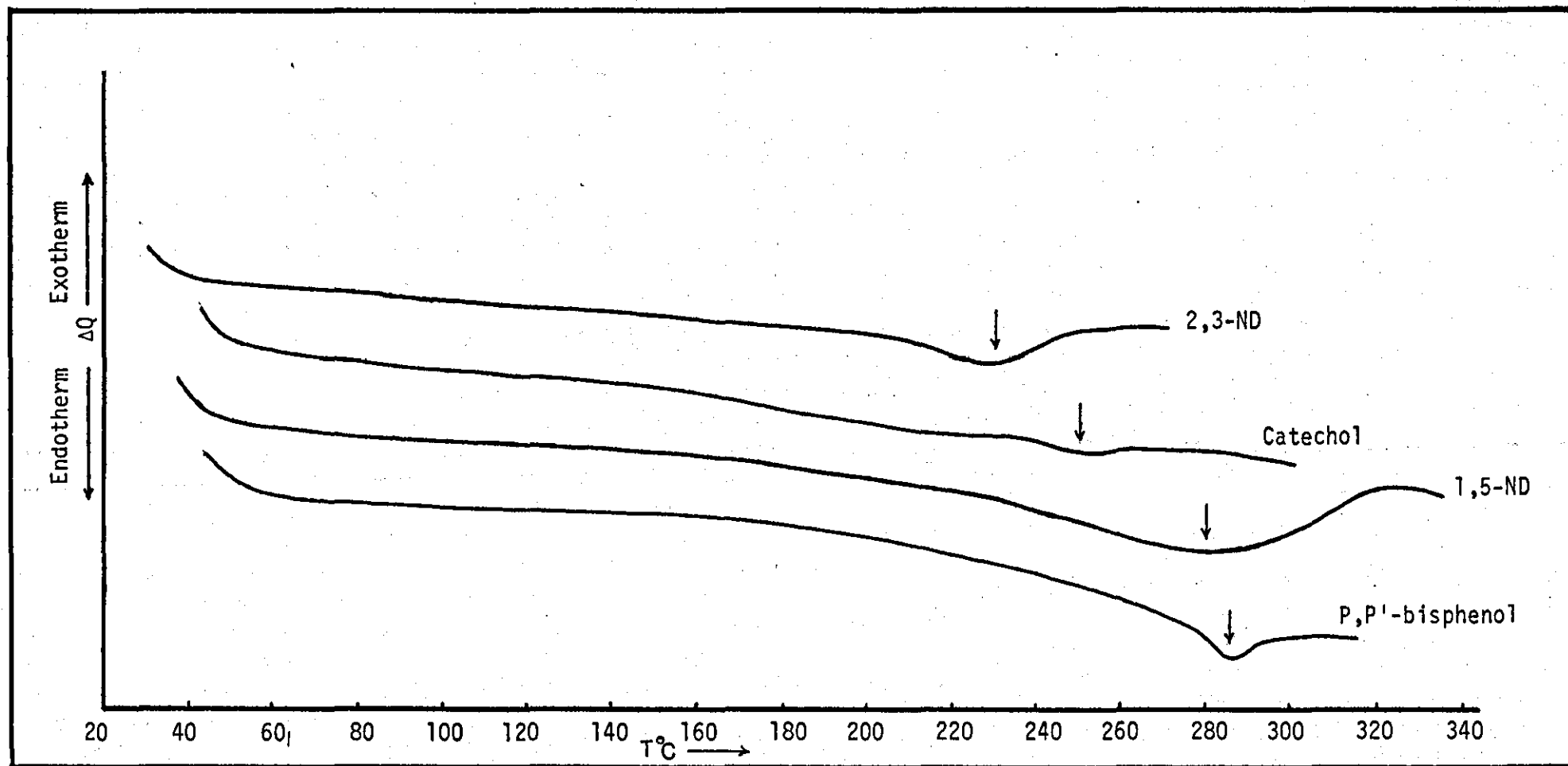


FIGURE 3.30: DSC Scans of Different Chain Extender Based Polyurethane Elastomers (arrow designates the position of transitions).
 PU type: Capa 225/CHDI/chain extender
 Molar ratio: 1 / 2 / 1

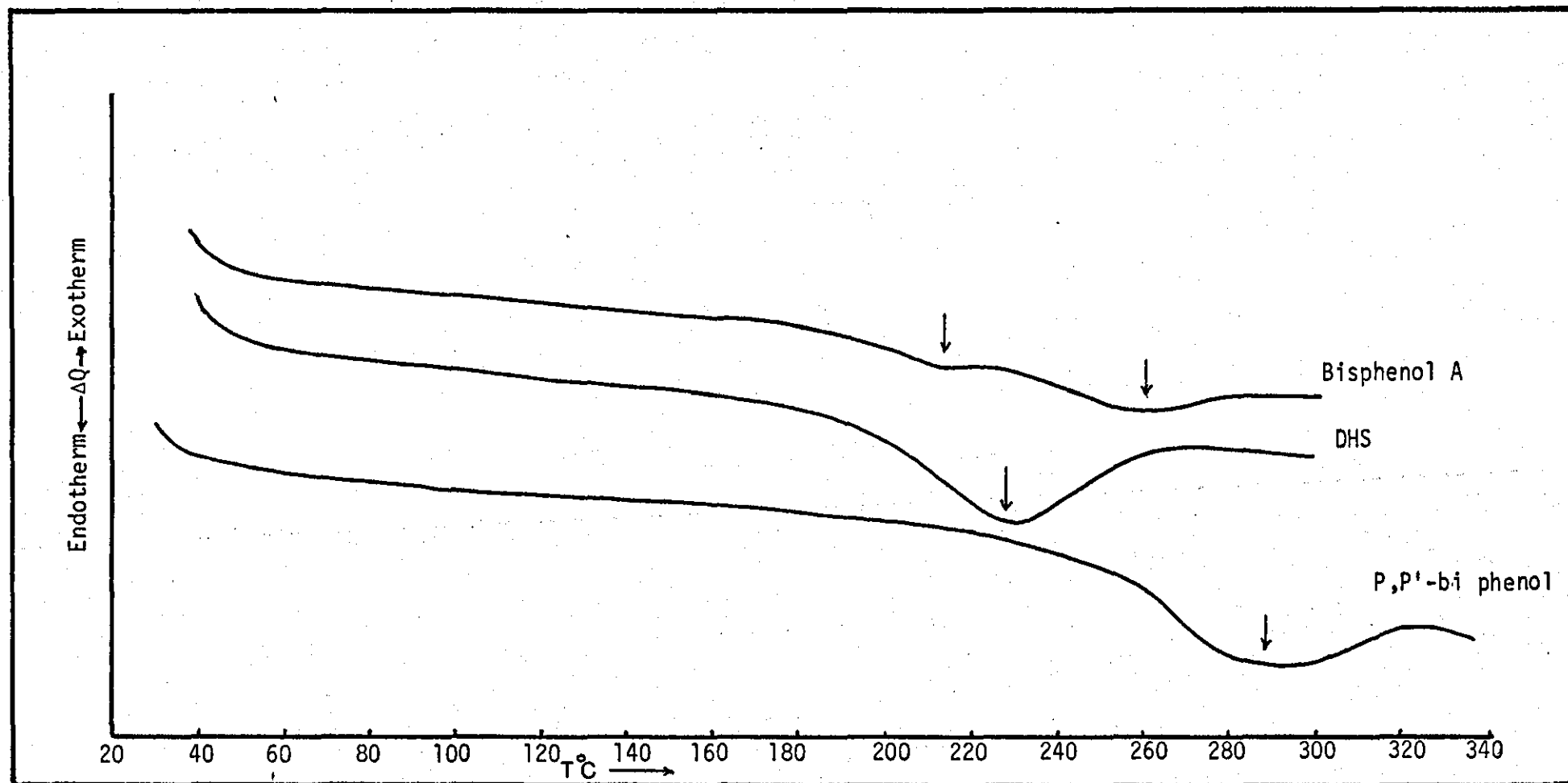


FIGURE 3.31: DSC Scans of Different Chain Extender Based PU Elastomer (arrow designates the position of transition)
 PU type: Capa 225/CHDI/chain extender Molar ratio: 1/2.6/1

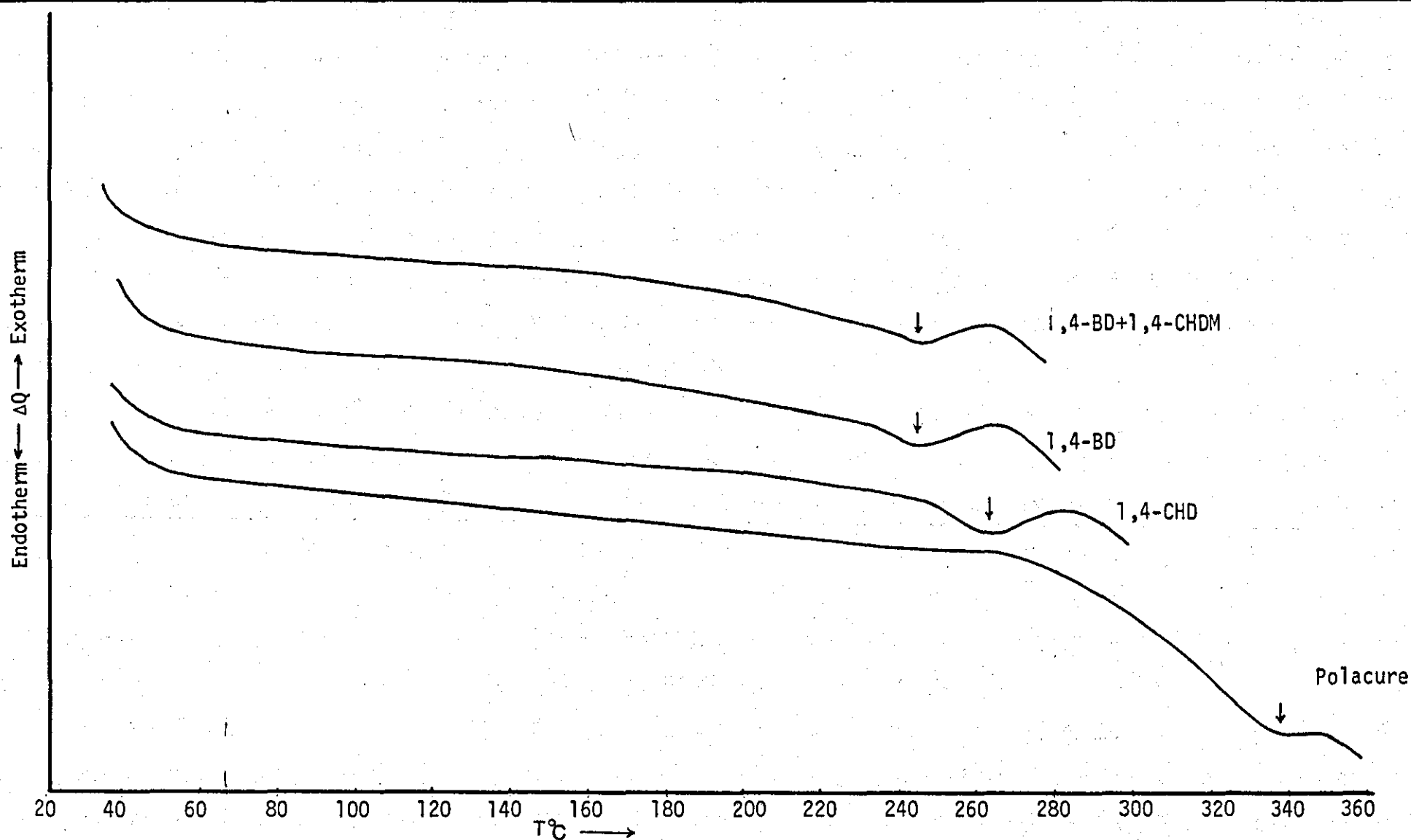


FIGURE 3.32: DSC scans of diamine and diol extended polyurethane elastomers. (Arrow designates the position of the transition)

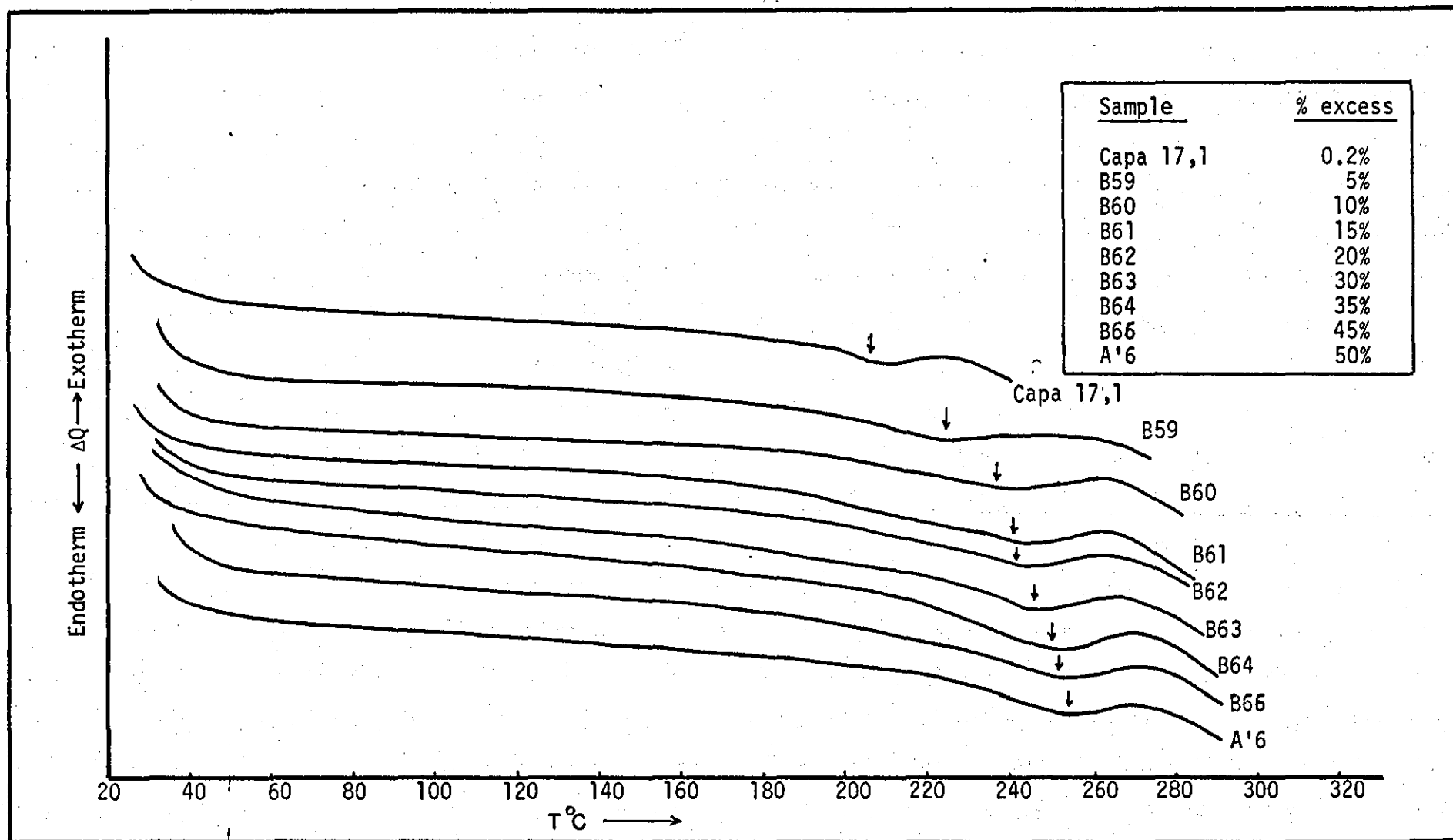


FIGURE 3.33: DSC scans of crosslinked PU elastomer in the case of using excess diisocyanate (arrow shows the position of transition)
 PU type: Capa 225/CHDI/1,4-BD
 Molar ratio: 1/2/1

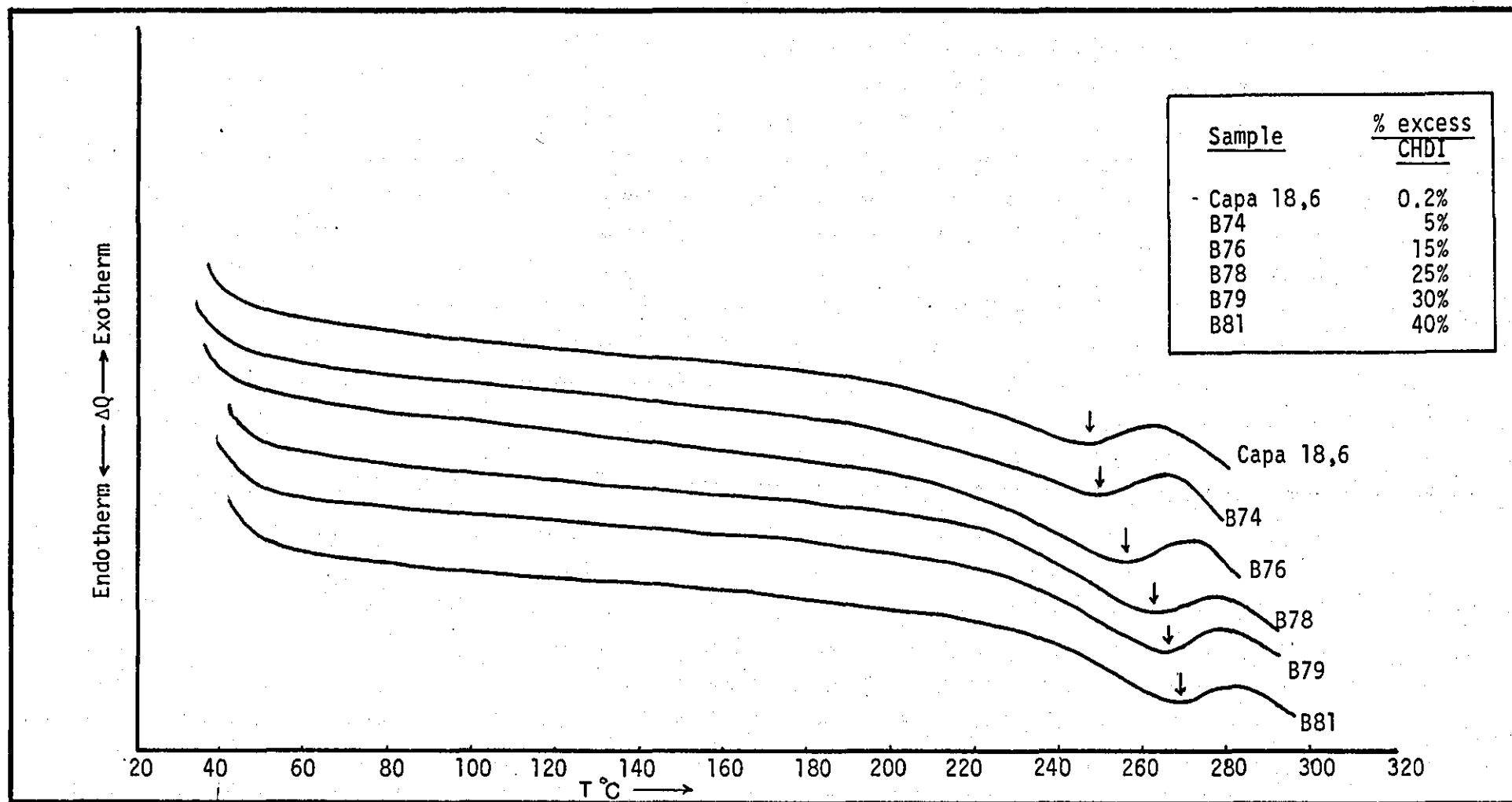


FIGURE 3.34: DSC scans of crosslinked PU elastomer in the case of using excess CHDI (arrow shows the position of transitions).
 PU type: Capa 225/CHDI/1,4-BD+1,4-CHDM
 Molar ratio: 1:3:2

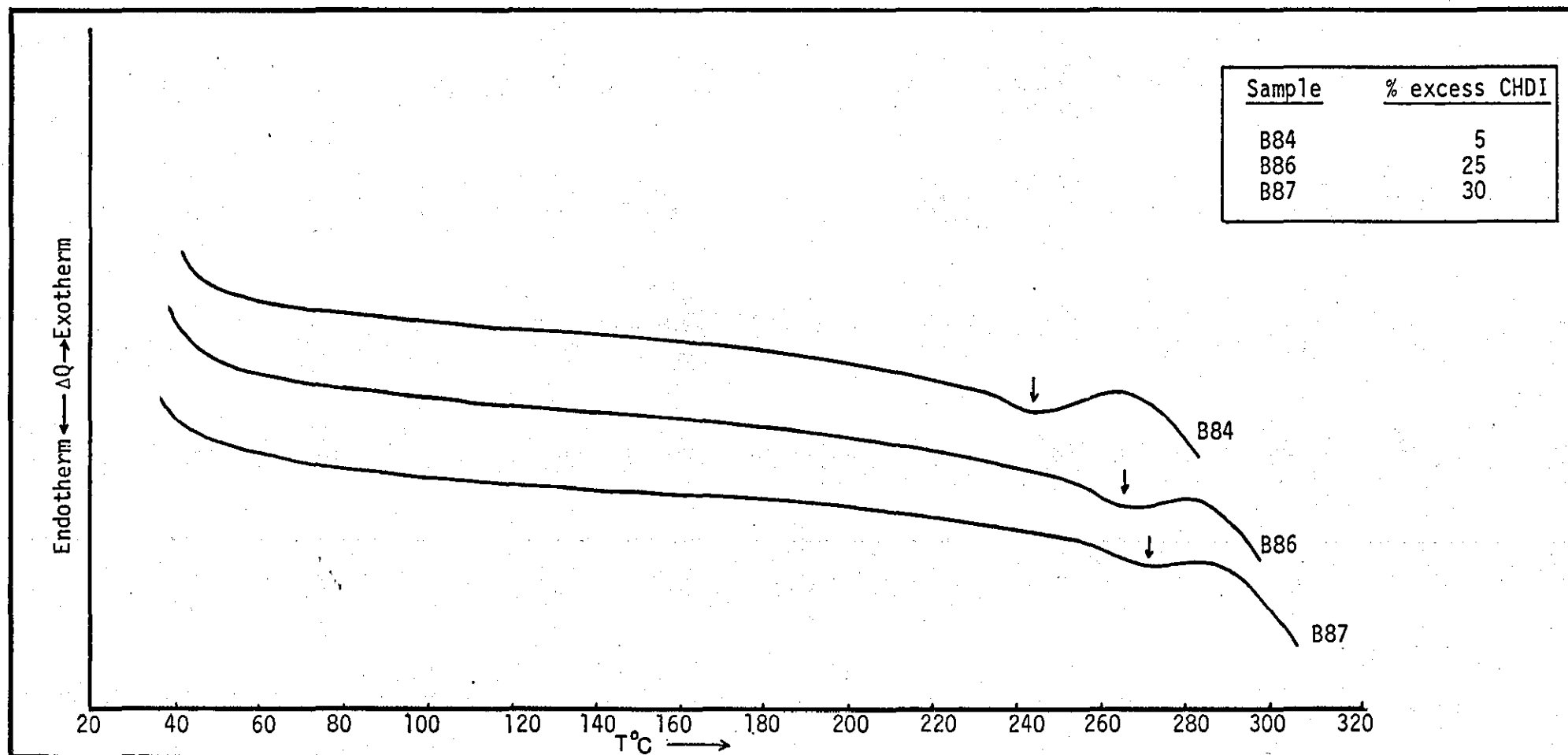


FIGURE 3.35: DSC scans of 1,4-BD based PU elastomer with block ratio 1/3/2. (Arrows show the position of transitions)

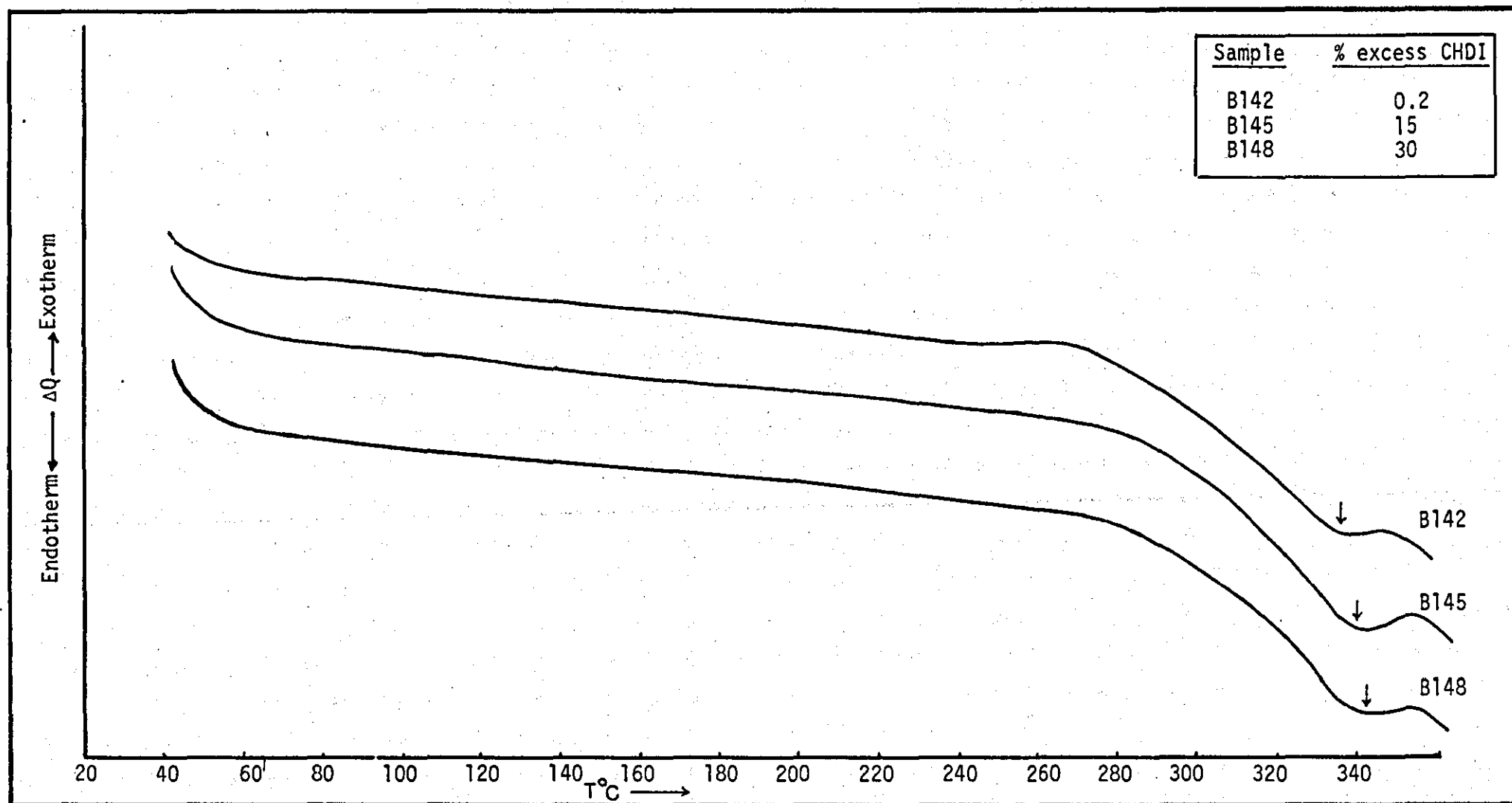


FIGURE 3.36: DSC scans of Polacure based polyurethane elastomers in the case of using different amounts of CHDI. (Arrow shows the position of transition)

FIGURE 3.37: DSC scans of mixed chain extender (1,4-BD+1,4-CHDM) based PU elastomer as a means of observing soft and hard segment transitions. (Arrow shows the position of transitions)

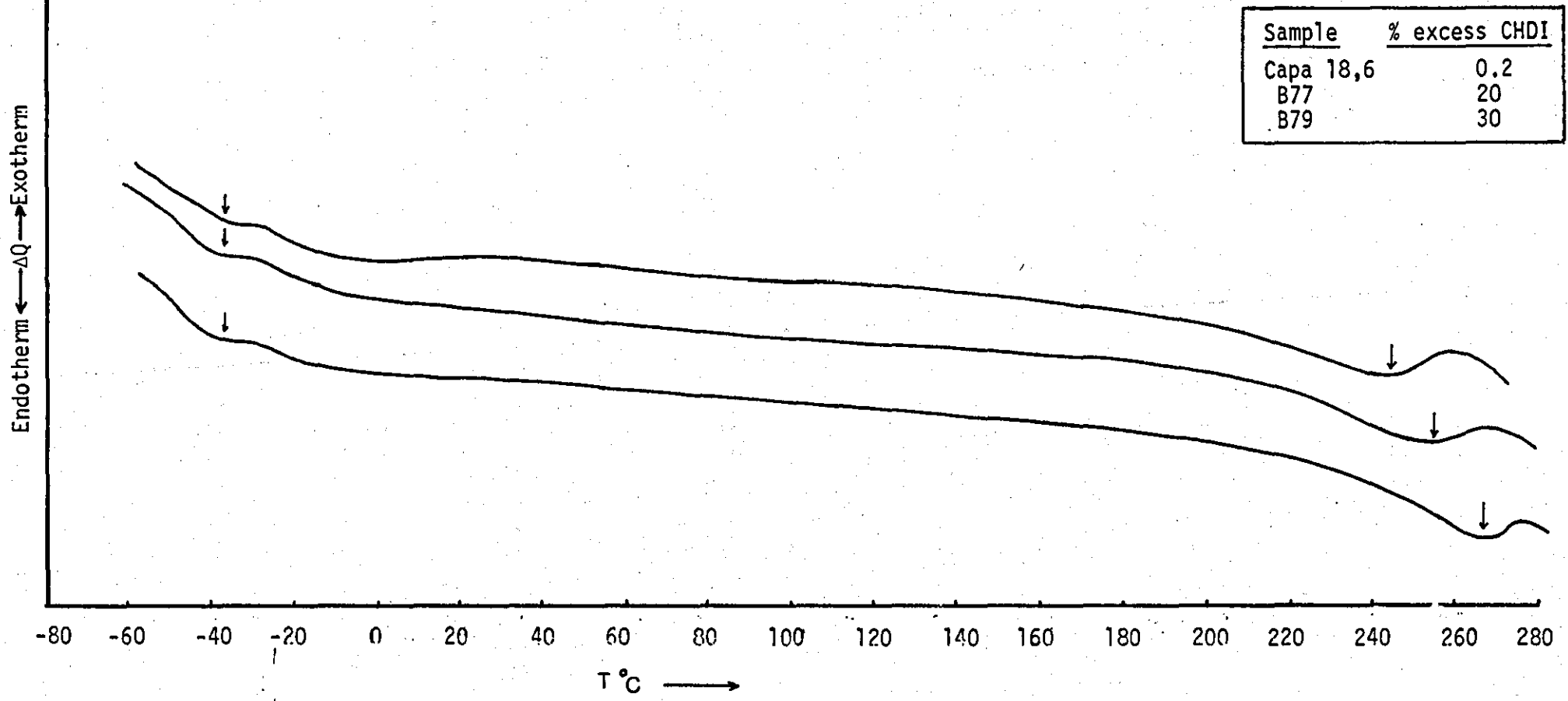
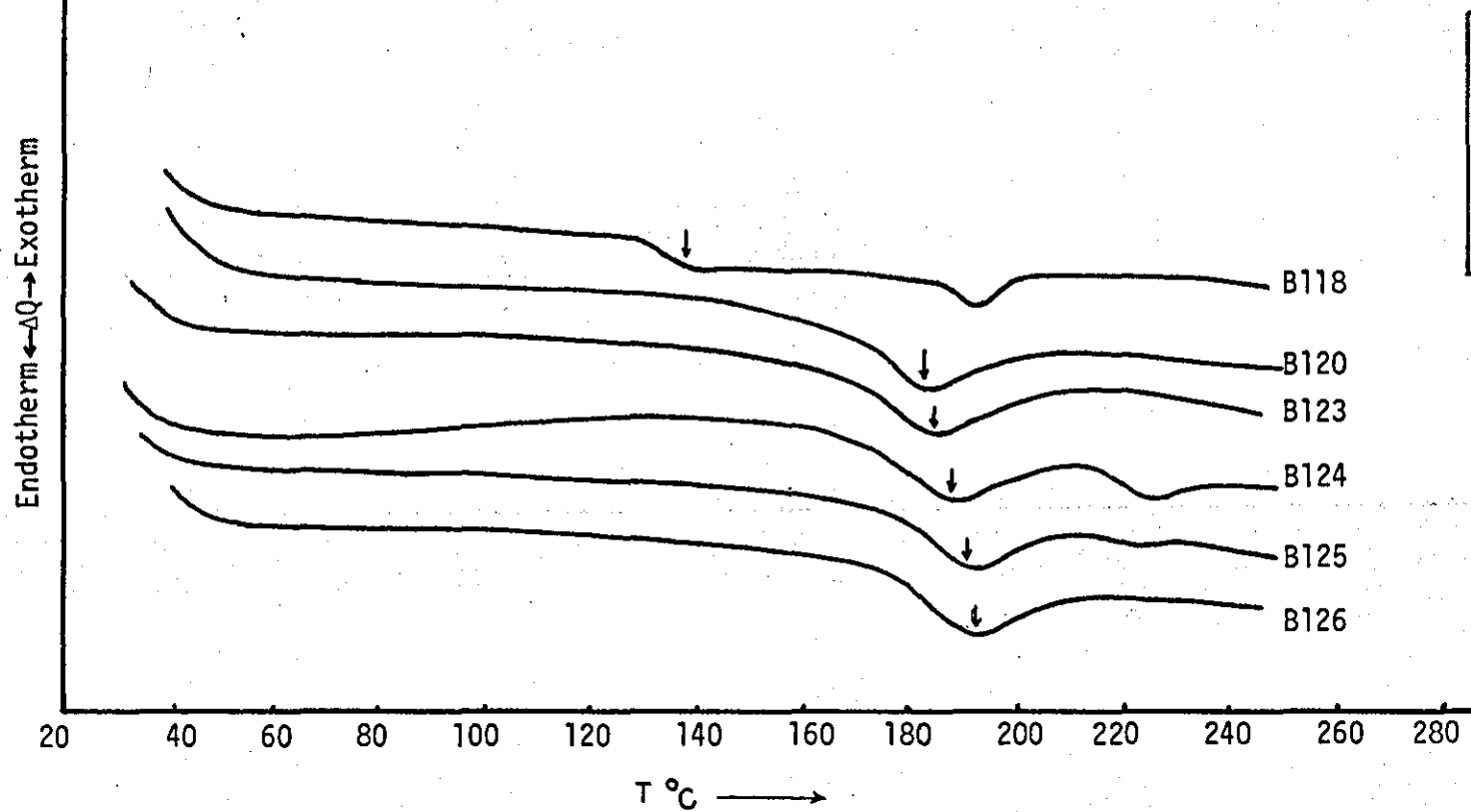


FIGURE 3.38: DSC scans of PPDI based PU elastomers. (Arrows show the position of transitions)



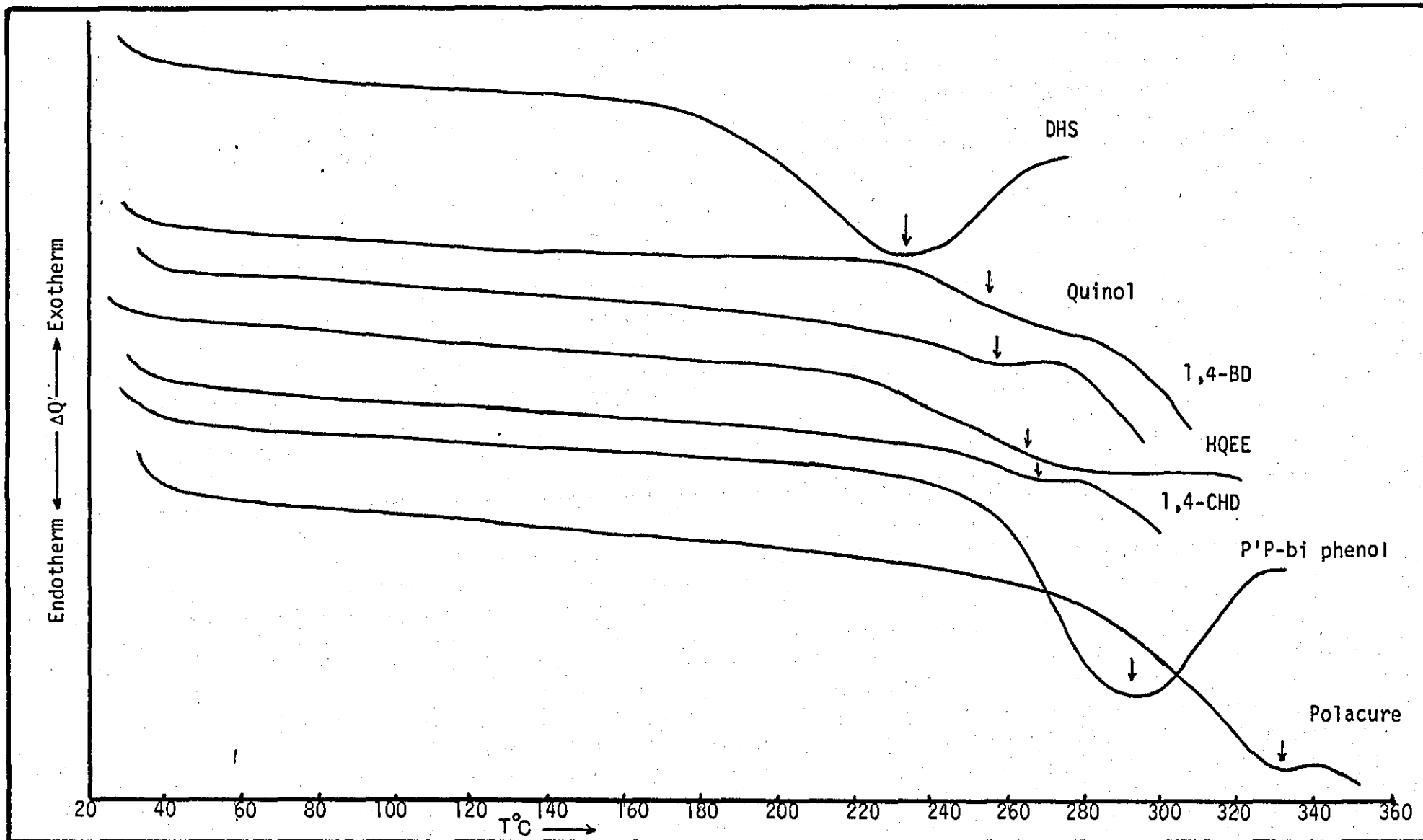
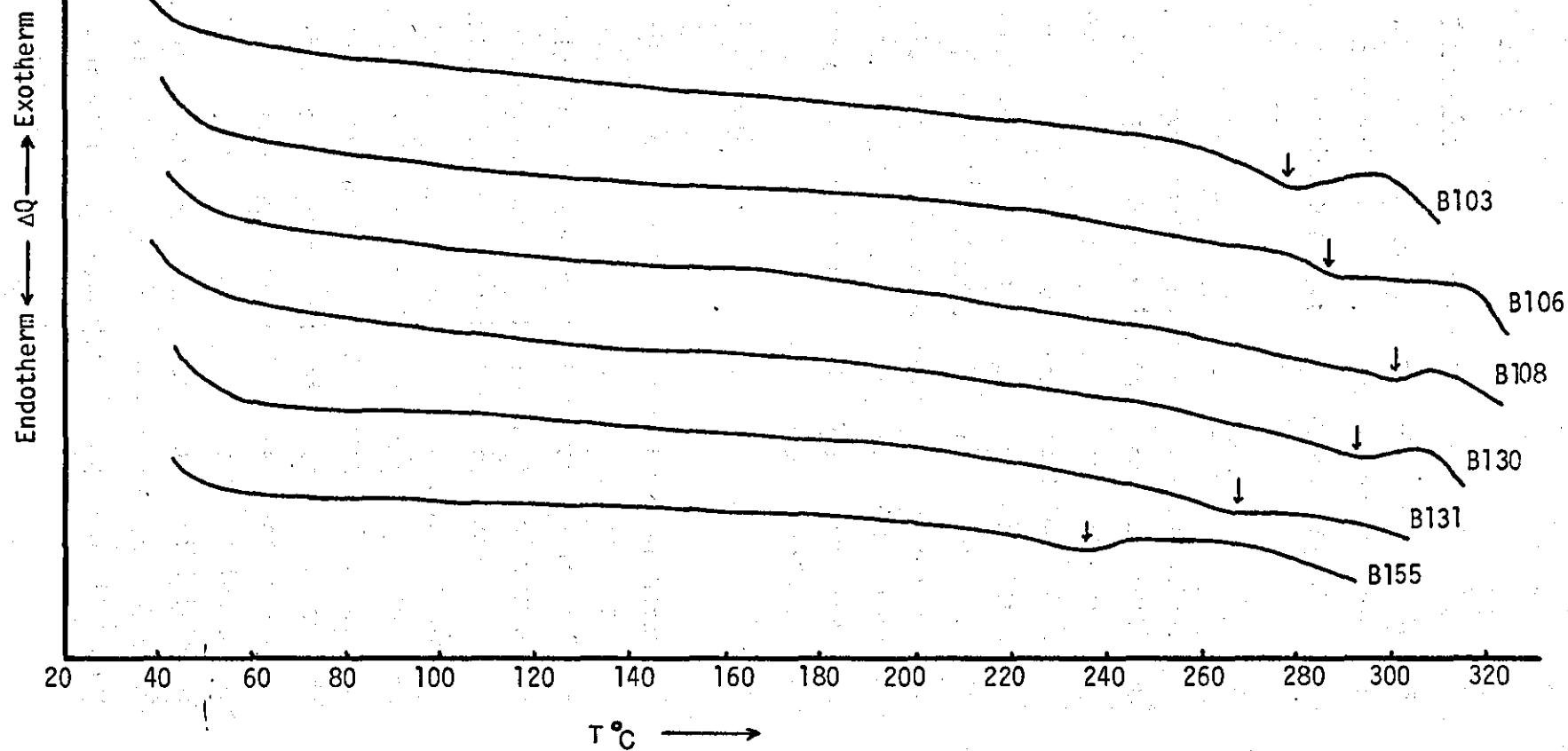


FIGURE 3.39: DSC Scans of Crosslinked PU Elastomer based on different diamine and diols chain extenders

FIGURE 3.40: DSC scans of PU elastomer of soft polymer series (arrows show the position of transitions)



3.2.3 Infrared Spectroscopy

3.2.3.1 Introduction

The molecular structure of polyurethane elastomers was investigated by infrared (IR) spectroscopic analysis. Spectra were examined for characteristic group absorption bands due to component groups present in the polyurethane bonding.

In polar polymers like polyurethanes, hydrogen bonding which sometimes dominates the crystalline structure, influences physical properties of the amorphous state through relatively strong interchain interactions or through the formation of paracrystalline. As mentioned earlier, the extent and possible forms of hydrogen bonding is dependent on many factors including the electron donating ability and relative proportion and spatial arrangement of the proton acceptor groups in the polymer chains. In a typical hydrogen bonded polyurethane the NH group of urethane units (-NH-C(=O)-O-) serves as a proton donor and the proton acceptors can be carbonyl groups (C=O) from the urethane unit and/or polyester chain.

Analysis of IR spectra to estimate the degree of hydrogen bonding between NH protons and possible proton acceptors was one of the methods used for evaluating the degree of phase segregation. Estimation of hydrogen bonding is based on the resolution of urethane NH and carbonyl bond into the bonded and non-bonded components. In a polyether urethane the determination of phase separation or phase mixing through hydrogen bonding is simple, as the only proton acceptors are the C=O group of the urethane hard segment and the ether oxygen of the polyether soft segment which give absorbances at different wavelengths. Polyester urethane on the other hand, due to containing two different carbonyl groups (one each belonging to hard and soft segment units respectively) and thus four possibilities of absorption peaks exist and hence the much broader carbonyl absorption regions which result in making the hydrogen bonding estimation difficult.

3.2.3.2 Infrared Technique

Infrared spectra are normally observed using a double beam infrared spectrophotometer. This consists basically of a source of infrared radiation, and a dispersion system to give a spectrum of varied wavelength radiation. Prisms of inorganic salts and diffraction gratings are commonly used as light beam dispersion agents. A beam of monochromatic radiation is split into two beams of equal intensity by means of a system of mirrors. One beam is arranged to pass through the sample, and the other through a suitable reference medium. If the frequency of vibration of the sample molecule falls within the range of the instrument, the molecule will absorb energy at this frequency, resulting in a difference in the intensities of the sample and reference beams which is detected by a photocell system. The final spectrum is recorded on a chart recorder which is coupled to the dispersion and detection systems. Spectra show peaks corresponding to absorption, plotted against wavelength (or frequency).

Absorption of infrared radiation by the sample can be brought about using two techniques:

1. Transmission of radiation in which infrared radiation is passed directly through the sample.
2. Reflection of radiation in which infrared radiation is reflected from the sample.

In this research programme, the infrared reflection method was adopted and used for the polyurethane elastomers under investigation.

3.2.3.3 Infrared Reflection Spectroscopy

Opaque materials clearly demand some kind of reflectance technique, but a spectrum obtained by reflection of the radiation from the surface

of a chemical material is usually very poor. A technique known as Attenuated Total Reflectance (ATR) was conceived by Fahrenfort¹⁵¹ in 1961. This enables reflection spectra of satisfactory quality to be produced. The infrared ATR unit consists essentially of a flat crystal (usually ^htallium iodide or mixed ^htallium iodide and bromide), arranged in the sample beam of the spectrophotometer so that infrared radiation can pass through it by total internal reflection. Samples are clamped firmly on either surface of the crystal. When radiation is totally internally reflected at the surface of the crystal, a small proportion actually passes through the surface of the sample and may be absorbed. On repeated internal reflection along the crystal, the sum intensity of absorption increases. Therefore the emerging radiation has a lower intensity than the reference beam, and a spectrum is obtained in the usual way. Figure 3.41 shows the optical path in a simple ATR unit and also shows the totally internally reflected infrared radiation. (overleaf).

3.2.3.4 Experimental Procedure

In the present investigation the spectra of the prepared polyurethane elastomer were recorded using a Beckman TR-9 ATR unit (giving nine internal reflections), installed in a Pye-Unicam SP3-200 grating infrared spectrophotometer. Samples of polymer sheet (approximately 2 mm thick) were cut so as to cover the two surfaces of the crystal. Samples were dried in a vacuum oven at about 60°C immediately before investigation, to remove any surface moisture which would give rise to characteristic OH absorption bands. With the samples clamped firmly against the crystal surfaces, spectra were recorded between 4000 cm^{-1} and 600 cm^{-1} (2.5 μm to 16.5 μm) using a normal scanning mode.

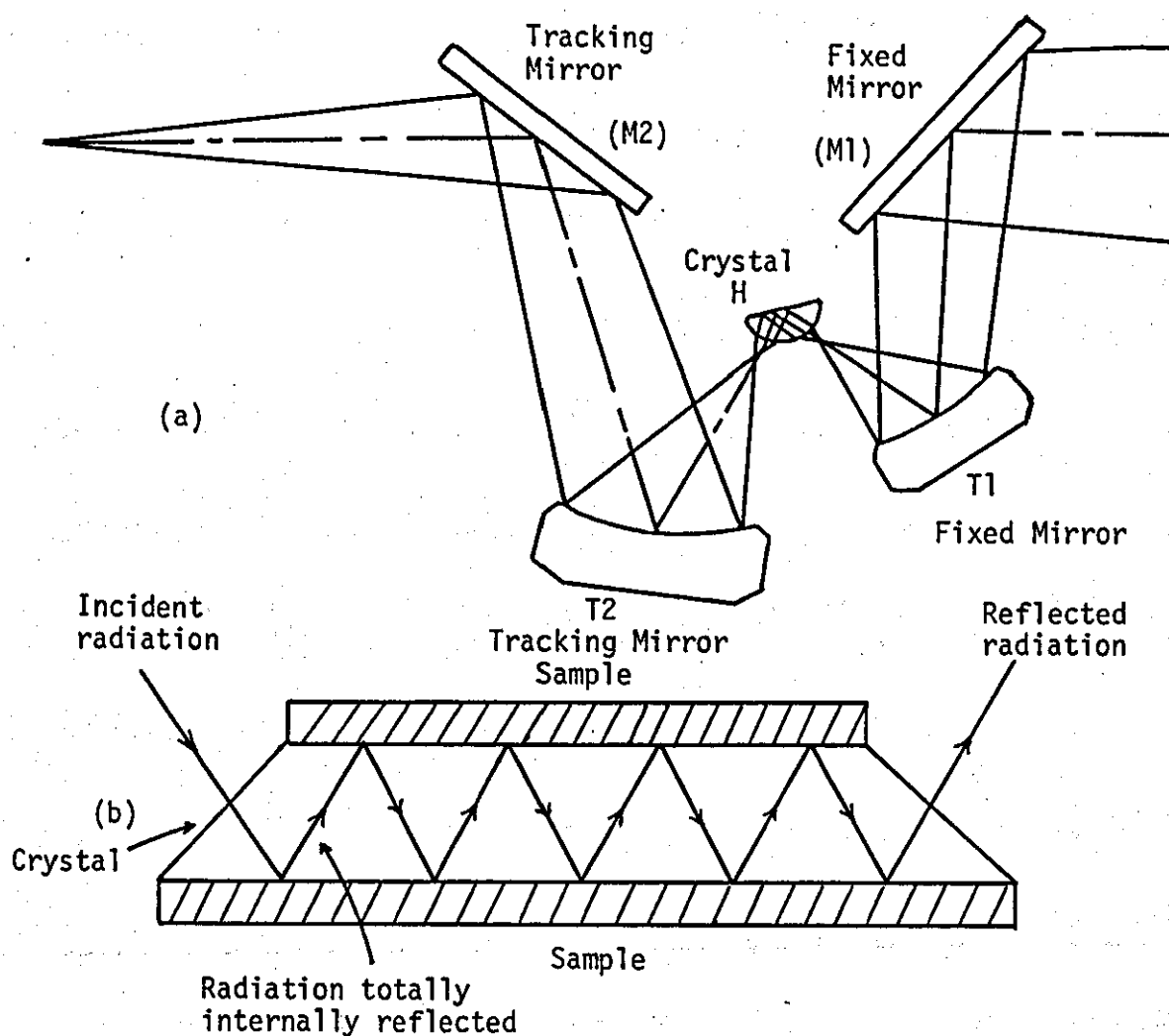


FIGURE 3.41: (a) The optical path in a simple ATR unit;
(b) Totally internally reflected IR radiation

3.2.3.5 Extent of Hydrogen Bonding in PU Elastomer

In a pure urethane hard domain, hydrogen bonding results from the hydrogen atoms of NH groups serving as proton donors and the C=O groups acting as proton acceptors. When the urethane hard segment and the CAPA soft segment are mixed at the molecular level, the carbonyls in the CAPA backbone also act as proton acceptors in forming hydrogen bonds with the NH groups of the hard segment urethane groups.

The major absorption bands which appear between 1600 cm^{-1} and 4000 cm^{-1} are particularly useful in determining percent hydrogen bonding and hence the interurethane and urethane-soft segment linkages. From the IR spectra,

by using the 'baseline density' method¹⁵² the absorbances at the absorption maxima were calculated according to Beer-Lambert's law of absorption which states:

$$A = \log_{10} \left(\frac{I_0}{I} \right) = E.C.L.$$

where A = absorbance

I_0 = intensity of incident radiation

I = intensity of transmitted radiation

E = extinction coefficient

C = concentration of the NH groups

L = radiation path length (cm)

The absorbance A_b of the hydrogen bonded absorption maximum is given by:

$$A_b = E_b \cdot C_b \cdot L_b$$

Similarly, for the free NH absorption maximum

$$A_F = E_F \cdot C_F \cdot L_F$$

As an approximation, assuming $E_b = E_F$, then:

$$A_b = K C_b$$

and

$$A_F = K C_F$$

where K is a constant.

Values of A_b and A_F were calculated from the IR spectra using the 'baseline density' method as shown in Figure 3.47.

From Figure 3.47 $A_b = \frac{AC}{BC}$

$$A_F = \frac{DF}{EF}$$

The proportion of bonded NH groups is then given by:

$$\text{Percent hydrogen bonded NH} = \frac{A_b}{A_b + A_F} \times 100$$

The values of hydrogen bonding were calculated from the spectra of prepared polyurethane materials are given in Tables 3.34 to 3.37.

3.2.3.6 Results and Discussion

Spectra of all polyurethane elastomers were found to be very similar to Figures 3.43 to 3.45 which are respectively the representatives of a typical 1,4-BD, Polacure and TMP-cured polyurethanes. Assignments of the most pronounced absorption bands in these spectra are given in Table 3.33.

Figure 3.43 shows the IR spectra of the 1/2/1 composition of the Capa 225/CHDI/1,4-BD series. Very similar IR spectra are observed for a 1/3/2 composition of the Capa 225/CHDI/1,4-BD+1,4-CHDM series. All polyurethane elastomers gave spectra showing the absence of an isocyanate (NCO) absorption band at 2240 cm^{-1} , indicating the complete reaction of diisocyanates. The spectra of CHDI are shown in Figure 3.42.

It is known that a band near 3300 cm^{-1} is caused by the hydrogen bonded NH group while the non-hydrogen bonded NH group appears near 3440 cm^{-1} as a shoulder of the bonded NH group.

The carbonyl region shows splitting of the absorption band into two peaks at 1740 cm^{-1} and 1670 cm^{-1} in 1,4-BD and 1,4-BD+1,4-CHDM extended PU elastomer, which is attributed to the free and bonded C=O groups respectively. The urethane NH bending appears at 1530 cm^{-1} in both series and the presence of a distinct absorption band at 1412 cm^{-1} suggests the presence of an isocyanurate structure in the polyurethane elastomers. The isocyanurate C=O absorption band also

The spectra of diol based PU shows the absence of a distinct band at 1640 cm^{-1} , assigned to the urea C=O stretching mode. This is reasonable, as only urethane groups would be anticipated in the diol extended polymers. The urea C=O stretching mode at 1640 cm^{-1} can be seen present in Polacure chain extended polyurethanes.

[typical]

IR spectra of Capa 225/PPDI/TMP based polyurethane shows benzene ring stretching at 1600 cm^{-1} and 1500 cm^{-1} (Figure 3.45) due to the structure of PPDI while these stretching vibrations are absent in CHDI based PU elastomers. The TMP based polyurethane also shows a broad C=O absorption band at 1720 cm^{-1} . A similar C=O absorption band is observed for the CHDI based urethane extended with Capa 305 (Figure 3.46). It is worth mentioning that both TMP and Capa 305 are trifunctional diols with 154 and 540 molecular weight respectively. These trifunctional chain extenders act as a crosslinking agent in polyurethanes.

The extent of hydrogen bonding in the polyurethanes investigated in this research are shown in Tables 3.34-3.37. It is apparent from the Tables 3.34-3.37 that all the PU elastomers, studied by infrared

spectroscopy, exhibited hydrogen bonding between 50-60%. Using excesses of diisocyanates in the formulation of the isocyanurate crosslinked series showed relatively little effect on hydrogen bonding (about 4-8%). The lower values of hydrogen bonding in the TMP extended polymer can be explained by considering the reduction in intermolecular attractive forces that result from a special separation of chains due to increased crosslinking.

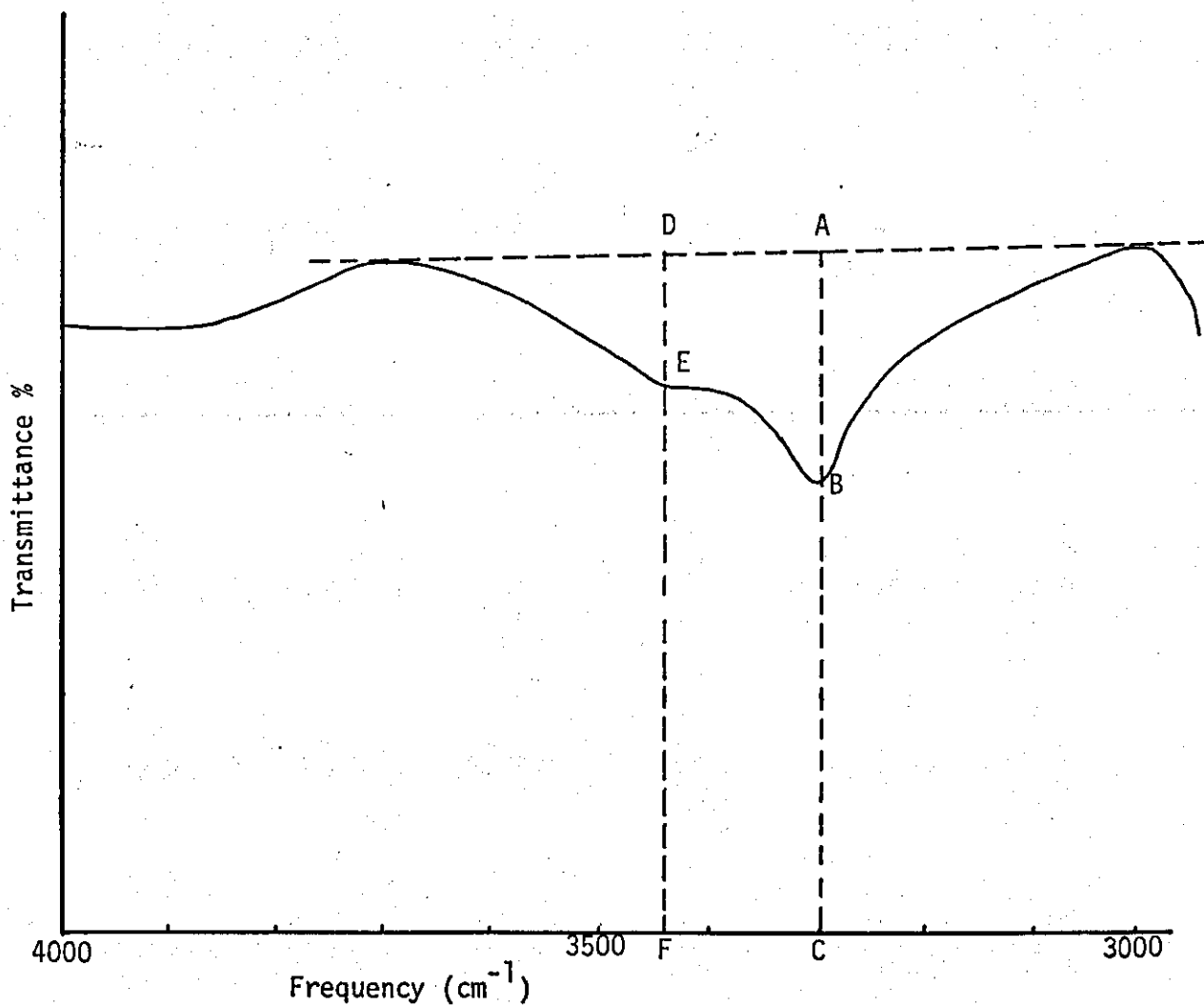


FIGURE 3.47: Showing Baseline Density Method in a Typical NH Absorption Band of PU Elastomer

TABLE 3.33: Major Infrared Band Assignment for Prepared PU Elastomers

Frequency (cm^{-1})	Assignment	Relative Intensity
3440	Free N-H stretching	Sh, W
3300	Bonded N-H stretching	S
2925	CH_2 asymmetry stretching	VS
2850	CH_2 symmetry stretching	S
1720	Free C=O stretching	VVS
1709-1689	isocyanurate C=O stretching	sh, S
1670	Bonded C=O stretching	VVS
1625	Urea C=O stretching	S
1600	C=C stretching in aromatic group	m
1530	N-H bending and C-N stretching	VS
1500	C=C stretching in aromatic group	m
1450	CH_2 bending	m
1412	Isocyanurate group	m
1150	C-O-C stretching	S
1060-1090	C-O-C stretching	S
770	$\begin{array}{c} \text{O} \\ \\ \text{C-O-} \end{array}$ out of plane bending	m
730	C-H bending of four adjacent H-atoms	m

TABLE 3.34: Extent of Hydrogen Bonding in Polyurethane Elastomers Chain Extended with BD

Samples (a)	% Excess CHDI	Hard Segment Weight Fraction (b) (%)	Hydrogen Bonded N-H Groups (%)	Hydrogen Bonded C=O Groups (%)
Capa 17.1	2	17.66	59.1	28.0
B59	5	17.99	58.2	32.0
B60	10	18.55	56.0	30.0
B61	15	19.10	56.0	34.0
B62	20	19.63	55.0	30.0
B56	25	20.17	54.0	43.0
B63	30	20.69	52.0	41.0
B64	35	21.21	51.0	43.0
B65	40	21.72	59.0	35.0
B66	45	22.23	57.0	29.0

(a) All the samples are based on Capa 225/CHDI/1,4-BD

(b) Calculated as weight percentage of CHDI and 1,4-BD per total polymer weight

TABLE 3.35: Extent of Hydrogen Bonding in PU Elastomers Chain Extended with BD and CHDM

Samples (a)	% Excess CHDI	Hard Segment Weight Fraction (b) (%)	Hydrogen Bonded N-H Groups (%)	Hydrogen Bonded C=O Groups (%)
Capa 18.6	0.2	26.81	54	51
B74	5	27.47	52	48
B75	10	28.12	55	48
B76	15	28.76	51	45
B77	20	29.38	51	47
B78	25	30.00	53	48
B79	30	30.61	51	48
B80	35	31.20	51	47
B81	40	31.79	51	47

(a) All the samples are based on Capa 225/CHDI/1,4-BD+1,4-CHDM

(b) Calculated as weight percentage of CHDI and chain extender per total polymer weight

TABLE 3.36: Extent of Hydrogen Bonding in Polacure Chain Extended Based PU Elastomer

No	Sample	% Excess CHDI	Hard Segment Weight Fraction (a)	Hydrogen Bonded NH Groups (%)
B142	Capa 225:CHDI:Polacure	0	36.03	53
B148	Capa 225:CHDI:Polacure	30	38.94	51

(a) Calculated as weight percentage of CHDI and Polacure per total polymer weight

TABLE 3.37: Extent of Hydrogen Bonding in PPDI Based Polyurethane Elastomers

Sample No (a)	Chain Extender	% Excess PPDI	Hard Segment Weight Fraction (b)	Hydrogen Bonded NH Groups (%)
B103	Dianol (22+33)	30	39.09	60
B106	Dianol (22+33)+TMP(1+1)	30	34.28	61
B108	TMP	30	28.64	47

(a) Samples are based on Capa 225/PPDI/chain extender

(b) Calculated as weight percentage of PPDI and chain extender per total polymer weight

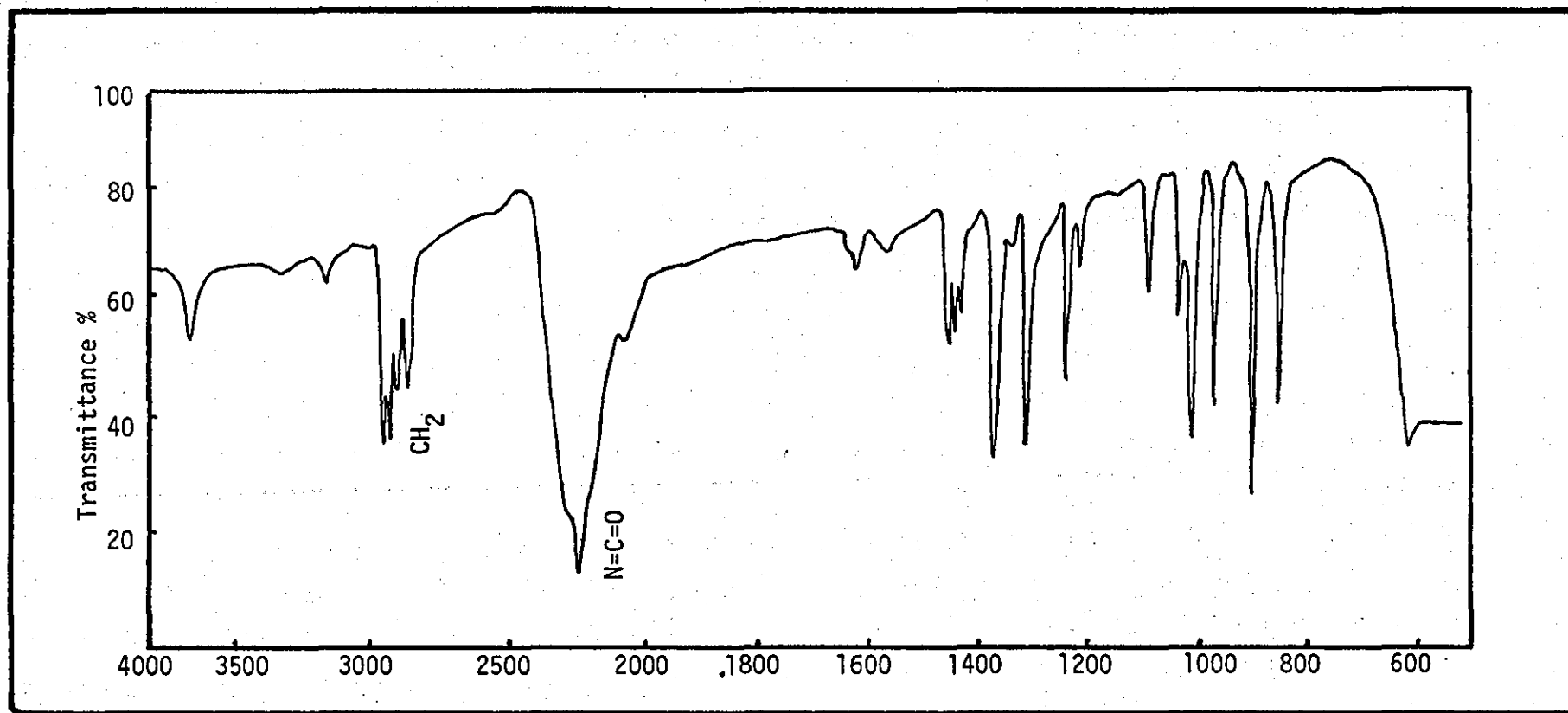


FIGURE 3.42: Infrared Spectrum of 1,4-cyclohexane diisocyanate (CHDI)

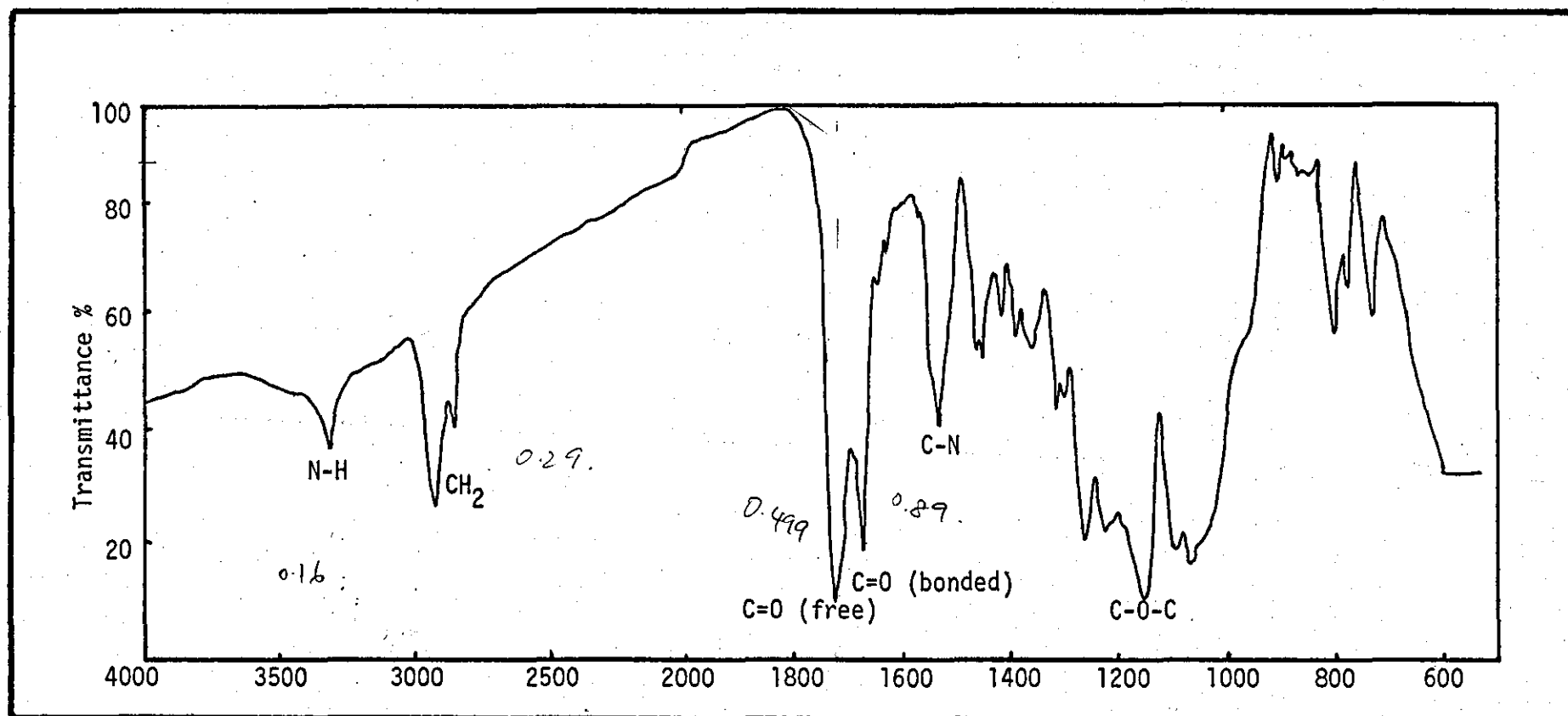


FIGURE 3.43: A Typical Infrared Spectra of Capa 225/CHDI/1,4-BD Based PU Elastomer

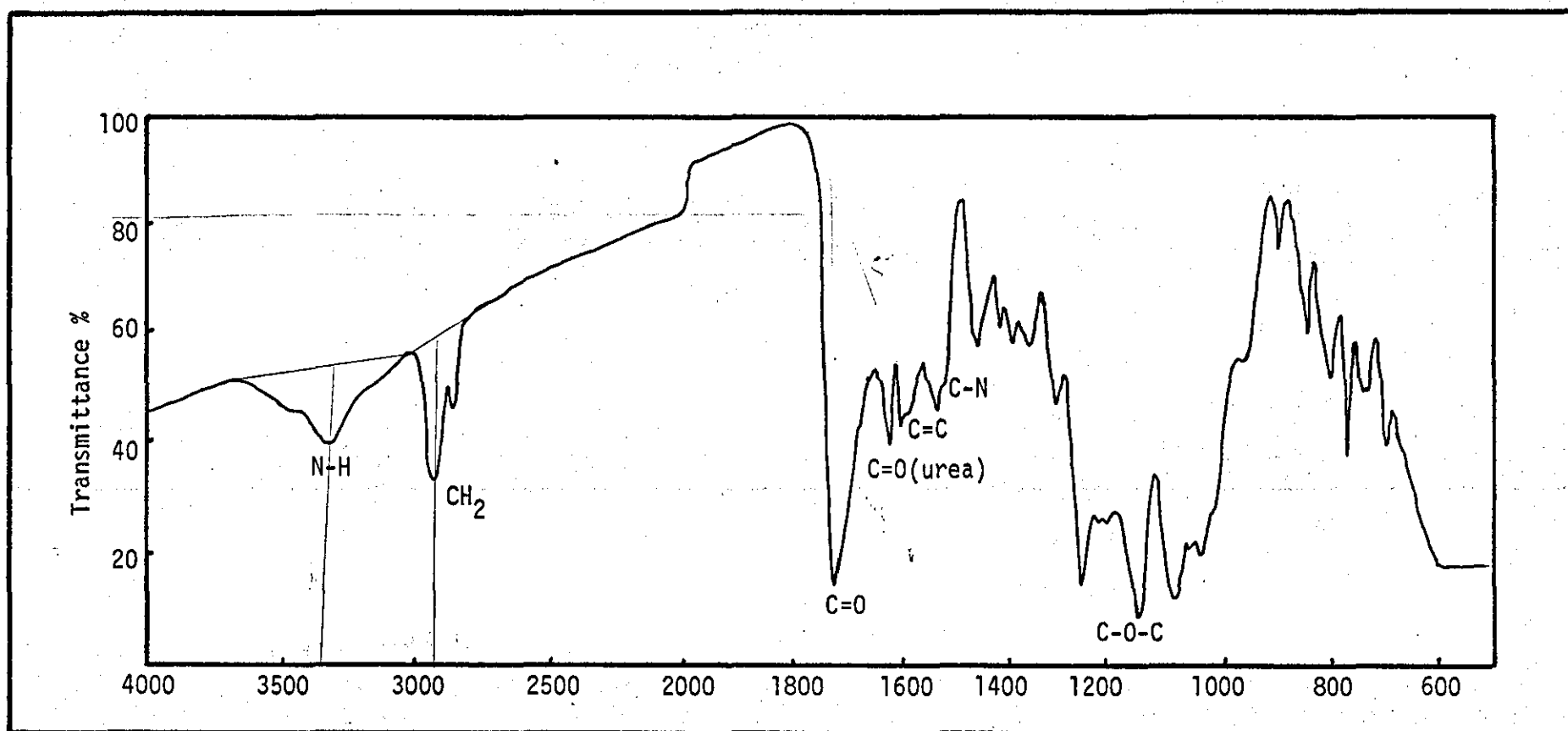


FIGURE 3.44: A typical infrared spectra of Capa 225/CHDI/Polacure based PU elastomer

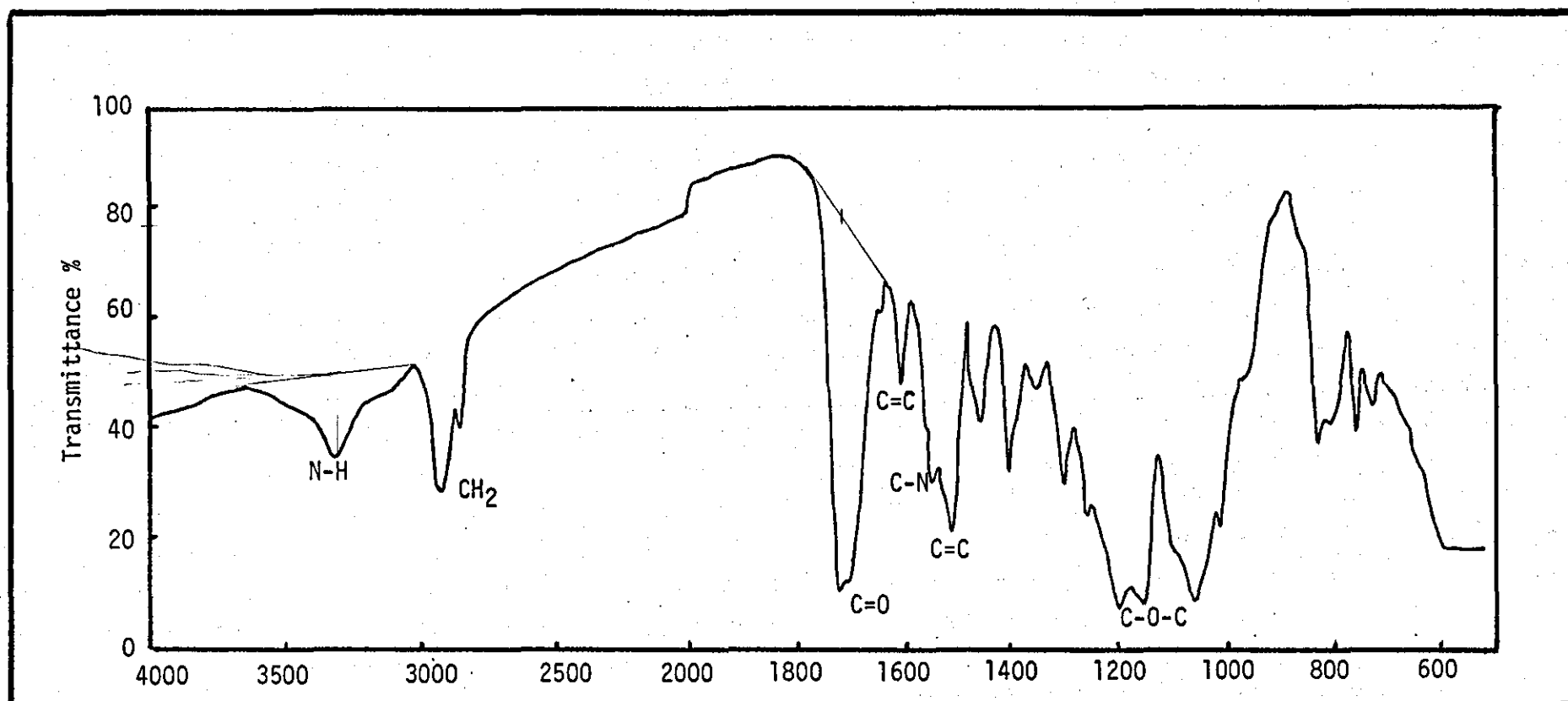


FIGURE 3.45: A Typical Infrared Spectra of Capa 225/PPDI/TMP Based PU Elastomer

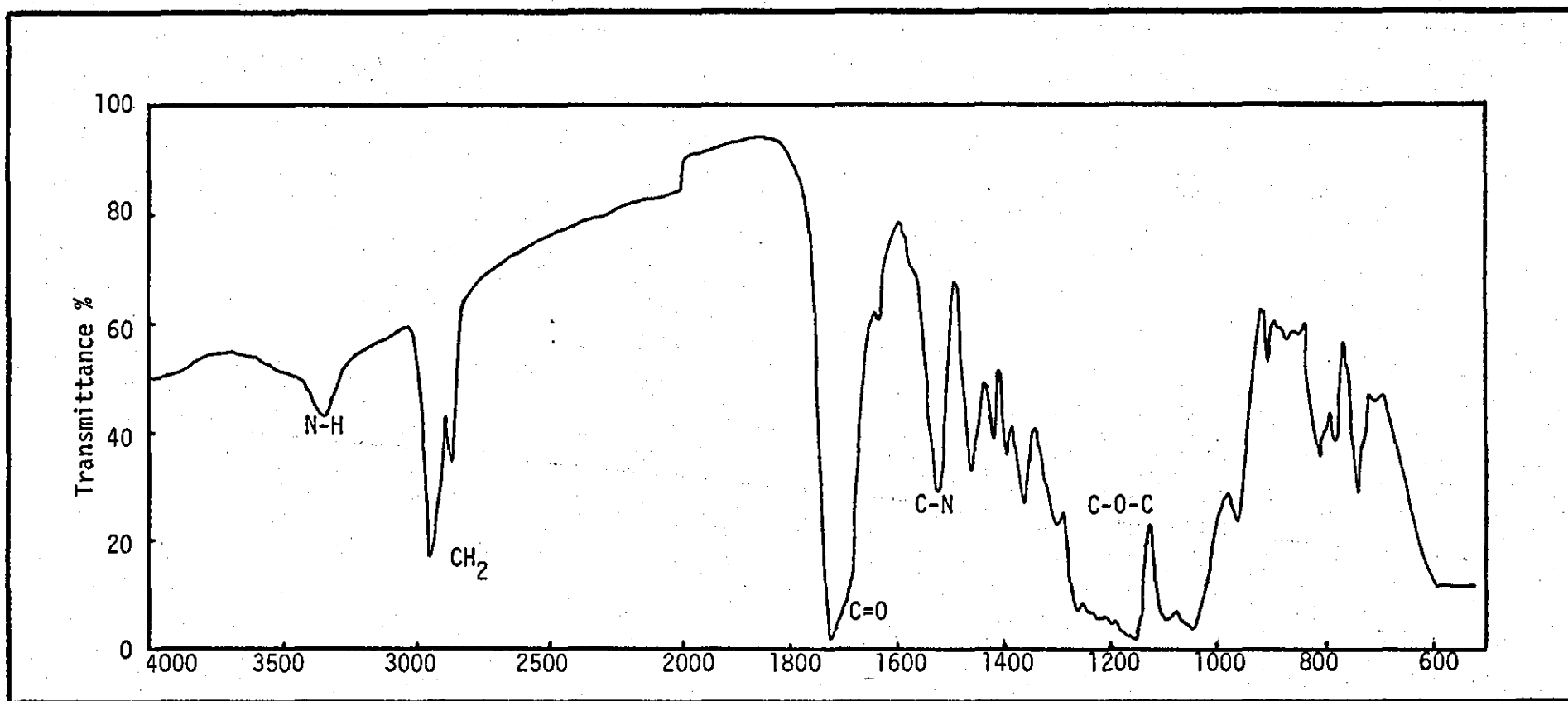


FIGURE 3.46: Infrared Spectra of Capa 230/CHDI/Capa 305 Based PU Elastomer

3.2.4 X-ray Diffraction

3.2.4.1 Introduction

The presence of ordered arrangements of atoms or molecules within a solid substance can be investigated by using X-ray diffraction methods. X-rays are generated by the bombardment of electrons on a metal (copper) target in an evacuated tube, causing ionisation of surface atoms and subsequent jumping of electrons into vacant orbitals. By this process, radiation is produced consisting of several distinct wavelength maxima, and by use of a suitable filter (nickel), radiation of a well-defined specific wavelength ($\lambda = 1.542 \text{ \AA}$) is obtained. The beam is collimated with suitable pinholes, passes through and is diffracted by the sample which is placed in the path of the X-ray beam. A flat plate camera is used for the record of the entire diffraction pattern. The distance between sample and plate is kept constant throughout. The general features of the unit are shown in Figure 3.49.

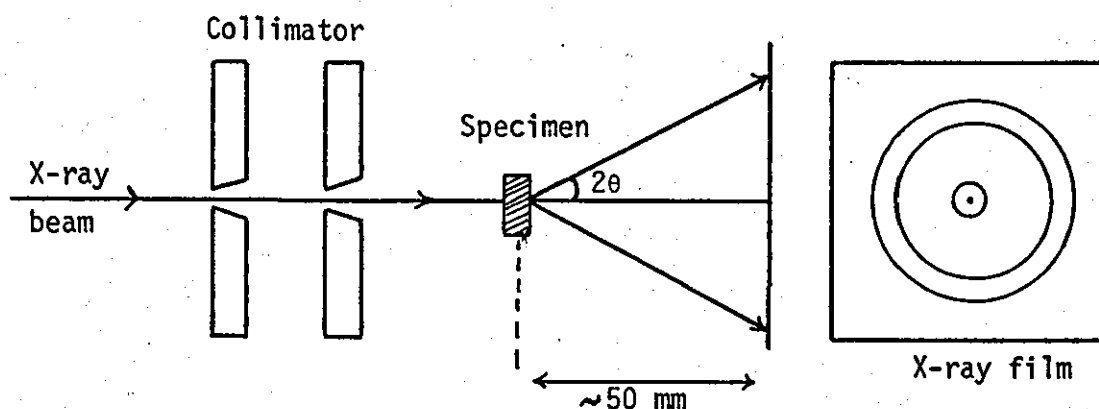


FIGURE 3.49: Essential Features of the X-ray Diffraction Instrument (WAXS)

As the wavelength of X-rays are comparable to interatomic distances in crystals, diffraction effects will occur when X-rays are exposed to a solid substance containing regularly arrayed atoms. Constructive interference of X-rays reflected from parallel atomic layers, are governed by Bragg's laws:

$$n\lambda = 2d \sin\theta \quad (A)$$

where λ is the wavelength of the radiation, d is the distance between the parallel planes in the crystallites, θ is the angle of incidence and reflection X-ray beams and n is an integer.

Knowing the distance between the sample and the camera plate, the angle θ can readily be determined. Using equation (A) and inserting the value of λ for the radiation used and also the appropriate value of n , the d spacing can be obtained.

The reinforced waves reflected by all the small crystallites produce diffraction rings, or haloes, which are sharply defined for highly crystalline materials and become increasingly diffuse when the amorphous content is high.

3.2.4.2 Experimental Procedure

Wide-angle X-ray diffraction patterns of prepared polyurethane elastomers were obtained using nickel-filtered CuK_α radiation generated by a Jeol Model DX-G0-S X-ray generator at 37.5 Kilovolts and 36 milliamperes. Photographs were obtained using a flat plate camera for the recording of the entire diffraction pattern with an exposure time of $1\frac{1}{2}$ hours. Samples in the form of a small rectangular strip (15 x 7 x 2 mm) were mounted in the path of the X-ray beam with the face of the largest surface area perpendicular to the beam. Photographs were taken using a sample to camera distance of 5.8 cm.

Wide-angle X-ray photographs of a few stretched PU elastomers were also taken. Elastomer samples in the form of long strips 7 mm wide and 2 mm thick were stretched to the desired elongation (300 %) and clamped onto a perspex mounting bracket. The bracket is so designed that the stretched sample passes across a hole in the perspex, through which the X-ray beam is arranged to pass.

Exposed X-ray films were developed in the normal way and the photographs were obtained by contact printing, so scattered X-rays show up as light regions on a dark background.

3.2.4.3 Results and Discussion

WAXS photographs illustrating the different scattering patterns observed are shown in Figures 3.50 to 3.53. As the figures show, there is no distinct sign of crystallinity in any of the samples, as indicated by the absence of any sharp diffraction rings and the appearance of only a diffuse amorphous halo at 0.45 nm. Increasing the concentration of the hard segments and consequently their length, enhances the structural arrangements of the hard segments and promotes some microcrystallinity of the domains. The effect of increasing the concentration of the hard segment is shown in the WAXS pattern of 1,4-BD based (samples numbered B59→A'6) and 1,4-BD+1,4-CHDM based (samples numbered Capa 18/6→B79) PU elastomers where some weak diffraction is observed in polyurethanes with higher hard segment content (samples numbered A'6 and B79). This is due to the use of excess diisocyanate in which the WAXS pattern of the polymers is sharper and gives a better defined diffraction pattern, suggesting that some short-range ordering is caused by the hard segment.

Polacure based PU elastomers also show WAXS patterns similar to those given by the 1,4-BD based PU and 1,4-BD+1,4-CHDM based PU elastomers (Figure 3.52). The presence of only a diffuse halo indicates the absence of crystallinity in these materials. These results are in agreement with DSC results from which there is no evidence of a sharp crystalline melting point. Although WAXS results did not suggest any substantial crystallinity in prepared polyurethane samples, the possibility of some small degree of crystallinity certainly cannot be ruled out. These results are also supported by those of Abouzahr et al¹⁵³ on MDI/BD/PTMO-2000 type polyurethanes. They found no detectable crystalline diffraction for samples with less than 35% hard segment content.

Figure 3.53 illustrates the effect of elongation on the WAXS pattern of sample B79 at approximately 300% extension; the resulting diagram is considered to represent para-crystallisation of the polyester soft segment.

3.2.5 Scanning Electron Microscopy (SEM)

3.2.5.1 Introduction

Scanning electron microscopy was used in a detailed study of prepared PU; sample surface morphology through direct observation of sample surfaces. The scanning electron microscope is a device which produces images of rough and smooth surfaces at magnifications of up to about 50,000 times with a best resolution of about 10 nm. A schematic diagram of a scanning electron microscope is shown in Figure 3.54. The essential features of a scanning electron microscope are:

1. An electron source
2. A means of focusing a tiny spot of electron from the source on the specimen
3. A means of scanning the spot across the specimen
4. A means of detecting the response from the specimen
5. A display system, capable of being scanned in register with the incident scan
6. A means of transmitting the response from the specimen to the display system.

The obvious advantages of the scanning electron microscope are:

- a) large depth of focus;
- b) the possibility of direct observation of the external form of real objects at high magnification;
- c) the ability to switch over a wide range of magnification;
- d) the ease of operation, and the large space available for dynamic experiments on the specimen.

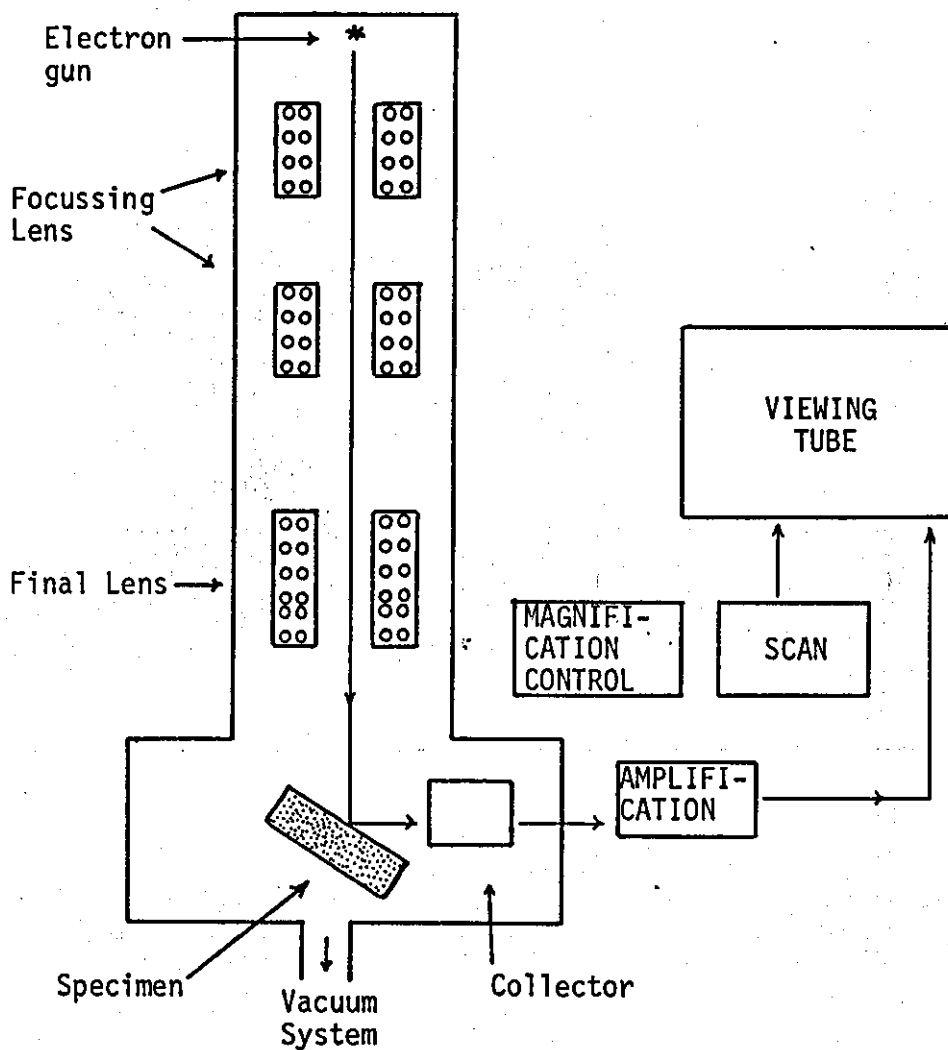


FIGURE 3.54 : A Schematic Diagram Showing the Operation of a Scanning Electron Microscope

3.2.5.2 Experimental Procedure

SEM specimen preparation is often extremely simple. In many applications, the specimen merely has to be attached to a stub using a quick setting adhesive and a conductive path provided from the specimen to the stub using conducting paint to bridge the thin adhesive layer. The stub fits simply into the specimen stage which is normally provided

with controls for translation, tilt and rotation. If the specimen is non-conductive a conductive coating must be applied to the surface, usually by evaporating or sputtering a metal (often gold or gold-palladium alloy). This is to prevent charging, which disrupts the image. In addition to the problem of charging, polymers suffer radiation damage, and artefacts may develop while viewing sometimes so quickly that the original structure may not be recorded.

All the polyurethane samples examined in this instance were prepared for scanning electron microscopy (SEM) by cutting from cast sheets and applying a gold coating. Micrographs were obtained at x2000 magnification using a Cambridge Stereoscan model 2A.

3.2.5.3 Results and Discussion

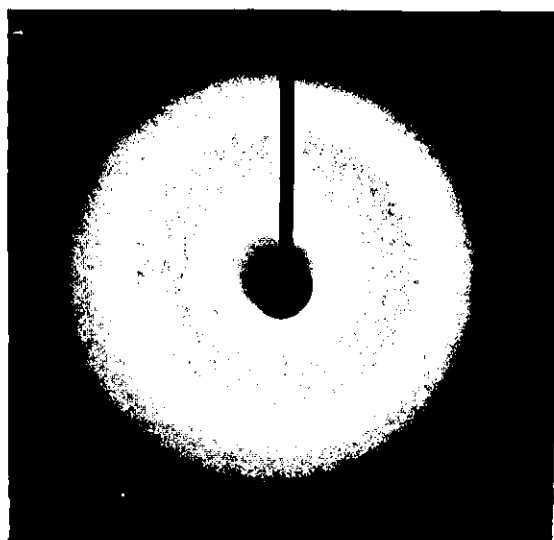
It was recorded in the literature^{59,60,61} that the presence of a crystallizable segment in a segmented polyurethane elastomer system can lead to the development of large scale structures which can be termed superstructures. The superstructure entities (spherulites) contain preferentially oriented domains, which are formed by aggregation of hard segment units.

SEM micrographs of prepared PU elastomers which are shown in Figures 3.55 and 3.56 are based on Capa 225/CHDI/1,4-BD+1,4-CHDM and Capa 225/CHDI/1,4-BD respectively. The micrographs in Figure 3.55 show that as the series proceeds from a→c, the degree of discrete spherulitic structure becomes more pronounced. In fact, for sample(a) with 0.2% excess CHDI no well defined spherulitic boundaries exist. The explanation for the systematic change in morphology of these polymers is considered to be the result of the increasing hard segment content which gets proportionally higher in the case of using the greater excess CHDI.

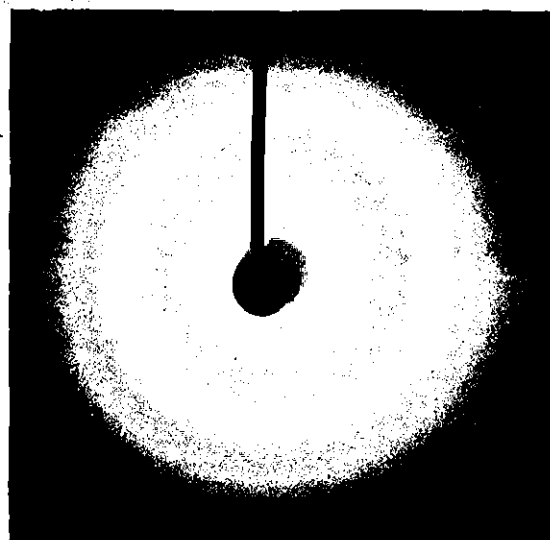
The SEM results are in good agreement with the X-ray results in which the WAXS pattern of the polymer with a higher amount of excess CHDI was

sharper and better defined. This shows the presence of more microcrystalline hard segments in polyurethane elastomers that have higher percentages of excess CHDI (30%) in comparison with those PU samples with lower percentages of excess CHDI (0.2%). It is thought that it is the presence of excess amounts of diisocyanate which is capable of creating some isocyanurate structure in the polymer, and that this enhances the domain structure because of the higher hydrogen bonding ability resulting in segregation of the hard segments. The thermal stability and mechanical properties of such polyurethane elastomers are observed to be improved by this domain structure formation.

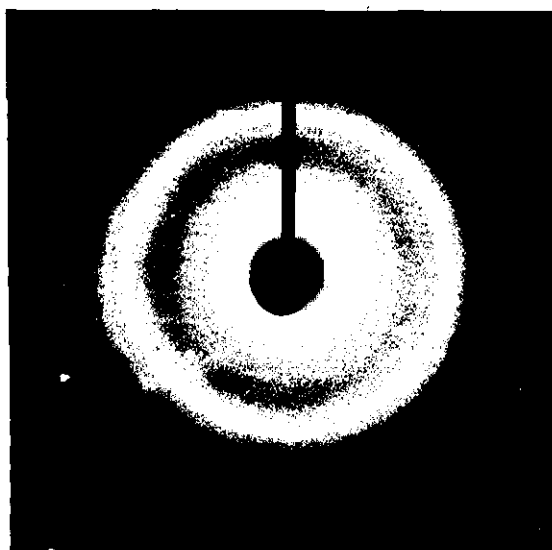
SEM studies of Capa 225/CHDI/1,4-BD based PU elastomers (Figure 3.56) show similar results to those shown in Figure 3.56 for the 1,4-BD+1,4-CHDM based PU elastomer system.



(a)



(b)



(c)

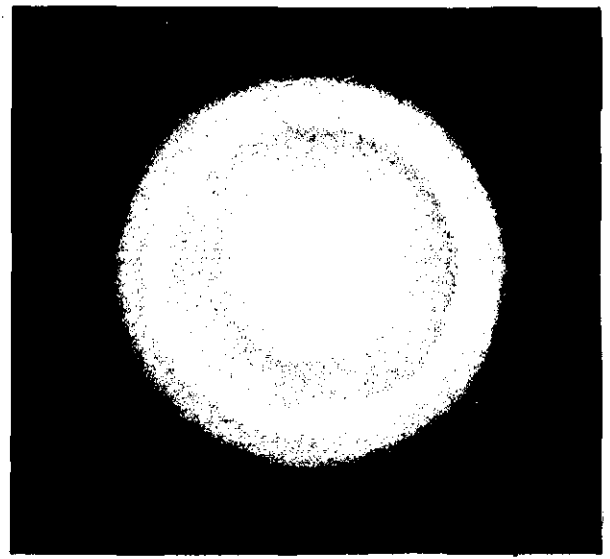
FIGURE 3.50: Wide angle X-ray diffraction patterns of Capa 225/CHDI/1,4-BD series with different percentages of excess CHDI:

- a) 5%;
- b) 30%;
- c) 50%.

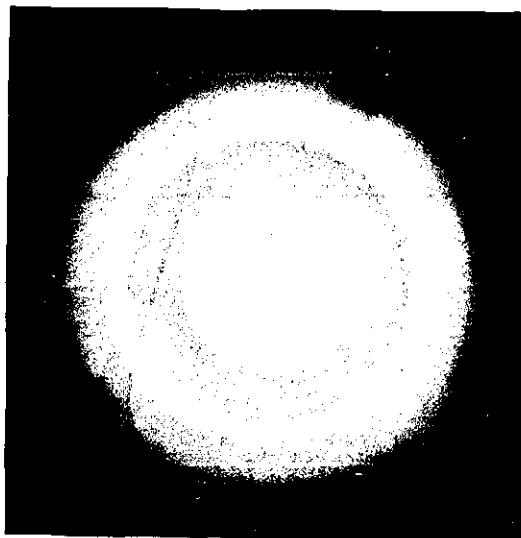
(Unstained samples)



(a)



(b)



(c)

FIGURE 3.51: Wide angle X-ray diffraction patterns of Capa 225/CHDI/1,4-BD+1,4-CHDM series with different percentage of excess CHDI; (a) 0.2%; (b) 5%; (c) 30%. (Unstained samples)

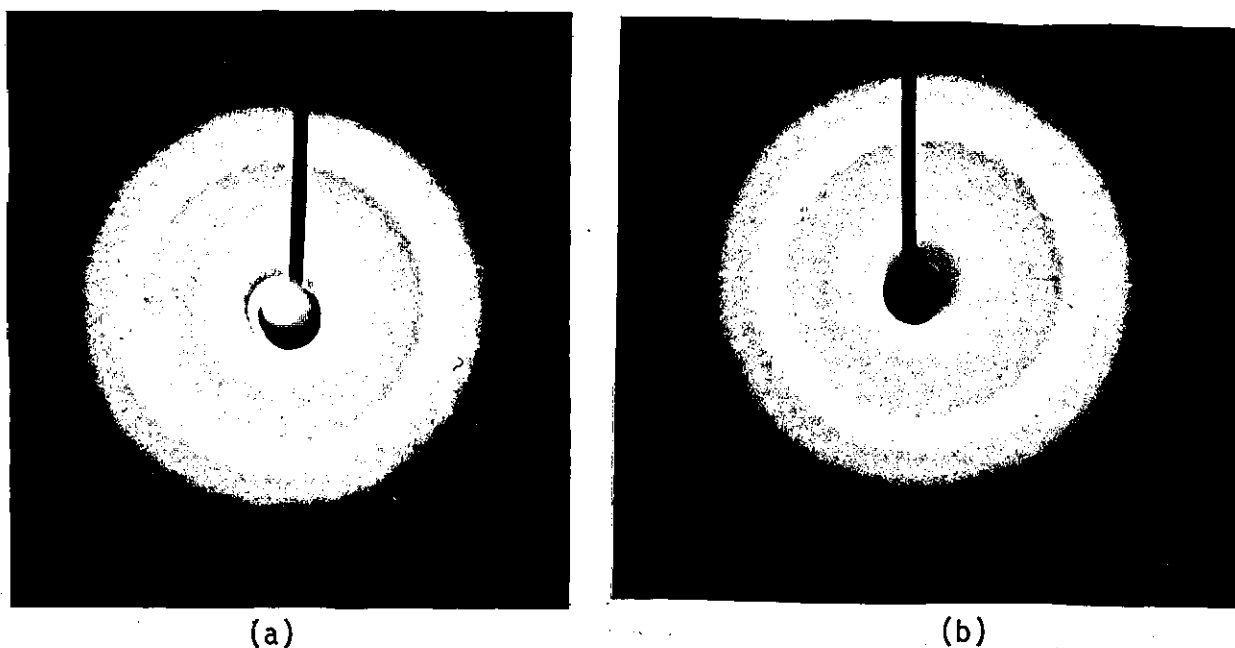


FIGURE 3.52: Wide angle X-ray diffraction patterns of Capa 225/CHDI/Polacure series with different percentage of excess CHDI: (a) 0.2%; (b) 30%. (Unstained samples)

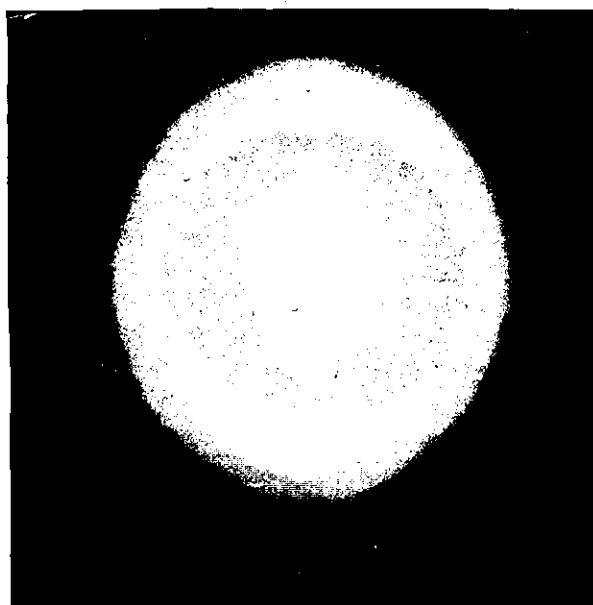
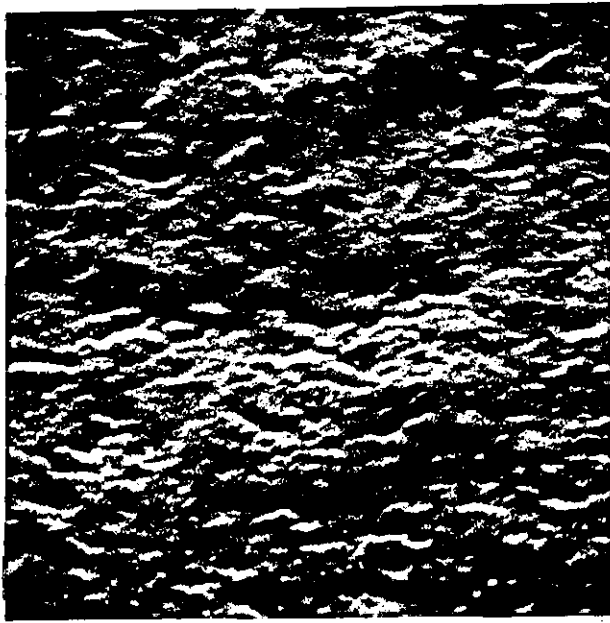
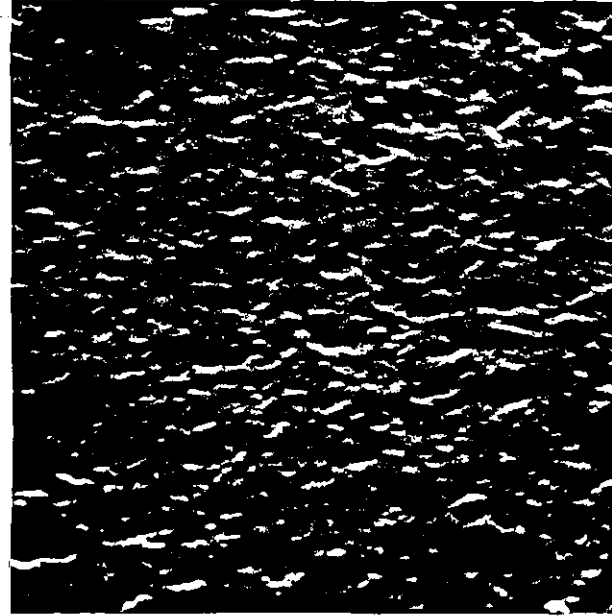


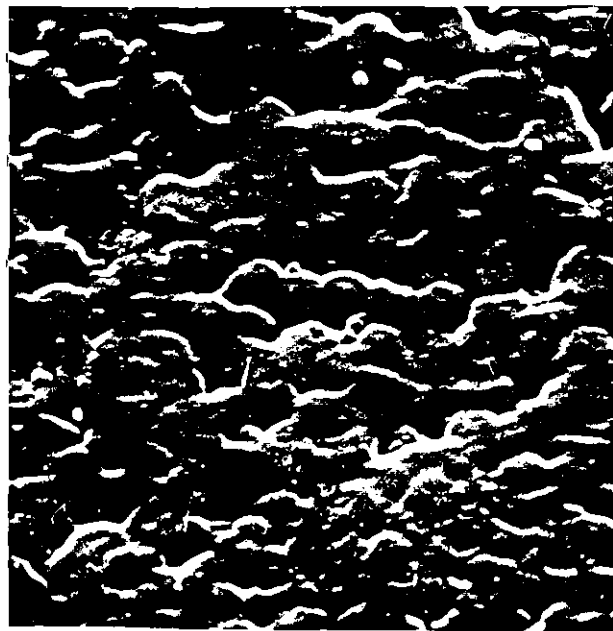
FIGURE 3.53: Wide angle X-ray diffraction pattern of Capa 225/CHDI/1,4-BD+1,4-CHDM series with 30% excess CHDI at 300% extension (arrow shows the direction of extension)



(a)

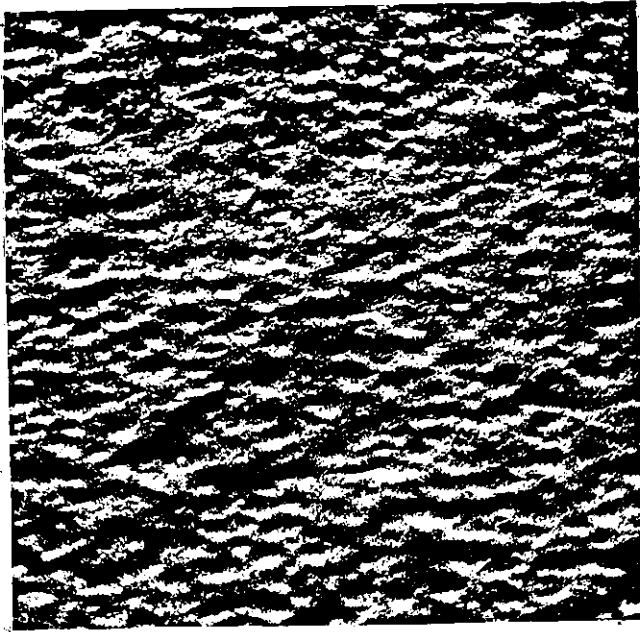


(b)

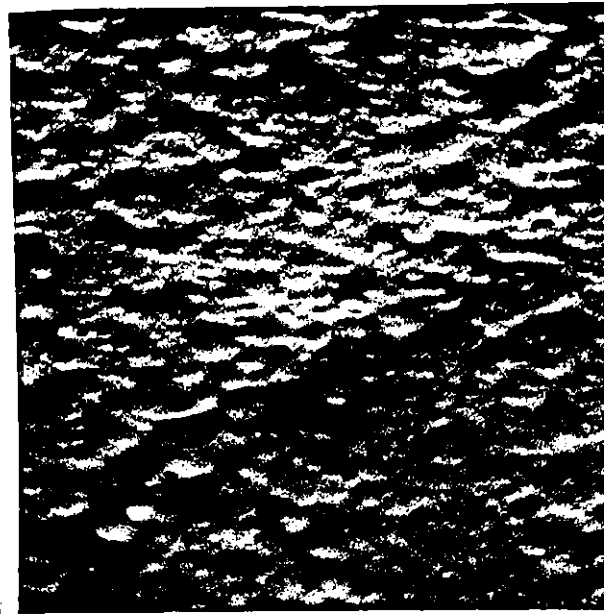


(c)

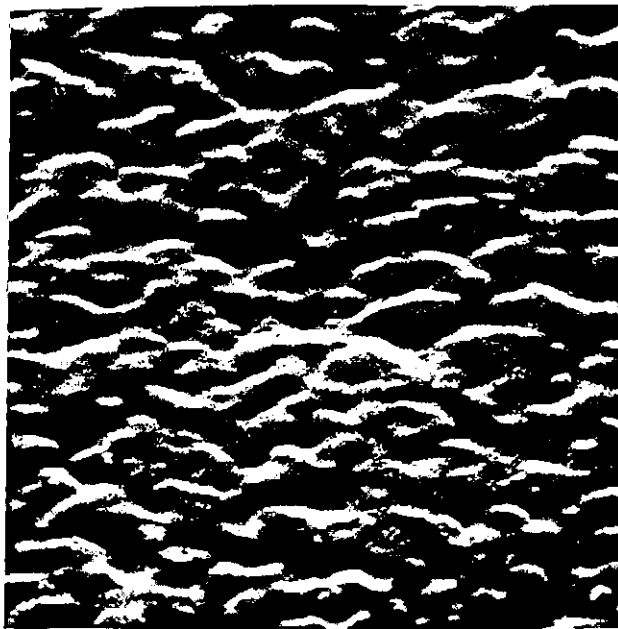
FIGURE 3.55: SEM micrographs (2000X magnification) showing the surface morphologies of Capa 225/CHDI/1,4-BD+1,4-CHDM based PU elastomer having different percentage of excess CHDI: (a) 0.2%; (b) 5%; (c) 30%.



(a)



(b)



(c)

FIGURE 3.56: SEM micrographs (2000X magnification) showing the surface morphologies of Capa 225/CHDI/1,4-BD based PU elastomer having different percentage of excess CHDI: (a) 5%; (b) 30%; (c) 50%.

3.2.6 Determination of Crosslink Density by Swelling

3.2.6.1 Introduction

As mentioned in Chapter 1, the crosslinking of polymer chains is of primary importance in controlling many polymer properties. In the case of a polyurethane elastomer, crosslinking can be produced by the use of either an excess of the diisocyanate or a branched polyol having functionality greater than two.

Basic Principles:

Swelling measurements are often used to measure the crosslink density of elastomers. The degree of swelling (the amount of solvent imbibed) is known to be dependent upon the crosslink density of polymer networks; the greater the crosslink density, the less is the degree of swelling. Percentage swelling by volume of the polymer samples can be determined by using the following formula¹⁵⁴:

$$\% \text{ swelling by volume} = \frac{\text{Gain in weight}}{\text{Specific gravity of solvent}} \times \frac{\text{Specific Gravity of specimen}}{\text{Original weight of specimen}} \times 100$$

The number average molecular weight between crosslinks, M_c , can be calculated from the Flory-Rehner¹⁵⁵ equation:

$$-\ln[(1-V_r) + V_r + \chi V_r^2] = \rho V_s M_c^{-1} (V_r^{1/3} - V_r/2) \quad (B)$$

where V_r is the volume fraction of polymer in the swollen gel at equilibrium

χ is the polymer-solvent interaction parameter

V_s is the molar volume of solvent

M_c is the number average molecular weight between crosslinks

ρ is the density of polymer.

The volume fraction of polymer (V_r) can be calculated from the equation:

$$V_r = \frac{m_1 d_s}{m_1 (d_s - d_r) + m_2 d_r} \quad (C)$$

where m_1 is the weight of the polymer before swelling

m_2 is the weight of the polymer after swelling

d_s is the density of solvent

d_r is the density of polymer.

The polymer-solvent interaction parameter (χ) was determined from the Bristow and Watson¹⁵⁶ semi-empirical equation:

$$\chi = \beta_1 + (V_s/RT)(\delta_s - \delta_p)^2 \quad (D)$$

where β_1 is the lattice constant, usually about 0.34
 V_s is the molar volume of solvent
 R is the universal gas constant
 T is the absolute temperature
 δ is the solubility parameter and the subscripts s and p refer to the swelling agent and polymer, respectively.

The solubility parameters of polyurethane and the solvent (toluene) are $10.0 \text{ (cal/cc)}^{1/2}$ and $8.9 \text{ (cal/cc)}^{1/2}$ respectively, according to the data taken from polymer handbooks¹⁵⁷.

The molar volume of solvent is determined from the equation:

$$V_s = \frac{M}{d}$$

where: M is the molecular weight of solvent
 d is the density of solvent.

The crosslink density, defined as $\frac{1}{2M_c}$ can therefore be calculated.

3.2.6.2 Experimental Procedure

Swelling experiments were conducted on small rectangular (approximately $20 \times 10 \times 2 \text{ mm}$) specimens of the synthesised PU's in toluene at room temperature for one week. A swelling time of one week was chosen as the basis of the test results on several samples which showed no significant changes after one week of immersion in toluene. At the end of the immersion period the sample was removed, rapidly blotted with tissue and transferred to the weighing bottle to obtain the swollen weight of the sample. The crosslink density was calculated, based on the values of V_r and V_s obtained, using equation (B). Crosslink density was expressed as moles of crosslink per gram of insoluble network.

3.2.6.3 Results and Discussion

As the polymer-solvent interaction parameter χ was necessary to calculate the crosslink density from the swelling data, it was determined ($\chi = 0.56$) from the equation (D).

The results of swelling tests for five series of prepared polyurethane elastomers are given in Tables 3.38 to 3.42 and Figure 3.57. The results indicate that:

1. The crosslink density values of the polyurethanes significantly increased with increasing amounts of excess diisocyanate in the original gel.
2. The swelling capacity (or ability of the network to imbibe solvent) decreases with increasing the degree of crosslinking.
3. Swollen volume of polyurethanes based on 1/2/1 block ratio was greater than the swollen volume of urethanes based on 1/3/2; this means samples with lower block ratio have lower crosslink density.
4. Swollen volume of the Polacure based urethane was greater than the swollen volume of the 1,4-BD+1,4-CHDM based urethanes (as is clear from Tables 3.39 and 3.40).
5. Crosslink density of polyurethanes cured by Polacure exhibited higher values than the polyurethanes cured with the 1,4-BD+1,4-CHDM chain extension agent (see Figure 3.57).
6. Polyurethanes extended by the Dianol (22+33) chain extension agent showed a lower crosslink density than those extended by Dianol (22+33)+TMP (1/1) or TMP alone. These results illustrated that more crosslinks were formed during the chain extension of polyurethane with TMP chain extender (see Table 3.42) than where it was not used in the chain extension system.

TABLE 3.38: Crosslink Density and Swollen Volume of Polyurethane Elastomer Based on Capa 225/CHDI/1,4-BD (Block ratio 1/2/1)

Sample No	% Excess CRDI	V_r	% Volume Swollen	Crosslink Density (mole/g)
Capa 17,1	2	0.4862	235	72.7×10^{-5}
B59	5	0.4939	232	77.44×10^{-5}
B60	10	0.5049	228.3	84.76×10^{-5}
B61	15	0.5200	222.3	95.58×10^{-5}
B62	20	0.5295	219	103.04×10^{-5}
B56	25	0.5512	211	121.93×10^{-5}
B63	30	0.5601	209	130.34×10^{-5}
B64	35	0.5690	206.6	139.15×10^{-5}
B65	40	0.5860	201	157.72×10^{-5}
B66	45	0.5882	201	160.24×10^{-5}
A'6	50	0.5929	199	165.85×10^{-5}

TABLE 3.39: Crosslink Density and Swollen Volume of Polyurethane Elastomer Based on Capa 225/CHDI/1,4-BD + 1,4-CHDM (Block ratio 1/3/2)

Sample No	% Excess CHDI	V_r	% Volume Swollen	Crosslink Density (mole/g)
Capa 18,6	0.2	0.5751	204	146.47×10^{-5}
B74	5	0.5895	200	167.14×10^{-5}
B75	10	0.5966	198	170.49×10^{-5}
B76	15	0.6024	197	177.72×10^{-5}
B77	20	0.6066	196	182.46×10^{-5}
B78	25	0.6159	194	194.97×10^{-5}
B79	30	0.6251	191	208.15×10^{-5}
B80	35	0.6382	188	228.16×10^{-5}
B81	40	0.6398	188	230.71×10^{-5}

TABLE 3.40: Crosslink Density and Swollen Volume of Polyurethane Elastomer Based on Capa 225/CHDI/Polacure (Block Ratio 1/3/2)

Sample No	% Excess CHDI	V_r	% Volume Swollen	Crosslink Density (mole/g)
B142	0.2	0.6067	200	177.61×10^{-5}
B143	5	0.6362	192	227.12×10^{-5}
B144	10	0.6502	189	241.78×10^{-5}
B145	15	0.6623	186	262.23×10^{-5}
B146	20	0.6642	185	266.32×10^{-5}
B147	25	0.6879	180	314.59×10^{-5}
B148	30	0.6962	179	332.10×10^{-5}

TABLE 3.41: Crosslink Density and Swollen Volume of Polyurethane Elastomer Based on Capa 225/PPDI/1,4-BD (Block Ratio 1/2/1)

Sample No	% Excess CHDI	V_r	% Volume Swollen	Crosslink Density (mole/g)
B119	0.2	0.5637	210	131.79×10^{-5}
B120	5	0.5639	209	132.32×10^{-5}
B121	10	0.5676	208	136.05×10^{-5}
B122	15	0.5773	205	146.08×10^{-5}
B123	20	0.5789	204	147.30×10^{-5}
B124	25	0.5882	203	157.79×10^{-5}

TABLE 3.42: Crosslink Density and Swollen Volume of Soft Polyurethane Elastomer
(Block Ratios 1/3/2)

Sample No	Polyol	Diisocyanate	Chain Extender	V_r	% Volume Swollen	Crosslink Density (mole/g)
B103	Capa 225	PPDI	Dianol (22+33)	0.4851	241	69.27×10^{-5}
B106	Capa 225	PPDI	Dianol (22+33) + TMP	0.5409	219	108.94×10^{-5}
B108	Capa 225	PPDI	TMP	0.7227	208	400.64×10^{-5}
B131	Capa 240+ Capa 305 (3/1)	PPDI	TMP	0.4806	240	678.80×10^{-5}
B133	Capa 225	CHDI	TMP	0.5663	207	135.86×10^{-5}
B155	Capa 231	CHDI	Capa 305	0.4014	278	33.55×10^{-5}

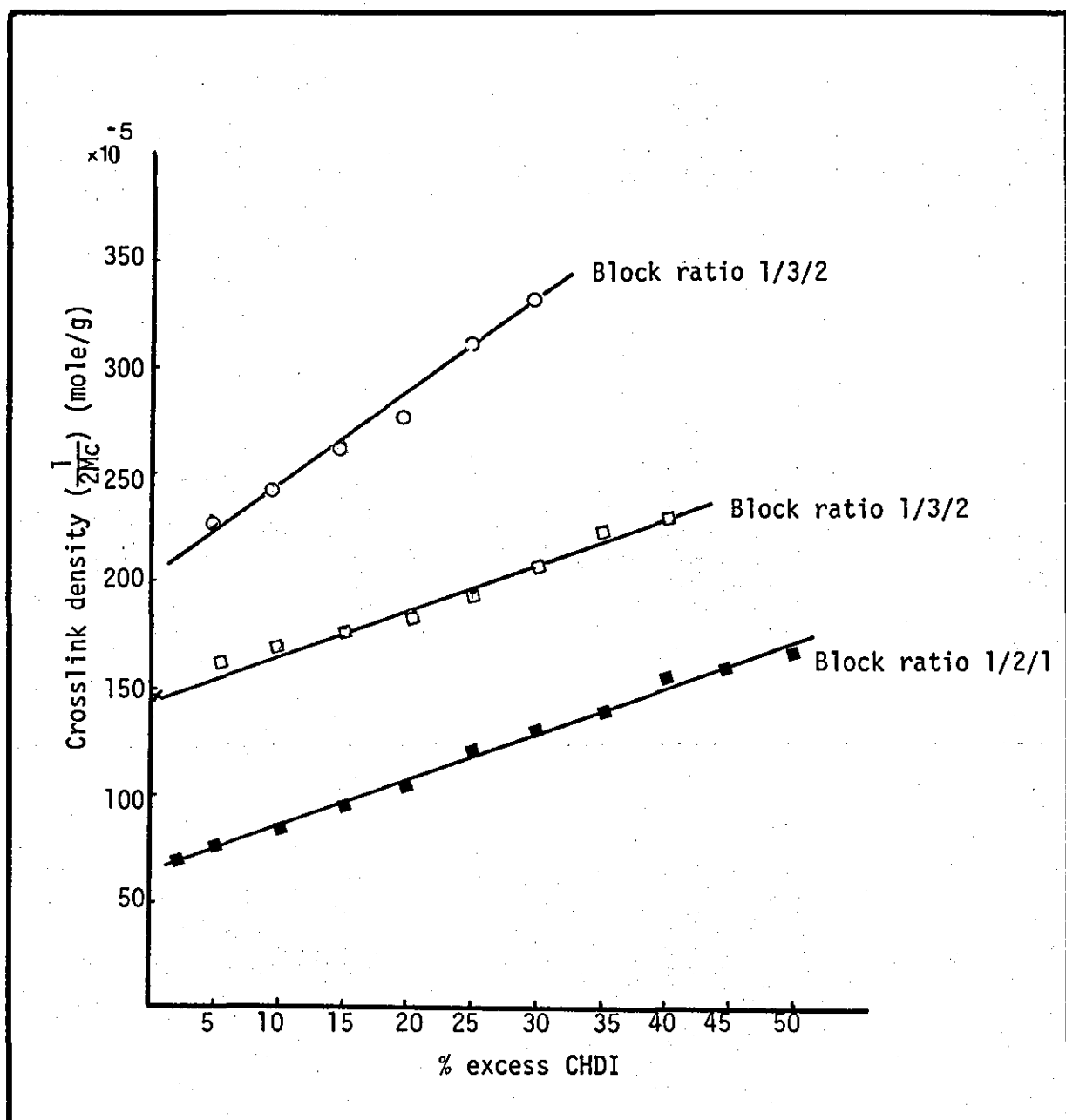


FIGURE 3.57: Crosslink density vs % excess CHDI for the polyurethane elastomer based on Capa 225/CHDI/chain extender: (o) Polacure; (\square) 1,4-BD+1,4-CHDM; (\triangle) 1,4-BD

CHAPTER 4

GENERAL PHYSICAL AND MECHANICAL PROPERTIES

The present chapter deals with the measurement of physical and mechanical properties of the prepared polyurethane elastomers. These include the tensile properties, tear strength, compression set, hardness, tension set, density, skid resistance, fatigue life, heat generation, hysteresis and ageing of the polymers.

4.1 TENSILE STRENGTH PROPERTIES

The stress-strain properties were carried out in accordance with BS 903: Part A: 1971. The JJ tensile testing machine* Model T5002 was used in conjunction with an X-Y plotter (PL 100 of JJ) while the crosshead speed was maintained at 100 mm/minute and a load cell giving a maximum load of 500 Newtons was employed throughout. Test specimens were BS dumbbell type 2 cut from 2-3 mm thick cast sheets using a die punch cutter. Four to five specimens were used for each determination and all the samples were conditioned for at least 2 weeks at room temperature (23°C) and 60% relative humidity prior to testing. The following tensile parameters were calculated and the results cited in appropriate tables:

i) Ultimate tensile strength

Ultimate tensile strength is calculated from the recorded load at break using the following formula:

$$\text{Ultimate tensile strength} = \frac{\text{Force at break}}{\text{Initial cross-section area}} \quad (\text{MPa})$$

* J J Lloyd Instruments Ltd, Warsash, Southampton, England

ii) Modulus at 100% and 300% strain

Modulus at a given tensile strain is a tensile stress at a given strain and obtained as follows:

$$\text{Modulus (at 100\% or 300\%)} = \frac{\text{Force at a given strain}}{\text{Initial cross-section area}} \quad (\text{MPa})$$

iii) Elongation at break (%)

It was calculated by subtracting the initial distance between the reference lines on the dumbbell test piece from the distance between the lines at breaking point and expressing the results as a percentage of the initial distance. For type 2 test pieces, the initial distance is 20 mm.

Tensile properties were also measured at elevated temperature in order to correlate crosslinking effect and structural variation with strength properties.

4.1.1 Results and Discussion

The results of tensile properties of prepared polyurethane elastomers are presented in Tables 4.1 to 4.7. Table 4.1 shows the properties of polymers which are based on the Capa 225/CHDI system and chain extended with different diol chain extenders. The block ratio varied from 1:2:1 to 1:2.6:1 for some samples i.e. increasing hard segment content by using excess CHDI. The hardness, tensile strength and modulus increase with

increasing hard segment content, this shows the effect of excess diisocyanate on improving physical properties. A similar effect is demonstrated in the Capa 225/CHDI/1,4-BD based polymers where the increase in CHDI from stoichiometric ratio to 30% excess improved tensile properties (see Tables 4.2 and 4.4).

In order to measure thermal stability and strength retention, tensile properties of polyurethanes are also measured in elevated temperatures using a hot air environmental chamber to enclose the grips of a JJ Lloyd tensile testing machine. The tensile properties at room temperature and up to 210°C of the two series of polyurethane elastomers based on Capa 225/CHDI/1,4-BD and Capa 225/CHDI/1,4-BD+1,4-CHDM studied are given in Tables 4.4 and 4.5 respectively. In both these series the percentage of free isocyanate allowed to be present in the elastomer on first casting was varied from 0-50% in 5% steps.

Influence of % Free NCO on the Properties of the PU Elastomer at Room Temperature

For both the PU systems studied there is an increase in the hardness values of 8-9° Shore A as the amount of molar excess of isocyanate available for crosslinking increases from 0 to 50%. In the 1,4-BD extended polymer (Table 4.4) tensile strength values increase from about 17 MPa at 0% free NCO to a maximum of nearly 61 MPa at 30% excess NCO; this is an increase by a factor of 3.58. In parallel, for the mixed 1,4-BD+1,4-CHDM extended PU system (Table 4.5) an initial tensile strength of 25.4 MPa increases to a maximum of 62.45 MPa at 30% excess diisocyanate. Elongation at break values remain consistently high for both systems and are nearly always in the range 500-800%. The elastomers produced, though stiff in nature, were highly elastic materials possessing ready flexibility and good elastic recovery characteristics. Modulus values were consistently high and increased steadily with increasing NCO levels.

Strength Properties at Elevated Temperature

The changes in tensile properties, as the temperature rises from 23°C to 210°C, follow a consistent pattern and decrease uniformly. It is specially observed that these polyurethanes show no sharp melting points accompanied by rapid loss in dimensional stability. This is a characteristic usually only shown by the traditional covalent crosslinked rubbers such as NR, CR and the like and is of importance in engineering applications where it is essential to avoid failures of a catastrophic nature which may occur if a polymer possesses a sharp melting point.

Retention of tensile strength at elevated temperature is seen to reach a maximum at the excess NCO % content of 40% with the 1,4-BD extended polyurethanes and at 30% with the mixed 1,4-BD+1,4-CHDM extended polymers. With both systems elongation at break values remain at consistently high levels throughout the temperature range 23-210°C. Also the polyurethanes remained dimensionally stable and elastic as demonstrated by their possession of measurable elastic modulus at the highest test temperatures used.

There is some indication from a few tensile test results that the systems may remain elastic at 240°C (see Table 4.5); this aspect was not pursued as it was considered that ultimate tensile strength values of about 5-7 MPa for the 1,4-BD system at 240°C and 5-9 MPa for the 1,4-BD+1,4-CHDM systems at 210°C represent the lower strength limits of a useful engineering elastomer.

Systematic trends in physical properties, with respect to the percentage of excess diisocyanate used, are readily detectable and illustrated in Figures 4.1 and 4.2 which show all physical properties to reach maximum values at specific values of the initial excess of diisocyanate which is usually in the 30-40% range.

NR = Natural Rubber
CR = Chloroprene Rubber

Tensile properties of polyurethane elastomers based on Capa 225/CHDI and extended with different diols and diamine are given in Table 4.6 to compare the effect of diols and diamine on tensile properties.

As the table shows in the case of Polacure based PU elastomer, the hardness and modulus are higher and the elongation at break is lower. This is believed to be due to the formation of urea linkages in the polymer backbone which is affected on crosslinking and hydrogen bonding formation and gives more rigidity to the polymer.

The tensile properties of some soft polyurethanes are also given in Table 4.7. It is seen that the hardness and modulus increase and ultimate tensile strength and elongation at break decrease by using TMP as a mixed chain extender with Dianol (22+33) or alone (see Figure 4.4). This is perhaps due to more crosslinking and poor molecular ordering in these systems. Moreover, the low level of tensile strength properties exhibited by these materials indicates the presence of a disordered system having mixed hard and soft segments.

4.2 HARDNESS

The hardness of all polyurethane elastomers was determined using a Durometer hardness tester (Shore A and Shore D) according to ASTM D-2240.

4.2.1 Results and Discussion

Values of hardness (Shore A and Shore D) of all prepared polyurethanes are given in Tables 2.3 and 2.4. The hardness values of some polyurethane elastomers are also given in Tables 4.1 to 4.7. Symmetrical, bulky diisocyanate and chain extenders give rise to materials of higher hardness while asymmetrical diisocyanates and chain extenders give much softer materials, indicative of relatively poor packing of hard segments. Increased hard segment content by using higher block ratio or using excess diisocyanate gives a marked increase in hardness.

TABLE 4.1: Tensile Properties of Polyurethane Elastomers Based on Capa 225/CHDI/chain extender (see table) with 1/2/1 molar ratio

Sample No	% Excess CHDI	Chain Extenders Used	UTS	EB	M ₁₀₀	M ₃₀₀	Hardness	
							A	D
B57	0	1,5-naphthalene diol	13.44	545	5.09	9.64	72	22
B58	0	Quinol	16.34	500	7.89	12.83	85	31
B93	30	Quinol	22.11	410	10.49	17.44	90	38
B67	0	Catechol	17.62	440	6.92	13.36	82	25
B68	0	2,3-naphthalene diol	11.81	485	5.33	8.58	78	27
B69	0	2,4-dihydroxybenzo-phenone	25.73	685	6.63	12.66	81	28
-	0	P,P'-biphenol	16.69	570	6.7	11.21	85	29
B92	30	P,P'-biphenol	22.13	450	9.91	15.95	92	39
B94	30	Di(4-hydroxy)sulphone	28.83	440	10.4	19.23	89	37
B95	30	Bisphenol A	24.17	515	7.36	14.66	84	29

Key: UTS = Ultimate Tensile Strength in MPa
 EB = Elongation at Break, %
 M₁₀₀ = Modulus at 100% strain in MPa
 M₃₀₀ = Modulus at 300% strain in MPa
 A and D = Hardness in Shore

TABLE 4.2: Tensile Properties of Polyurethane Elastomers Based on Capa 225/CHDI/1,4-BD with 1/3/2 molar ratio

Sample No	% Excess CHDI	UTS	EB	M ₁₀₀	M ₃₀₀	Hardness	
						A	D
B1	0	25.36	480	9.92	16.5	90	38
B84	5	32.8	600	10.95	17.49	92	43
B85	10	44.46	720	11.80	19.18	92	44
B86	25	55.0	675	14.24	25.41	96	49
B87	30	52.73	630	14.38	27.39	96	49

Key: As in Table 4.1

TABLE 4.3: Tensile Properties of Polyurethane Elastomers Based on Capa 225/PPDI/1,4-BD with 1/2/1 molar ratio

Sample No	% Excess PPDI	UTS	EB	M ₁₀₀	M ₃₀₀	Hardness	
						A	D
B118	0	26.93	550	11.23	16.29	88	40
B119	0.2	54.89	720	11.06	18.67	89	40
B120	5	50.7	650	11.01	19.38	89	41
B121	10	52.01	650	10.75	18.76	90	42
B122	15	50.68	640	10.39	18.04	89	41
B123	20	51.6	645	10.82	19.52	89	42
B124	25	52.17	630	11.28	21.04	90	42
B125	30	56.59	600	10.19	21.06	90	42

Key: as in Table 4.1

TABLE 4.4: Tensile Properties of Polyurethane Elastomers Based on Capa 225/CHDI/1,4-BD with 1/2/1 molar ratio at room and elevated temperature

Sample No	% Excess CHDI	Test Temperature											
		23 ^o C				120 ^o C				150 ^o C			
		UTS	EB	M ₁₀₀	M ₃₀₀	UTS	EB	M ₁₀₀	M ₃₀₀	UTS	EB	M ₁₀₀	M ₃₀₀
A27	0	17.02	630	6.73	10.69	4.10	30	-	-	-	-	-	-
Capa 17,1	2	43.80	820	7.33	12.35	7.15	385	5.04	6.48	4.87	325	3.82	4.77
B59	5	44.27	790	9.5	16.12	11.5	580	5.82	8.06	6.23	460	3.64	4.83
B60	10	53.36	830	9.5	16.73	12.71	575	6.81	9.12	8.12	395	6.15	7.39
B61	15	53.50	745	9.88	17.40	13.52	570	6.85	9.23	8.45	435	5.28	6.88
B62	20	56.56	750	10.61	18.82	17.07	650	7.07	9.81	10.45	525	5.15	7.18
B56	25	57.48	710	11.42	20.79	19.74*	660*	8.40	11.52	14.32	640	7.37	9.68
B63	30	60.97	715	11.52	20.79	21.66*	670*	9.44	12.57	15.8	590	8.72	10.86
B64	35	60.69	690	11.96	22.17	23.23*	660*	9.51	13.10	17.88	665	7.44	10.41
B65	40	55.24	570	12.85	24.59	28.16*	670*	10.66	14.10	16.13	430	8.54	12.09
B66	45	54.20	580	13.12	25.57	25.43*	660*	8.94	14.89	18.74	580	8.4	11.47
A'6	50	51.48	675	12.55	22.81	20.6	635	10.1	13.57	13.39	505	7.38	9.99

* Sample did not break (because of limitation of oven's length)

TABLE 4.4 ... continued

Sample No	% Excess CHDI	Test Temperature												Hardness	
		180°C				210°C				240°C				A	D
		UTS	EB	M ₁₀₀	M ₃₀₀	UTS	EB	M ₁₀₀	M ₃₀₀	UTS	EB	M ₁₀₀	M ₃₀₀		
A27	0	-	-	-	-	-	-	-	-	-	-	-	-	81	27
Capa 17,1	2	2.54	55	-	-	-	-	-	-	-	-	-	-	83	34
B59	5	3.06	60	-	-	1.77	30	-	-	-	-	-	-	85	35
B60	10	5.75	330	5.12	5.65	3.12	20	-	-	-	-	-	-	86	37
B61	15	5.22	340	4.18	4.96	2.21	30	-	-	-	-	-	-	87	38
B62	20	7.03	434	4.67	5.75	3.57	80	-	-	-	-	-	-	88	39
B56	25	10.38	545	6.81	8.06	5.27	315	5.01	-	-	-	-	-	88	40
B63	30	10.26	510	6.61	7.99	5.47	250	5.01	-	-	-	-	-	89	41
B64	35	11.54	600	6.14	7.79	5.4	290	4.84	-	-	-	-	-	90	42
B65	40	11.69	365	8.08	10.33	7.13	330	5.9	6.87	5.28	100	5.28	-	90	43
B66	45	13.22	590	6.21	8.27	6.33	310	5.56	6.27	4.48	50	-	-	91	44
A'6	50	10.22	410	6.93	8.78	6.15	220	5.7	-	-	-	-	-	91	44

Note: Key as in Table 4.1.

TABLE 4.5: Tensile Properties of Polyurethane Elastomers Based on Capa/CHDI/1,4-BD+1,4-CHDM with 1/3/2 molar ratio at room and elevated temperature

Sample No	% Excess CHDI	Test Temperature											
		23°C				120°C				150°C			
		UTS	EB	M ₁₀₀	M ₃₀₀	UTS	EB	M ₁₀₀	M ₃₀₀	UTS	EB	M ₁₀₀	M ₃₀₀
A2	0	25.40	688	6.20	11.17	5.52	380	3.69	4.93	2.91	125	2.8	-
Capa 18,16	0.2	35.84	665	9.58	12.29	11.99	440	8.39	10.54	8.97	270	8.4	-
B74	5	49.27	790	12.05	19.59	15.10	505	9.67	11.82	9.55	355	7.72	8.97
B75	10	56.74	705	12.45	22.54	20.7*	675*	7.29	10.29	13.24	515	6.61	8.82
B76	15	56.91	715	12.25	22.03	24.18*	660*	9.0	12.35	15.52	500	8.70	11.17
B77	20	55.89	675	12.62	23.34	25.64*	670*	9.06	12.78	16.07	545	7.60	10.31
B78	25	57.44	650	12.94	24.88	29.18*	650*	10.23	14.60	21.21	570	9.96	12.76
B79	30	62.45	620	14.36	28.29	29.67*	680*	10.46	14.63	20.49	590	8.65	11.92
B80	35	54.82	560	14.80	28.84	28.01	540	11.22	16.11	19.96	445	10.35	13.96
B81	40	54.46	515	16.01	31.40	25.72	530	11.30	16.14	17.99	440	9.50	13.29
B82	45	54.90	475	17.20	33.74	-	-	-	-	-	-	-	-
B83	50	46.78	420	17.42	33.48	-	-	-	-	-	-	-	-

* Sample did not break (because of limitation of oven's length)

TABLE 4.5 ... continued

Sample No	% Excess CHDI	Test Temperature								Hardness	
		180°C				210°C					
		UTS	EB	M ₁₀₀	M ₃₀₀	UTS	EB	M ₁₀₀	M ₃₀₀	A	B
A2	0	2.8	35	-	-	-	-	-	-	92	42
Capa 18,6	0.2	5.84	90	-	-	-	-	-	-	92	42
B74	5	7.12	115	7.12	-	5.69	40	-	-	92	44
B75	10	7.77	375	5.99	7.0	5.67	110	5.67	-	92	45
B76	15	9.72	400	7.23	8.52	5.39	75	-	-	92	45
B77	20	8.58	375	6.04	7.61	5.54	140	5.29	-	93	46
B78	25	14.39	470	9.41	11.01	8.71	330	7.88	8.47	94	47
B79	30	13.12	490	7.41	9.58	7.34	295	6.58	-	94	48
B80	35	12.97	325	9.97	12.30	9.2	275	8.73	-	94	51
B81	40	12.81	395	8.72	10.93	9.2	310	8.25	8.95	95	52

Note: Key as Table 4.1.

TABLE 4.6: Tensile Properties of Polyurethane Elastomers Based on Capa 225/CHDI/chain extender (see Table) with 1/3.9/2 molar ratio

Sample No	Chain Extenders Used	UTS	EB	M ₁₀₀	M ₃₀₀	Hardness	
						A	D
B87	1,4-BD	52.73	630	14.38	27.39	96	49
B79	1,4-BD+1,4-CHDM	62.45	620	14.36	28.29	94	48
B97	1,4-CHD	29.6	380	15.47	23.99	95	48
B89	HQEE	36.19	380	19.24	28.59	98	56
B148	Polacure	39.92	310	21.73	37.35	95	53

Note: Key as in Table 4.1.

TABLE 4.7: Tensile Properties of the Soft Series of PU Elastomers

Sample No	Polyol	Diisocyanate	Chain Extender	UTS	EB	M ₁₀₀	M ₃₀₀	Hardness	
								A	D
B103	Capa 225	PPDI	Dianol(22+33)	31.61	440	3.04	10.86	62	21
B106	"	PPDI	Dianol(22+33)+TMP(1/1)	13.22	200	4.87	-	66	24
B108	"	PPDI	TMP	12.45	120	8.58	-	75	26
B155	Capa 231	CHDI	Capa 305	19.13	220	7.56	-	72	22
B131	Capa 240 +Capa 305 (3/1)	PPDI	TMP	15.56	165	6.45	-	70	26

Note: Key as in Table 4.1.

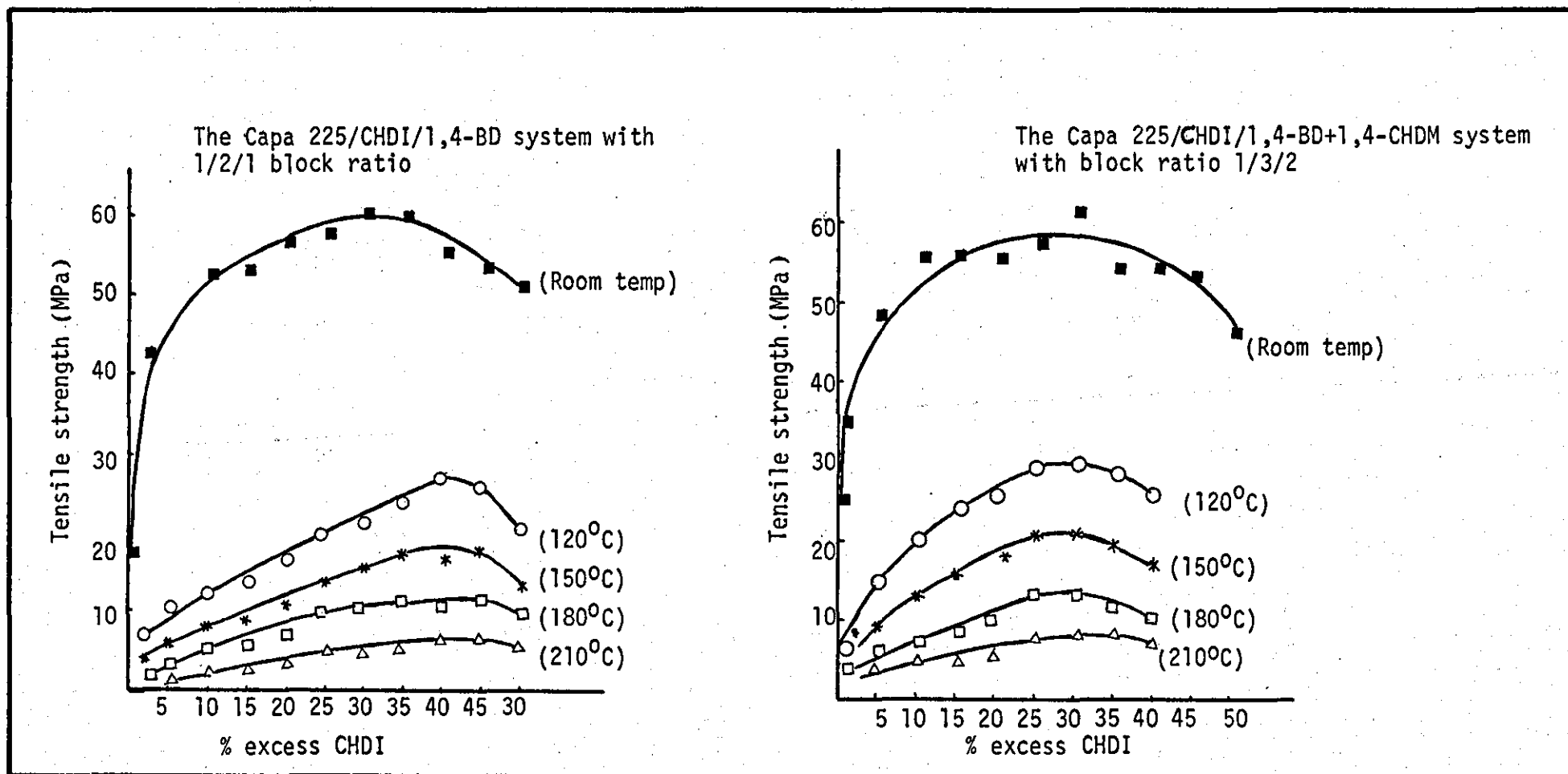


FIGURE 4.1: Relationship between tensile strength at different temperatures and the excess amount of diisocyanate used for crosslinking CHDI based polyurethane

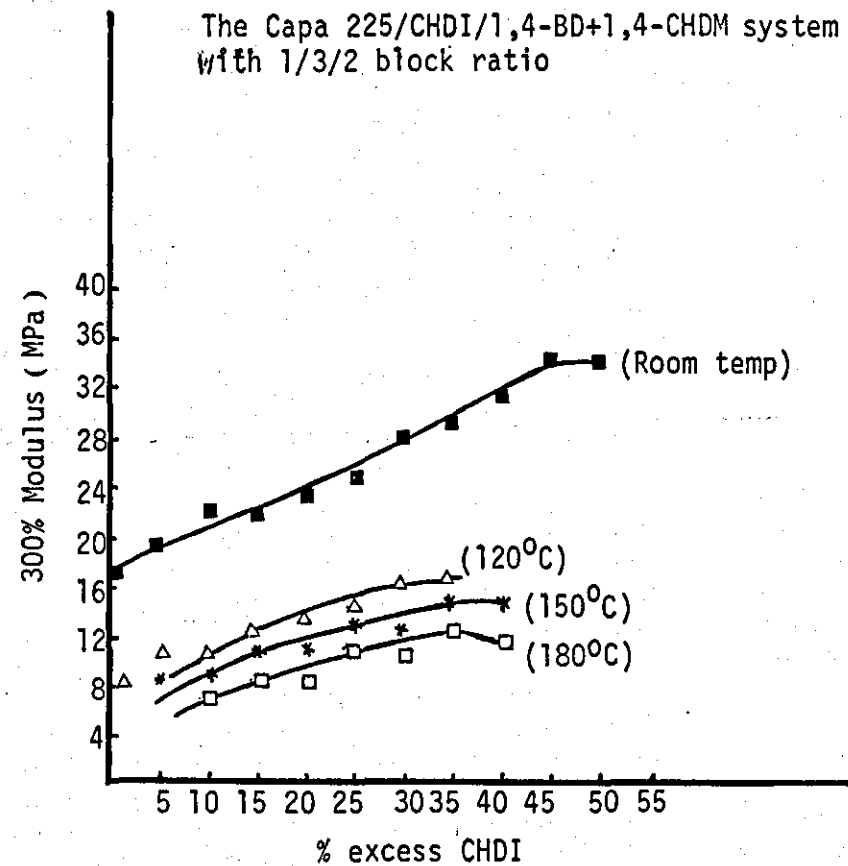
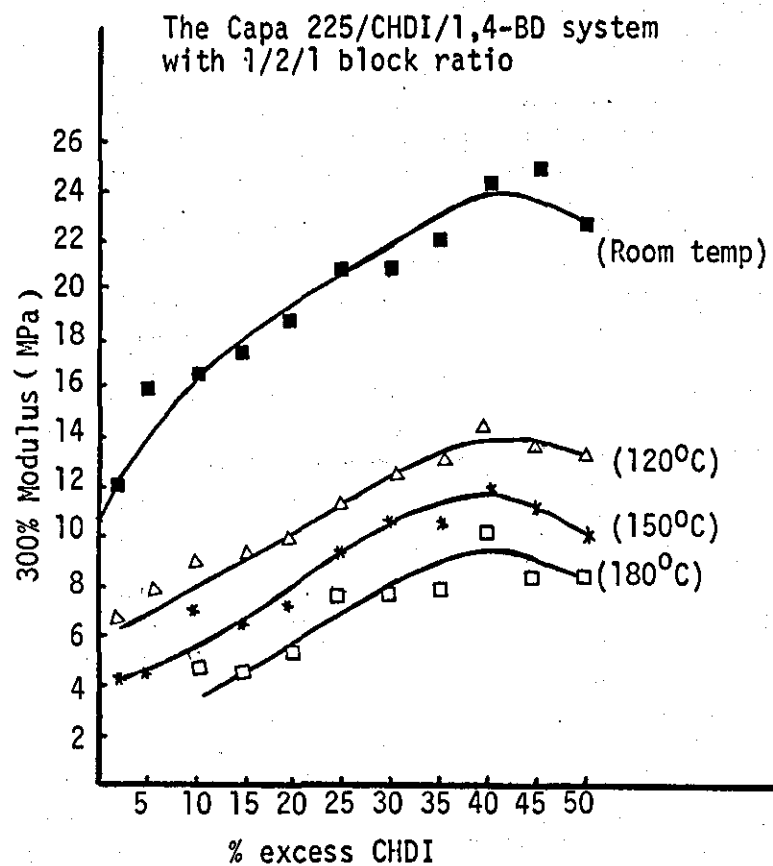


FIGURE 4.2: Relationship between 300% modulus and excess amount of diisocyanate in CHDI based polyurethane

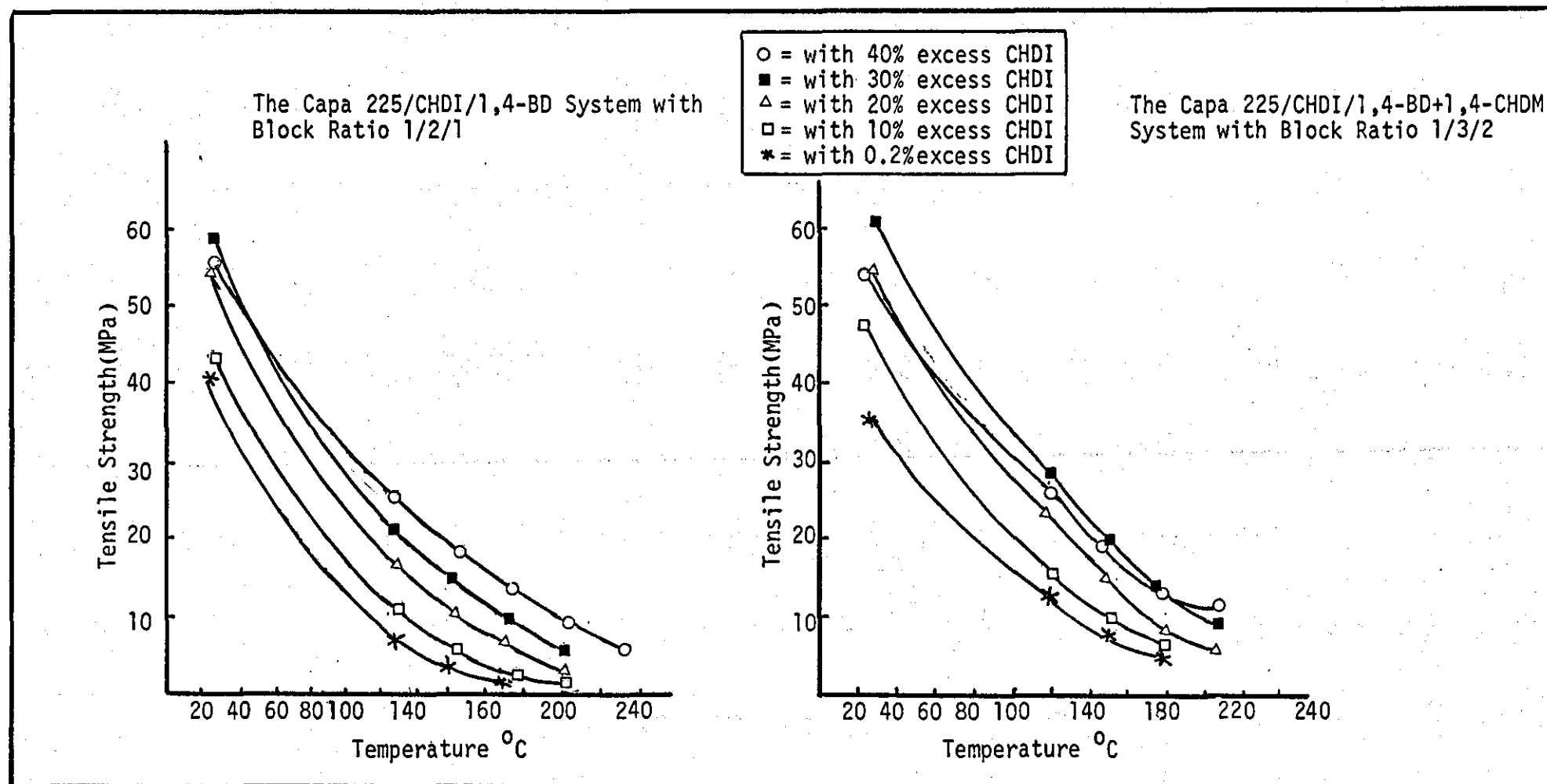


FIGURE 4.3: Relationship Between Tensile Strength and Temperature for Polyurethanes of Different Crosslinking Density

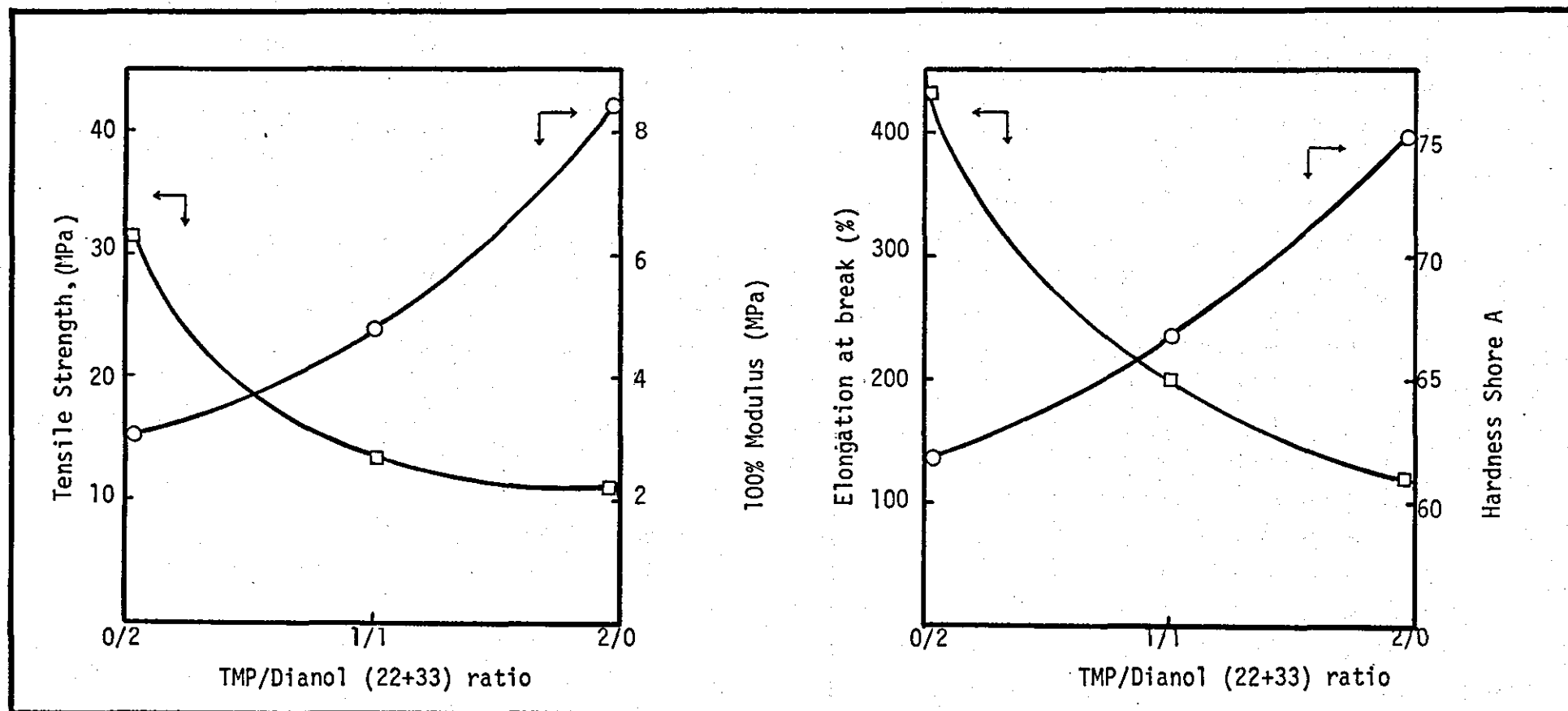


FIGURE 4.4: Effect of Crosslinking on Tensile Properties of Soft Series Polyurethanes

4.3 TEAR STRENGTH

A special type of tear test was designed and used to determine the tear properties of the polyurethane elastomers. Rectangular test pieces, of approximate dimensions 60 mm x 10 mm x 2 mm (see Figure 4.5) were die cut from the cast sheets. Each specimen was measured for thickness immediately after cutting. A nick was then cut in the test piece using the Wallace nick cutter and the resulting nicked specimen pulled apart on the JJ tensile testing machine at a constant crosshead speed of 100 mm/minute. The maximum force required to tear across the width of the uncut portion was measured. The following formula was used to calculate the tear strength (BS 903: Part A3: 1982):

$$\text{Tear strength} = \frac{F}{t}$$

where F = maximum force in kN

t = thickness of the test piece in m.

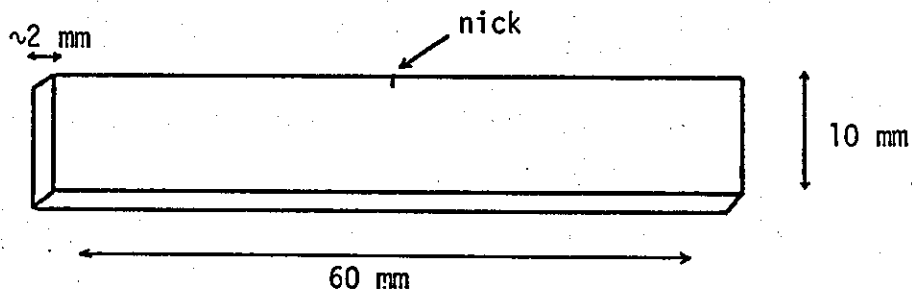


FIGURE 4.5: Tear Testing Sample and Tearing Mode

The result was expressed in kN/m.

4.3.1 Results and Discussion

High tear strength depends primarily on the presence of strong tie points throughout the polymer matrix. These tie points hinder the progress of crack growth and in polyurethanes may take the form of hard segment domains. The values of tear strength of the prepared polyurethane elastomers are given in Tables 4.8 to 4.10. Polyurethane elastomers having higher hard segment content are found to give higher values of tear strength. This is demonstrated by comparing sample Capa 18,6 (0.2% excess CHDI) with sample B74 (5% excess CHDI) in 1,4-BD+1,4-CHDM based polyurethanes; and B142 (0.2% excess CHDI) with B148 (30% excess CHDI) in the Polacure based polyurethane series. This is thought to be due to the presence of larger and more perfectly developed domains in the higher hard segment PU's which are more effective as crack growth inhibitors. Domain structures are affected, with respect to their tear strength, by strong intermolecular forces which exist in phase segregated polyurethanes.

4.4 COMPRESSION SET

This test is intended to measure the ability of polymers to retain elastic properties after prolonged compression. The compression set for the prepared polyurethanes was measured according to the BS 903: Part A: 1969 and the test piece used was a cylindrical disc of 13.0 ± 0.5 mm diameter which was compressed at 100°C for 24 hours. Then the compression set at constant strain (25%) was calculated as follows:

$$\text{Compression set at constant strain} = \frac{t_o - t_r}{t_o - t_s} \times 100$$

where t_o = original thickness of the test piece

t_r = thickness of the test piece after recovery

t_s = thickness of spacer (4.73 ± 0.01 mm)

4.4.1 Results and Discussion

Table 4.11 shows the values of compression set for some polyurethane elastomers. It can be seen that as the amount of hard segment content increases by using excess diisocyanate the compression set decreases. This is shown by comparing B142 (0.2% excess CHDI) with B148 (30% excess CHDI) in Polacure extended polyurethanes. It is generally concluded that higher crosslinked polyurethanes show lower compression set values.

TABLE 4.8: Tear Strength of Polyurethane Elastomers based on Capa 225/CHDI/1,4-BD (a) and Capa 225/CHDI+1,4-CHDM (b) Systems

Sample No	% Excess CHDI	Tear Strength (kN/m)	Sample No	% Excess CHDI	Tear Strength (kN/m)
Capa 17,1	2	127.15	Capa 18,6	0.2	133.02
B59	5	169.92	B74	5	162.15
B60	10	153.43	B75	10	142.57
B61	15	152.13	B76	15	145.70
B62	20	160.65	B77	20	144.82
B56	25	126.04	B78	25	145.18
B63	30	130.34	B79	30	146.29
B64	35	134.99	B80	35	147.91
B65	40	130.80	B81	40	148.33
B66	45	129.98			
A'B	50	138.62			

(a) Samples of Capa 17,1 to A'6

(b) Samples of Capa 18,6 to B81

TABLE 4.9: Tear Strength of Polyurethane Elastomers based on Capa 225/CHDI/Polacure (a) and Capa 225/PPDI/1,4-BD (b) Systems

Sample No	% Excess CHDI	Tear Strength (kN/m)	Sample No	% Excess PPDI	Tear Strength (kN/m)
B142	0.2	93.54	B118	0	97.63
B143	5	118.48	B119	0.2	134.11
B144	10	148.73	B120	5	126.54
B145	15	153.65	B121	10	128.51
B146	20	158.14	B122	15	146.37
B147	25	156.04	B123	20	128.09
B148	30	160.42	B124	25	117.43
			B125	30	101.46

(a) Samples of B142 to B148

(b) Samples of B118 to B125

TABLE 4.10: Tear Strength of Polyurethane Elastomers (Soft Series)

Sample No	Polyol	Diisocyanate	Chain Extender	Tear Strength (kN/m)
B103	Capa 225	PPDI	Dianol (22+33)	69.37
B106	Capa 225	PPDI	Dianol (22+33) + TMP	37.75
B108	Capa 225	PPDI	TMP	33.02
B131	Capa 240 + Capa 305 (3/1)	PPDI	TMP	19.8
B155	Capa 231	CHDI	Capa 305	31.28
Rubber (NR/SBR)*				56.02

* For formulation see Appendix 3.

TABLE 4.11: Compression Set of Polyurethane Elastomers

Sample No	Polyol	Diisocyanate	Chain Extender	Block Ratio	Compression Set
A5	Capa 225	CHDI	Dianol 22	1:2:1	59.19
A3	Capa 225	CHDI	1,4-CHDM	1:2:1	37.28
03	Capa 225	CHDI	1,4-BD+ Dianol 33	1:2:1	39.49
M2	Capa 225	CHDI	1,4-BD+ Dianol 33	1:3:2	56.54
B1	Capa 225	CHDI	1,4-BD	1:3:2	62.21
B79	Capa 225	CHDI	1,4-BD+ 1,4-CHDM	1:3.9:2	35.0
B142	Capa 225	CHDI	Polacure	1:3:2	57.5
B148	Capa 225	CHDI	Polacure	1:3.9:2	51.6
B151	Capa 225	CHDI	Polacure+ Benzoflex (10%)	1:3.9:2	65.96
B153	Capa 225	MDI	Polacure	1:3.9:2	94.62
B103	Capa 225	PPDI	Dianol (22+33)	1:3.9:2	19.0
B108	Capa 225	PPDI	TMP	1:3.9:2	8.5
B133	Capa 225	CHDI	TMP	1:3.9:2	8.5
B155	Capa 231	CHDI	Capa 305	1:3.9:2	14.36
Rubber (NR/SBR)*					64.9

* For formulation see Appendix 3.

4.5 TENSION SET

The tension set in polyurethane samples subjected to a constant elongation for a fixed length of time, was measured according to British Standard BS 903: Part A5, 1958, at room temperature. Specimens used were of the dumbell type 2 and marked with 20 mm bench marks using a very fine ink pen. The samples were then extended at a constant rate of 100 mm/minute to 300% extension on a JJ tensile testing machine. Samples were held at 300% extension for 10 minutes and were then relaxed at the same speed and left to recover for another 10 minutes before the tension set was calculated. The tension set was determined after 10 minutes and 1 hour recovery time using the following formula:

$$\text{Tension set (\%)} = \frac{l_1 - l_0}{l_s - l_0} \times 100$$

where l_0 = original unstrained reference length

l_s = strained reference length

l_1 = reference length after recovery

4.5.1 Results and Discussion

The tension set of polyurethane elastomers which were measured after 10 minutes and 60 minutes recovery time are given in Tables 4.12 to 4.15. Results indicate that tension set decreases with increased amount of excess diisocyanates. This is shown in Table 4.12 by comparing B59 with B66 in Capa 225/CHDI/1,4-BD series and in Table 4.13 by comparing B74 with B81 in Capa 225/CHDI/1,4-BD+1,4-CHDM based polyurethane elastomer. This effect is also illustrated by comparing B118 with B125 in Capa 225/PPDI/1,4-BD based polyurethane elastomer (see Table 4.14).

The relationship between tension set and excess CHDI in two different series of polyurethane elastomers are shown in Figure 4.6. Decreasing tension set in crosslinked polyurethanes is thought to be due to their high elasticity. In contrast non-crosslinked PU samples exhibited considerably higher set values presumably because of plastic deformation of hard segment domains or soft segment crystallization. Poor domain structure and mixed hard and soft segments are two factors which would be anticipated to give low set by minimising plastic domain deformation and soft segment crystallization.

TABLE 4.12: Tension Set of Polyurethane Elastomers Based on Capa 225/
CHDI/1,4-BD with Molar Ratio 1/2/1

Sample No	% Excess CHDI	Tension Set %	
		Relaxation Time (minutes)	
		10	60
Capa 17,1	2	45.8	43.3
B59	5	43.3	40.8
B60	10	41.6	38.3
B61	15	38.3	36.6
B62	20	36.6	35.0
B56	25	35.0	33.3
B63	30	35.0	31.6
B64	35	35.0	31.6
B65	40	35.0	30.8
B66	45	33.3	30.8
A'6	50	30.8	27.5

TABLE 4.13: Tension Set of Polyurethane Elastomers Based on Capa 225/
CHDI/1,4-BD + 1,4-CHDM with Molar Ratio 1/3/2

Sample No	% Excess CHDI	Tension Set %	
		Relaxation Time (minutes)	
		10	60
A2	0	80.0	78.3
Capa 18,6	0.2	45.0	43.3
B74	5	45.0	43.3
B75	10	43.3	41.6
B76	15	41.6	40.0
B77	20	40.0	38.3
B78	25	39.1	36.6
B79	30	38.3	35.8
B80	35	37.5	35.0
B81	40	36.6	35.0

TABLE 4.14: Tension Set of Polyurethane Elastomers Based on Capa 225/PPDI/1,4-BD with Molar Ratio 1/2/1

Sample No	% Excess PPDI	Tension Set %	
		Relaxation Time (minutes)	
		10	60
B118	0	58.3	56.6
B119	0.2	45.0	43.3
B120	5	45.0	43.3
B121	10	41.6	40.0
B122	15	41.6	40.0
B123	20	40.8	40.0
B124	25	38.3	36.6
B125	30	31.6	30.0
B125	35	30.8	30.0

TABLE 4.15: Tension Set of Polyurethane Elastomers (Soft Series)

Sample* No	% Excess PPDI	Tension Set %	
		Relaxation Time (minutes)	
		10	60
B103	30	1.6	0.83
B148	30	36.6	35.0
B153	30	28.3	25.0
B138	30	0.80	0.50

*See Table 2.4 for samples formulation.

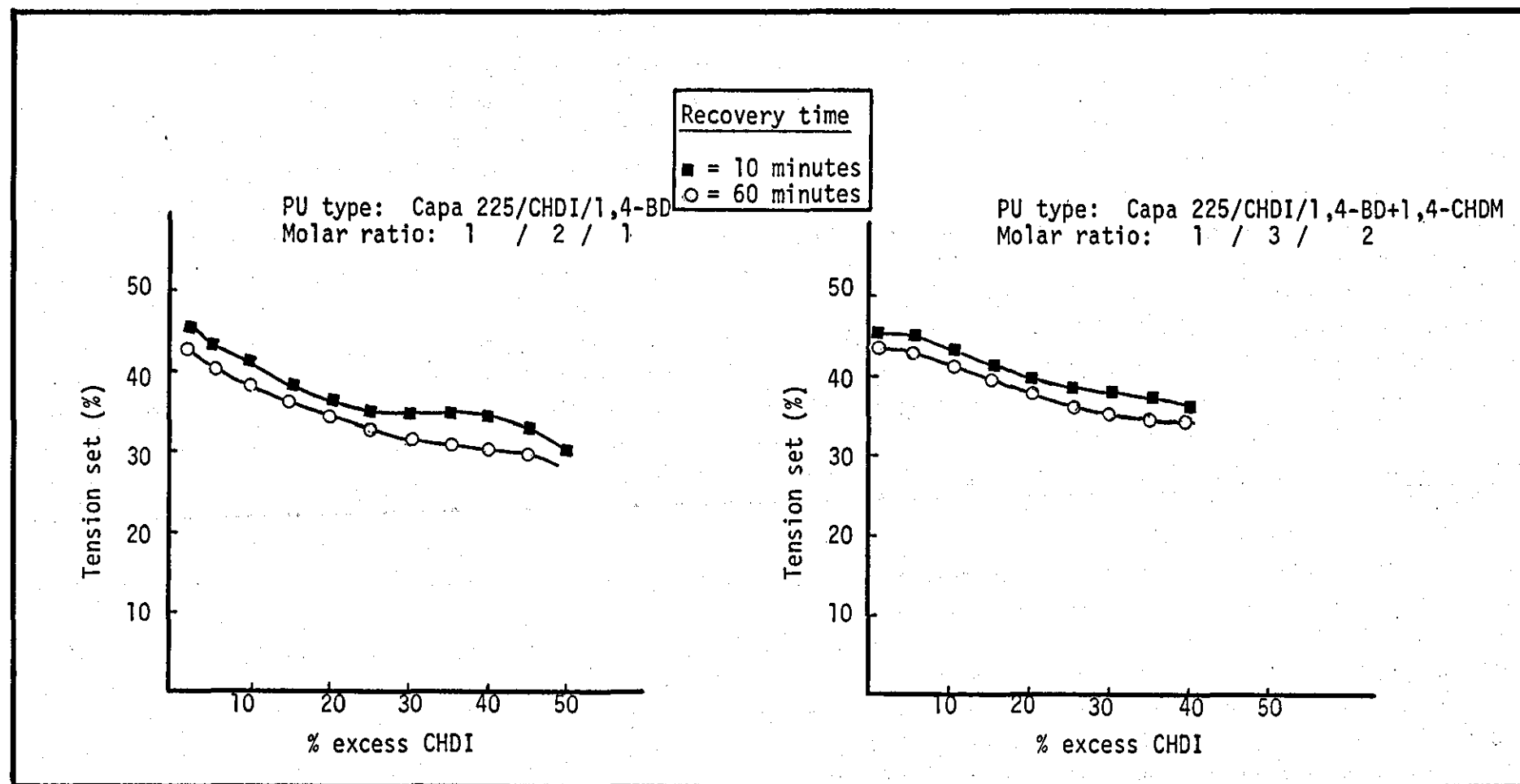


FIGURE 4.6: Relationship between tension set and percentage excess CHDI used for crosslinking of polyurethane elastomer

4.6 DENSITY

Density is the mass of a unit volume of material. The density of a polymer may in some cases be critical to the ultimate end use potential since a polymer with a low density will, obviously, occupy more volume or cover more surface per mass than one of higher density. In any event, density can add to the basic understanding of the material in every instance.

The Displacement Method is used to measure the density of the sample at room temperature (23°C) according to Method 509A of BS 2872:1970. Fine wire is used for the suspension of the specimen and air bubbles are removed by use of a minute quantity of detergent. Values of density are calculated according to the following formula:

$$\text{Density} = \frac{W_1}{W_1 - W_2} \times \rho$$

where W_1 = weight of specimen in air

W_2 = weight of specimen in water

ρ = density of the water, usually taken to be 1 kg/m³.

4.6.1 Results and Discussion

Table 4.16 shows the results of density measurements which are calculated in kg/m³. A slight increase in the density of 1,4-BD and 1,4-BD + 1,4-CHDM based polyurethanes is found by increasing amounts of excess CHDI into the polymer system. Relationship between density and percentage excess CHDI for these two series of polyurethane elastomers is shown in Figure 4.7.

TABLE 4.16: Density Value of Polyurethane Elastomers

Capa 225/CHDI/1,4-BD based urethanes		Capa 225/CHDI/1,4-BD +1,4-CHDM based urethanes		Capa 225/PPDI/1,4-BD based urethanes		Capa 225/CHDI/Polacure based urethanes		Soft Polymer Series*	
Sample No	Density (kg/m ³)	Sample No	Density (kg/m ³)	Sample No	Density (kg/m ³)	Sample No	Density (kg/m ³)	Sample No	Density (kg/m ³)
Capa 17,1	1125.6	Capa 18,6	1126.38	B118	1158.36	B142	1171.3	B155	1122.57
B59	1126.9	B74	1132.60	B119	1149.26	B143	1171.5	B133	1136.88
B60	1127.2	B75	1133.93	B120	1146.30	B144	1172.8	B131	1149.72
B61	1129.2	B76	1134.76	B121	1146.49	B145	1176.9	B103	1170.43
B62	1129.4	B77	1139.40	B122	1148.02	B146	1174.3	B106	1167.79
B56	1129.5	B78	1140.20	B123	1152.12	B147	1171.8	B108	1169.40
B63	1130.8	B79	1140.76	B124	1152.04	B148	1175.5		
B64	1132.7	B80	1142.10	B125	1152.80				
B65	1134.0	B81	1142.30	B126	1150.86				
B66	1134.4								
A'6	1134.5								

* For formulation see Table 2.4.

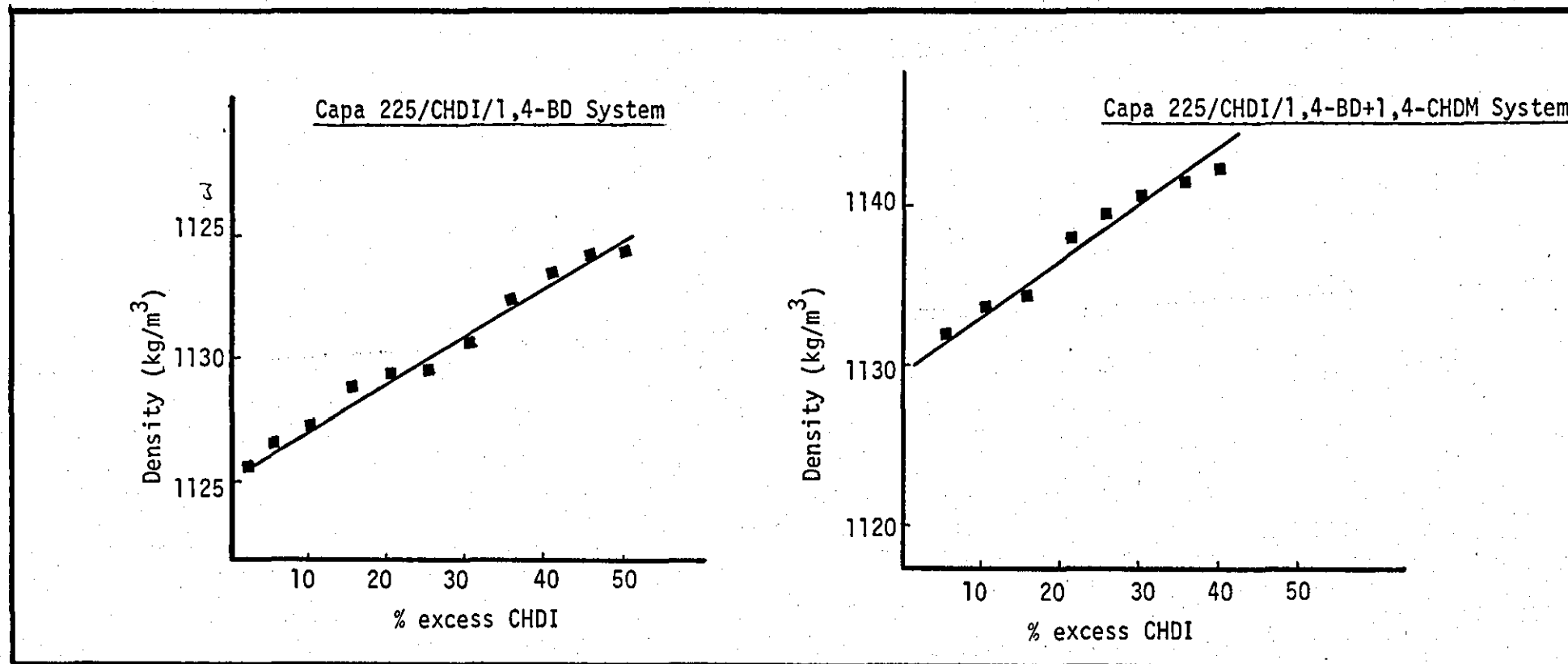


FIGURE 4.7: Relationship between density and % excess CHDI in polyurethane elastomers

4.7 SKID RESISTANCE

The skid resistance of some of the soft polyurethane elastomers was measured with a portable 'Skid-Resistance' Tester* developed by the Road Research Laboratory. This is a pendulum device, the movement of which is arrested by the foot of the pendulum skidding on the surface to be measured.

The results of these measurements are given in Table 4.17 for both dry and wet conditions.

TABLE 4.17: Skid Resistance Data of Some Soft PU Elastomers

Composition				Condition	
Sample No	Polyol	Diisocyanate	Chain Extender	Dry	Wet
				% Damping	% Damping
B103	Capa 225	PPDI	Dianol (22+33)	11	9
B108	Capa 225	PPDI	TMP	10	8
B155	Capa 231	CHDI	Capa 305	28	12
NR/SBR ^(a)				28	11

(a) Compositions are given in Appendix 3.

4.8 DETERMINATION OF INTERNAL HEAT GENERATION AND RESISTANCE TO FATIGUE

Fatigue can be defined as any change in the properties of a material caused by prolonged action of stress or strain. In many products, notably tyres, it is the loss in strength shown by cracking and/or complete rupture which is considered to be the important aspect of fatigue and this is the measure of fatigue which is normally used in laboratory tests on rubber. The manner of breakdown will vary according to the geometry of the component, the type of stressing or straining and environmental conditions.

4.8.1 Flex-Cracking and Crack Growth

Flex-cracking is the formation of cracks on the surface of a rubber subjected to repeated cycles of deformation. This phenomenon occurs in the side walls of tyres and in the base of grooves in the tread. In the 'crack growth' (or 'cut growth') test, an initial cut or nick is made in the test piece, and measurements are made of its growth during repeated deformation until ultimately the sample fails by breaking.

4.8.2 Experimental Procedure

Fatigue life of some of the prepared polyurethanes was determined on a De Mattia-type machine* (see Figure 4.7) for resistance to flex-cracking and cut growth by using a special test specimen. The test piece, which was a rectangular strip of approximate dimensions 100 mm x 10 mm x 2 mm, was die cut from the cast sheet and fixed in two clamps which move towards each other to extend and bend the strip. Repeated extending and bending or flexing causes cracks to develop in bending--part of the surface where tension strains or stresses are set up during flexing or, if the bending part of the surface contains a crack or cut this causes it to extend in a direction perpendicular to the strain or

* H W Wallace and Co Ltd., Croydon, England.

stress. The apparatus is operated at 300 cycles/minute and the tests are continued until complete failure of the test pieces occurs and then the number of cycles is recorded. Tests are made at a number of extensions for crack propagation and compounds are compared in terms of fatigue life at the same strain.

Initial cracks in the test piece are produced by piercing a 2 mm long cut at a mid-point perpendicular to the longest side and equidistant from the sides, using a suitable cutter and jig. The cut is accomplished by a single insertion and withdrawal of the tool.

4.8.3 Results and Discussion

The results of the crack initiation and crack propagation tests by the De Mattia machine are given in Tables 4.18 and 4.19. As the results show the flex-cracking resistance of polyurethane elastomers based on the Capa 225/CHDI/1,4-BD + 1,4-CHDM system decreases with increasing percent excess of CHDI. This is thought to be due to the higher modulus and lower extension at break ability of the more highly crosslinked polyurethanes, which have resulted from the use of excess diisocyanate. A similar trend of decreasing fatigue life is observed in the crack propagation test series, so both crack initiation and crack propagation resistance decrease with increasing crosslinking which occurred due to the use of the excess diisocyanate.

Figure 4.9 shows the relationship between fatigue life and percentage excess CHDI and also percentage applied strain of these PU elastomers for both the flex-cracking and cut growth tests. It is found through the Figure 4.9(c) that the relationship between fatigue life and applied strain is similar to the 'Wöhler curve'. The important feature of this curve is that on reducing the stress or strain towards a particular value, the fatigue life increases virtually to infinity giving rise to the concept of a limiting fatigue life and an ultimate failure strength or deformability.

Internal heat generation of the Capa 225/CHDI/1,4-BD + 1,4-CHDM based polyurethane elastomer was measured on the De Mattia-type machine by using a contact flat thermocouple head during the flex cracking resistance measurements. Temperature was recorded by a Comarck electric thermometer at time intervals which varied depending on the rate of temperature rise. The results are given in Tables 4.20-4.21 and Figures 4.10-4.11. Table 4.20 shows the results of heat generation of polymers subjected to 100% applied strain and Table 4.21 gives the results at 150% applied strain.

Figures 4.10 and 4.11 show the effect of using various levels of excess diisocyanate and also the percentage applied strain on heat generation of these PU elastomers. It can be seen that the heat generation of these polymers increases with both increasing percentage excess diisocyanate or the percentage applied strain e.g. the increase in temperature for a polymer with 0.2% excess CHDI at 100% strain was 20°C and this increased to 29°C for a 30% excess CHDI containing polymer. Also the increase in temperature for the polymer containing 30% excess CHDI is about 29°C at 100% applied strain and this increases to about 37°C at 150% applied strain. Figures 4.10 and 4.11 also show that the temperature of polymers sharply increases during the first five minutes of flexing and then stays approximately constant or show only a small change as flexing time continues.

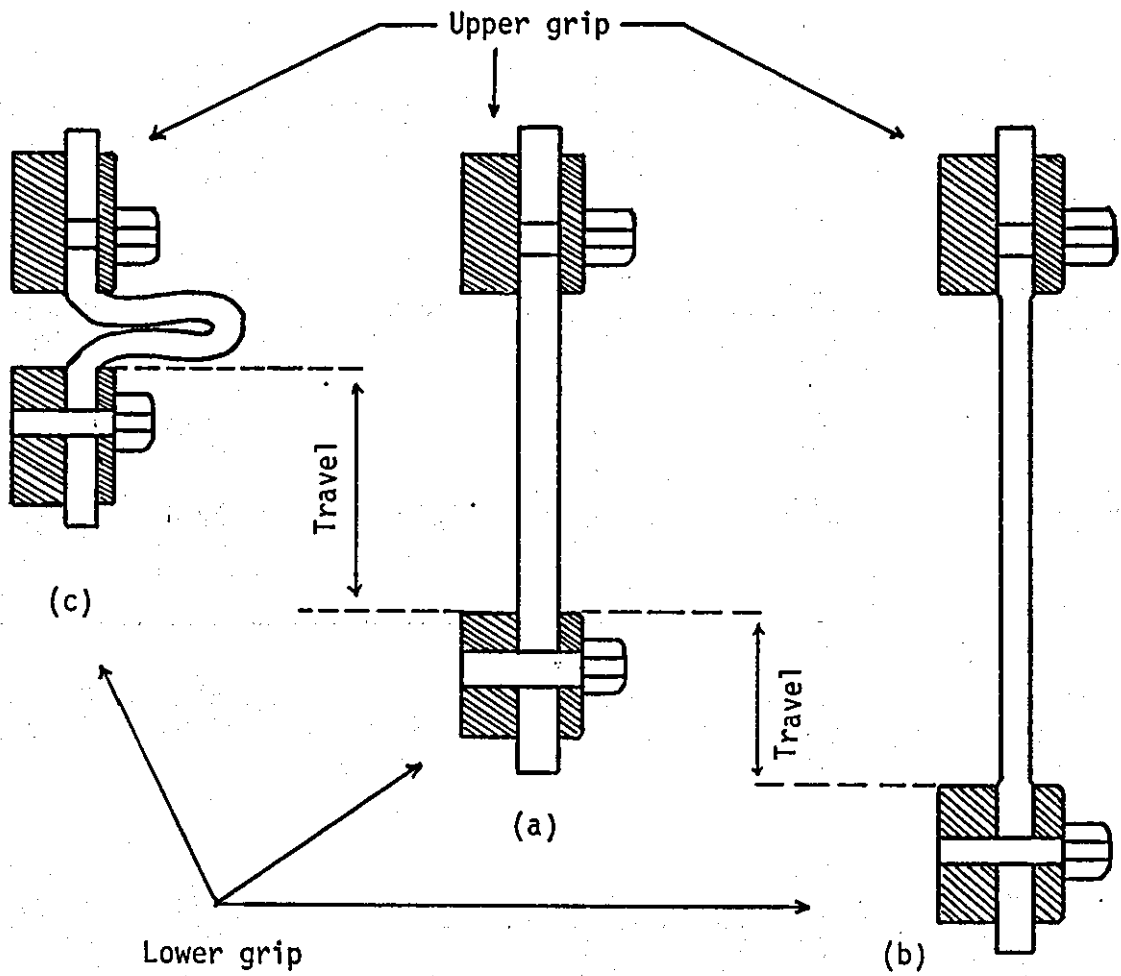


FIGURE 4.8: De Mattia-Type Machine:

- a) Sample shown in its original form unstressed
- b) Sample under strain
- c) Sample under stress

TABLE 4.18: Flex-cracking Resistance of Polyurethane Elastomer Based on Capa 225/CHDI/1,4-BD + 1,4-CHDM with Molar Ratio of 1/3/2 at 100% Strain

Sample No	% Excess CHDI	Kilocycles to Failure at 100% Strain
Capa 18,6	0.2	365
B74	5	340
B77	20	200
B81	40	30

TABLE 4.19: Crack Propagation Resistance of Polyurethane Elastomer Based on Capa 225/CHDI/1,4-BD + 1,4-CHDM with Molar Ratio of 1/3/2 at 0%, 10%, 20% and 25% Strain

Sample No	% Excess CHDI	Number of Kilocycles to Failure			
		0% Strain*	10% Strain	20% Strain	25% Strain
Capa 18,6	0.2	1000 (no failure)	1515 (no failure)	210	1.1
B74	5	"	1515 (failed)	132	0.88
B77	20	"	1070 (failed)	-	0.5
B79	30	"	72 (failed)	3.6	0.2
B81	40	"	13.4 (failed)	1.8	0.05

* At 0% strain the test was stopped after 1000 kilocycles

TABLE 4.20: Heat Generation Observed by Flexing of Polyurethane Elastomers Based on Capa 225/CHDI/1,4-BD + 1,4-CHDM at 100% Strain

$t_0 = 21^\circ\text{C}$

Time (mins)	Capa 18,6 (0.2% excess CHDI)		B74 (5% excess CHDI)		B79 (30% excess CHDI)	
	t	Δt	t	Δt	t	Δt
1	34	13	37	16	41	20
2	38	17	38	17	46	25
3	39	18	42	21	47	26
6	40	19	43	22	47	26
10	40	19	43	22	48	27
20	40	19	44	23	49	28
30	41	20	44	23	50	29
45	41	20	44	23	50	29
60	41	20	44	23	50	29
90	41	20	44	23	50	29

TABLE 4.21: Heat Generation Observed by Flexing of Polyurethane Elastomers Based on Capa 225/CHDI/1,4-BD + 1,4-CHDM at 150% Strain

$t_0 = 21^{\circ}\text{C}$

Time (mins)	B74 (5% excess CHDI)		B77 (20% excess CHDI)		B79 (30% excess CHDI)	
	t	Δt	t	Δt	t	Δt
1	40	19	45	24	48	27
2	44	23	48	27	54	33
3	44.5	23.5	48	27	55	34
4	45	24	49	28	56	35
10	47	26	50	29	57	36
15	47	26	50	29	58	37
20	47	26	50	29	58	37
30	48	27	50	29	58	37
65	48	27	50	29	58	37

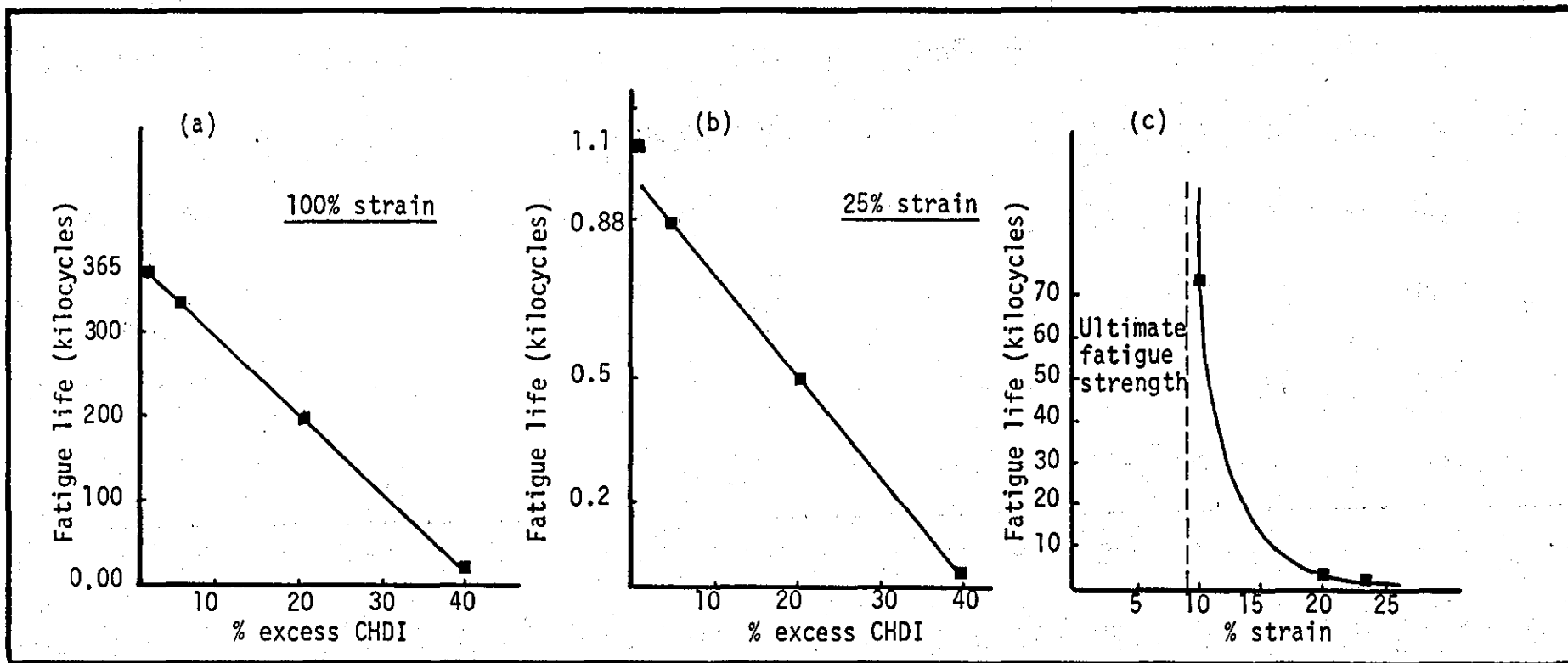


FIGURE 4.9: Relationship between fatigue life and % excess diisocyanate and also % applied strain of a polyurethane elastomer based on Capa 225/CHDI/1,4-BD + 1,4-CHDM.
 (a) Crack initiation; (b) and (c) Crack propagation

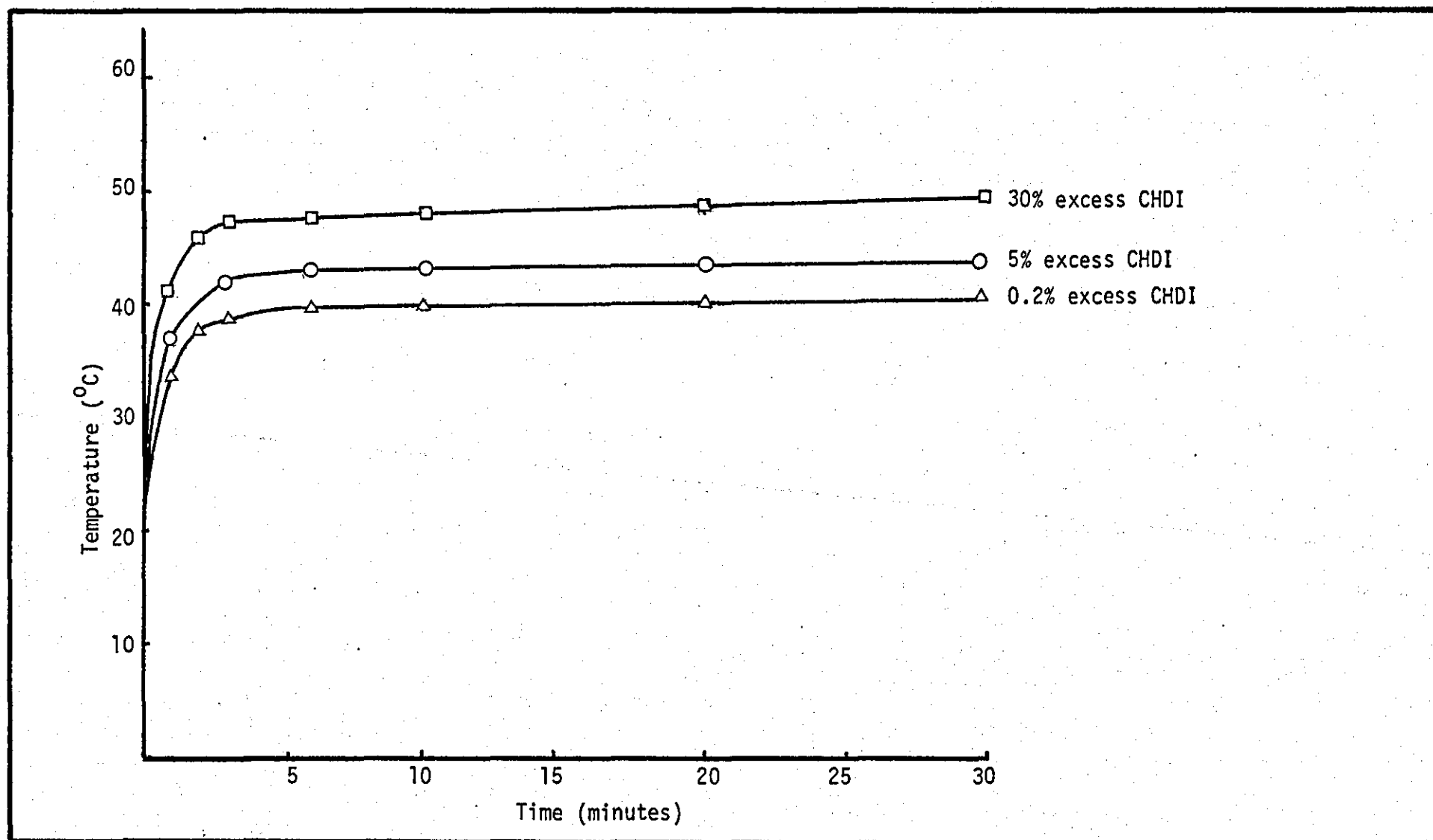


FIGURE 4.10: Heat Generation Against Time for Polyurethane Elastomers Based on Capa 225/CHDI/1,4-BD+1,4-CHDM with Different Amounts of Excess CHDI at 100% Strain

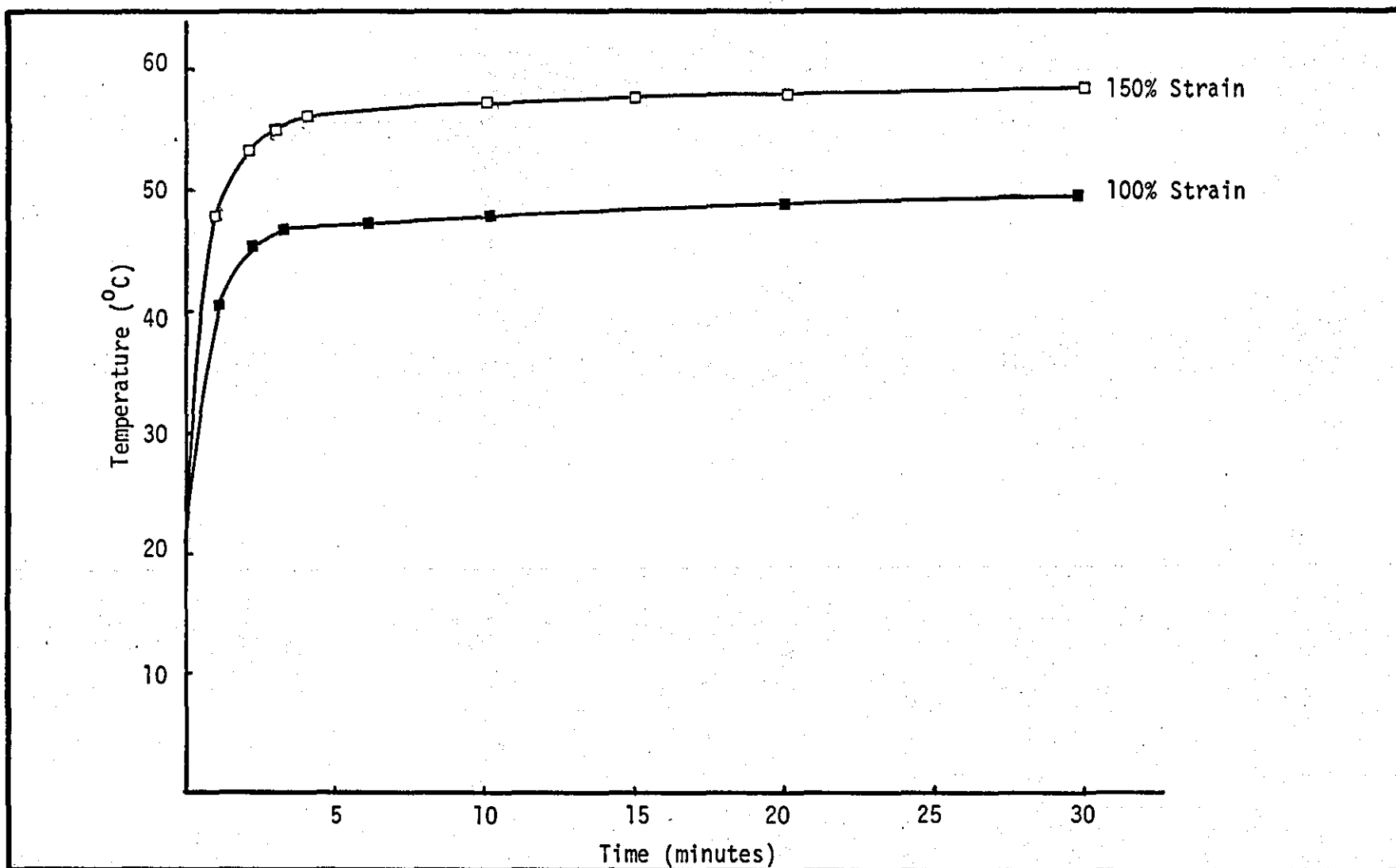


FIGURE 4.11: Heat Generation Against Time of Polyurethane Elastomers Based on Capa 225/CHDI/1,4-BD+ 1,4-CHDM with 30% Excess CHDI at Different % Strain

4.9 HYSTERESIS

4.9.1 Introduction

In service conditions, an elastomeric material may be required to withstand repeated deformation without significant loss in performance. A typical example is to be found in tyre applications where elastomeric materials are subjected to a cyclic compressive deformation. When an elastomeric material is deformed and then allowed to regain its original state, a net amount of work is performed on the material. This is shown in Figure 4.12 for an extension-retraction cycle. On extension of the material (AB), the amount of work is equal to the area under the loading curve (ABD). On retraction of the material (BC), the amount of work performed is equal to the area under the unloading curve (CBD). This network performed on the material is therefore given by the area bounded by the loading and unloading curves (ABCA) and this represents the energy dissipated as heat during the complete stress-strain cycle. The value of strain at which the unloading curve reaches zero stress (AC) is residual strain and represents a certain amount of permanent set in the material.

The aim of the present section was to investigate the effect of the hard segment structure as controlled by the use of excess diisocyanate, on hysteresis behaviour of polyurethane elastomers.

4.9.2 Experimental Procedure

Hysteresis measurements of certain prepared polyurethane elastomers were determined by subjecting samples to multiple stress-strain cycles. A JJ tensile testing machine (model T5002) was used with the crosshead speed of 100 mm/min and load cell of 500N. Test specimens were BS dumbbells, type 2, die cut from cast sheets and measurements were made at room temperature.

For a meaningful comparison of the hysteresis behaviour of different polyurethanes all the samples tested in this section were subjected to a series of preconditioning cycles prior to measurement of the final hysteresis cycle. Preliminary experiments showed the third and fourth cycles to follow almost identical paths. On this basis, all samples were preconditioned at test temperature (23°C) by cycling three times to 300% of previously calculated elongation at break.

The percentage hysteresis for a given cycle is calculated by the ratio of the area bounded by the loading-unloading curves to the total area under the loading curve. To find the area bounded by the curve of the hysteresis, the weight by difference method was used. According to this method the area bounded by the hysteresis curve is cut out and weighed to 4 decimal places. Then a standard square of the paper used for recording the curves is cut out and weighed to form a standard. The area within the hysteresis loop was determined by using the following formula:

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

where W_1 = weight of the area bounded by hysteresis curve

W_2 = weight of standard cut out square

E_1 = hysteresis energy

E_2 = energy related to the standard cut out square.

The hysteresis energies are expressed in joules per volume (m^3) to make them available for comparison purposes.

4.9.3 Results and Discussion

Hysteresis results of these polyurethane elastomers are given in Tables 4.22 to 4.25. Here, cycle (1) and cycle (3) refer to the initial and final cycles at 300% of the elongation at break. The first three extension/retraction cycles for a typical CAPA 225/CHDI/1,4-BD+1,4-CHDM based polymer are illustrated in Figure 4.13. It can be seen from the Tables 4.22-4.25 and also from the Figure 4.13 that the greatest proportion of hysteresis loss occurs in the first cycle, and that the second and third cycles show very little difference in hysteresis loss. During the first cycle, a relatively high stress is required for a given elongation and almost all the energy expended is retained in the restructured system. Second and third cycles undergo only minor restructuring of hard segments and therefore the stress required for a given elongation is reduced and the hysteresis loss is considerably lower. The high hysteresis loss in the first cycle is primarily associated with the high degree of structural reorganisation which takes place in the first cycle.

Tables 4.22 and 4.23 show that PU elastomers of higher hard segment content possess significantly greater net energy absorption e.g. compare B59 (5% excess CHDI) with B64 (40% excess CHDI) in the CAPA 225/CHDI/1,4-BD polyurethane series. Also compare B74 (5% excess CHDI) with B81 (40% excess CHDI) in the CAPA 225/CHDI/1,4-BD+1,4-CHDM polyurethane series.

This effect can be explained by the presence of larger domain structures associated with the longer hard segments. Dissociation of these domains and their subsequent formation into reorganised arrangements of hard segments could account for the higher net energy absorption observed.

Polacure based polyurethane (Table 4.25) shows higher hysteresis loss compared with the 1,4-BD+1,4-CHDM based PU elastomers (Table 4.23).

This might be due to the higher cohesive energy associated with the urea group present in Polacure based PUs whereas the 1,4-BD+1,4-CHDM based PU elastomers predominantly have urethane groups and no urea groups.

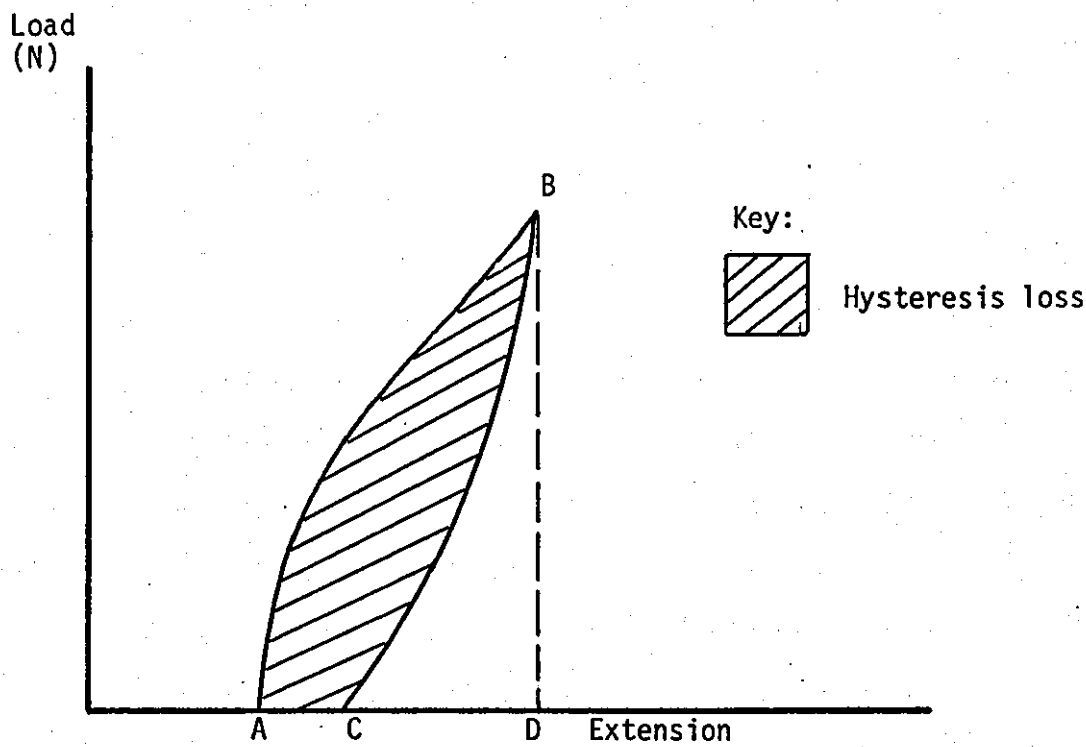


FIGURE 4.12: Typical Hysteresis Curve

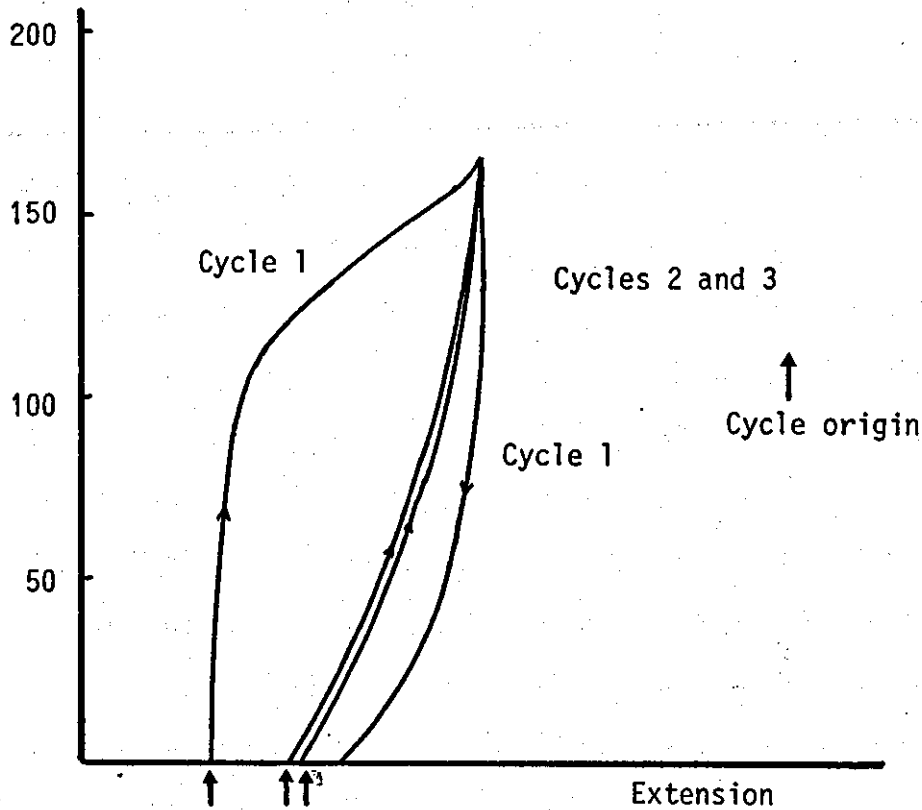


FIGURE 4.13: Typical Example of Hysteresis Curve of a PU Chain Extended with 1,4-BD+1,4-CHDM at room temperature; these are the first three cycles to which the PU was subjected when stretched to 300% of its elongation at break value

TABLE 4.22: Hysteresis Properties of Polyurethane Elastomers Based on Capa 225/CHDI/1,4-BD with the block ratio 1/2/1

Sample No	% Excess CHDI	Cycle (1)				Cycle (3)			
		E_i (MJ.m ⁻³)	E_o (MJ.m ⁻³)	E_a (MJ.m ⁻³)	$(\frac{E_a}{E_i})100\%$	E_i (MJ.m ⁻³)	E_o (MJ.m ⁻³)	E_a (MJ.m ⁻³)	$(\frac{E_a}{E_i})100\%$
Capa 17,1	2	15.26	2.81	12.44	81.52	5.33	2.81	2.51	47.09
B59	5	15.17	2.95	12.21	80.48	5.55	2.91	2.59	46.66
B60	10	16.38	2.99	13.39	81.74	5.81	2.99	2.82	48.53
B61	15	17.17	2.74	14.43	84.04	6.35	3.27	3.07	48.34
B62	20	17.18	3.03	14.15	82.36	5.99	3.03	2.96	49.41
B56	25	19.19	3.51	15.67	81.65	6.52	3.51	3.01	46.16
B63	30	18.83	3.56	15.26	81.04	6.65	3.56	3.08	46.31
B64	35	20.93	3.66	17.27	82.51	7.01	3.66	3.34	47.64
B65	40	23.16	3.97	19.19	82.85	7.56	3.97	3.59	47.48
B66	45	22.71	3.82	18.90	83.22	7.82	3.82	4.01	51.27
A'6	50	21.63	3.74	17.88	82.66	7.26	3.74	3.51	48.34

Key: E_i = energy absorbed on extension

E_o = energy released on retraction

E_a = net energy absorbed on complete cycle

$(\frac{E_a}{E_i})100 = \% \text{ energy absorbed in complete cycle, i.e. \% hysteresis}$

TABLE 4.23: Hysteresis Properties of Polyurethane Elastomers Based on Capa 225/CHDI/1,4-BD+1,4-CHDM with the block ratio 1/3/2

Sample No	% Excess CHDI	Cycle (1)				Cycle (3)			
		E_i (MJ.m ⁻³)	E_o (MJ.m ⁻³)	E_a (MJ.m ⁻³)	$(\frac{E_a}{E_i})100$ (%)	E_i (MJ.m ⁻³)	E_o (MJ.m ⁻³)	E_a (MJ.m ⁻³)	$(\frac{E_a}{E_i})100$ (%)
Capa 18,6	0.2	21.36	3.10	18.26	85.48	6.28	3.10	3.18	50.63
B74	5	21.00	2.87	18.12	86.28	6.29	2.87	3.42	54.37
B75	10	22.05	3.10	18.94	85.89	6.83	3.10	3.73	54.61
B76	15	22.37	2.85	19.52	87.25	6.50	3.43	3.65	56.15
B77	20	22.62	3.55	19.07	84.30	7.05	3.55	3.49	49.50
B78	25	24.48	3.62	20.85	85.17	7.61	3.62	3.99	52.43
B79	30	25.45	3.56	21.89	86.01	7.76	3.56	4.19	53.99
B80	35	26.27	3.63	22.63	86.14	7.96	3.63	4.33	54.39
B81	40	27.43	3.77	23.65	86.22	8.22	3.77	4.45	54.51

Note: Key as in Table 4.22

TABLE 4.24: Hysteresis Properties of Polyurethane Elastomers Based on Capa 225/PPDI/1,4-BD with the block ratio 1/2/1

Sample Number	% Excess PPDI	Cycle (1)				Cycle (3)			
		E_i (MJ.m ⁻³)	E_o (MJ.m ⁻³)	E_a (MJ.m ⁻³)	$E(\frac{a}{E_i})100$ (%)	E_i (MJ.m ⁻³)	E_o (MJ.m ⁻³)	E_a (MJ.m ⁻³)	$E(\frac{a}{E_i})100$ (%)
B118	0	17.76	2.47	15.28	86.03	4.33	2.47	1.86	42.95
B119	0.2	16.88	2.84	14.03	83.11	5.00	2.90	2.10	42.00
B120	5	19.23	2.76	16.46	85.59	5.76	3.28	2.48	43.05
B121	10	18.78	2.44	16.33	86.95	5.45	2.75	2.70	49.54
B122	15	18.68	3.29	15.39	82.38	5.75	3.40	2.45	42.61
B123	20	17.86	3.16	14.70	82.30	5.94	3.16	2.77	46.63
B124	25	19.21	3.27	15.94	82.97	5.94	3.27	2.67	44.95
B125	30	16.79	3.68	13.10	78.02	6.47	3.68	2.79	43.12
B126	35	16.51	3.41	13.09	79.28	6.43	3.41	3.01	46.81

Note: Key as in Table 4.22

TABLE 4.25: Hysteresis Properties of Polyurethane Elastomers Based on Capa 225 with Different Diisocyanates and Chain Extenders (see Table) with a Block Ratio of 1/3/2

Sample No	% Excess Diisocyanate	Diisocyanate	Chain Extender	Cycle (1)				Cycle (3)			
				E_{i-3} (MJ.m ⁻³)	E_{o-3} (MJ.m ⁻³)	E_{a-3} (MJ.m ⁻³)	$(\frac{E_a}{E_c})100(\%)$	E_{i-3} (MJ.m ⁻³)	E_{o-3} (MJ.m ⁻³)	E_{a-3} (MJ.m ⁻³)	$(\frac{E_a}{E_c})100(\%)$
B103	30	PPDI	Dianol (22+33) (1/1)	5.80	3.60	2.20	37.93	4.70	3.60	1.10	23.40
B138*	30	MDI	1,4-BD	5.46	4.26	1.20	21.98	4.85	4.26	0.58	11.96
B148	30	CHDI	Polacure	36.65	3.75	32.90	89.76	8.98	3.75	5.23	58.24
B153	30	MDI	Polacure	34.27	4.65	29.6L	86.40	13.44	4.65	8.79	65.40

* With block ratio of 1/2/1

Note: Key as in Table 4.22.

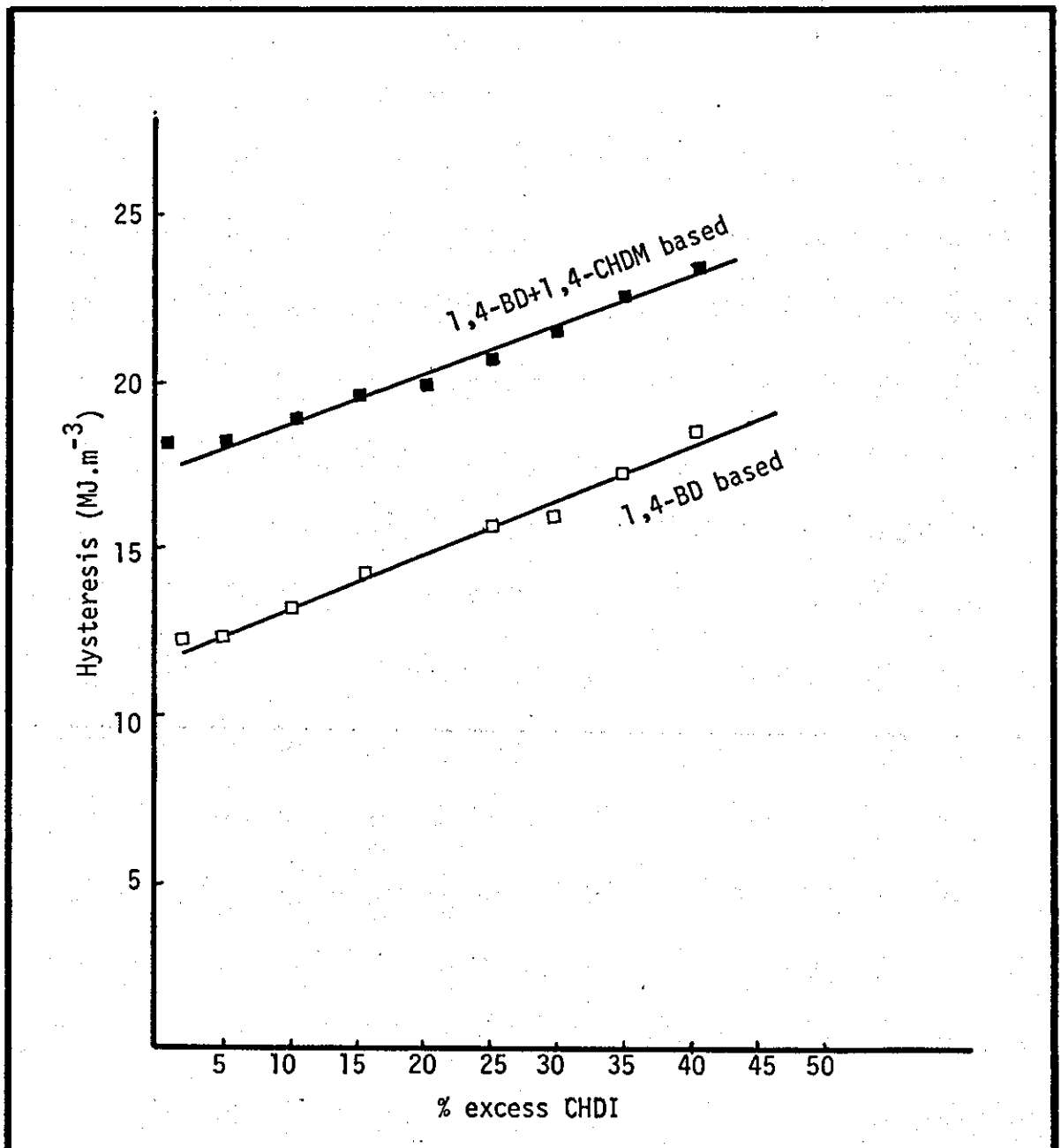


FIGURE 4.14: Relationship Between Hysteresis and % Excess Diisocyanate in Capa 225 Based Polymers Chain Extended with 1,4-BD and 1,4-BD+1,4-CHDM

4.10 HEAT AGEING OF POLYURETHANE ELASTOMERS

4.10.1 Introduction

The ageing of rubber and rubber-like polymers has been the subject of study for many years. It is generally agreed that oxygen attack is the chief cause of the degradation of rubber compounds⁹⁵ and the rate of ageing or degradation does however vary very widely depending upon the conditions and circumstances prevailing and also upon the compounding of the stock.

Various methods have been developed to provide information on the stability of rubber and rubber-like polymers against oxidative degradation. One of these methods, which has a good fundamental basis, is oxidative hot air oven ageing which is well documented for specification and evaluation purposes.¹⁶²

Heat ageing of polyurethanes is taken to mean the effect of elevated temperatures on the polymer for prolonged periods but heat ageing tests are carried out for two distinct purposes. First, they are intended to measure changes in the elastomer at the elevated service temperature and second they can be used as an accelerated test to estimate the degree of change which would take place over a much longer time at normal ambient temperature. The degree to which accelerated tests are successful in predicting long term life at ambient temperature is highly debatable but nevertheless such tests are very widely used in specifications and as a quality control test.

4.10.2 Experimental Procedure

The dry heat ageing of these experimental cast polyurethane elastomers was carried out using a cell type ageing oven at 150°C for 3, 7, 14 and 21 days. The cell type of oven is preferred because it is possible to comparatively age polymers of different compositions simultaneously in the same oven.

Test pieces in the form of dumbell type 2 of BS 903: Part A2: 1975 were used and aged by means of a Wallace-cell ageing block kept at 150°C with a constant rate of new air flow over the specimens. Losses in physical properties by hot air oven ageing was used to measure the degree of polyurethane elastomer deterioration. Test results were expressed as a percentage of change in the properties against ageing time according to the following formula:

$$\text{Change in property} = \frac{P - P_0}{P_0} \times 100$$

where P_0 = initial property of specimen

P = property of specimen after heating.

4.10.3 Results and Discussion

The results of the ageing behaviour of polyurethanes are given in Tables 4.26 to 4.29. Table 4.26 illustrates the original and the percentage change in tensile properties of the polyurethane elastomer series based on Capa 225/CHDI/1,4-BD at the block ratio of 1/3/2 with different levels of excess CHDI. The following observations were obtained: there was a decrease in tensile strength and elongation at break for the polyurethane elastomers with respect to air ageing at 150°C. There was also observed a decrease in the 100% and 300% modulus with increasing ageing time.

Table 4.7 illustrates the percentage change in physical properties with polyurethane elastomers based on Capa 225/CHDI/1,4-BD+1,4-CHDM. It can be seen that there is a continuous decrease in modulus, tensile strength and elongation at break at 150°C with increasing ageing time.

It is interesting to note that a pronounced improvement in heat ageing can result from an antioxidant addition; this is observed in polyurethanes based on Capa 225/CHDI/1,4-BD+1,4-CHDM (compare B79 with B79*

in Table 4.27). About 0.1% by weight of antioxidant (Irganox** 1010) was used in the case of the sample B79*.

The heat ageing properties of polyurethane elastomers based on Capa 225/CHDI or PPDI/1,4-BD with the block ratio of 1/2/1 are given in Table 4.28. There is a continuous decrease in tensile strength, elongation at break and modulus (100% and 300%) with increasing ageing time at the temperature of 150°C. PPDI based polyurethanes exhibit better resistance to ageing than CHDI based polyurethanes.

Table 4.29 shows heat ageing properties of the soft series of polyurethane elastomers. It can be seen that there is a decrease in tensile strength for the period of 3 days at 150°C followed by an increase with increasing ageing time. A continuous increase in elongation at break also occurs with increasing ageing time. The modulus is also decreased throughout the ageing periods at 150°C.

No significant change in hardness was observed in the polyurethane elastomers except for the sample B131 (with Capa 240 in polymer backbone). In this case the crystallisation occurred after ageing and the polymer became very hard increasing to about 100 Shore A compared with its original hardness of 73 Shore A.

The original colour of all the samples changed throughout the ageing periods and became darker and darker with increasing ageing time. The results are presented in Figures 4.15-4.19.

Figure 4.15 shows the effect of ageing time on the Capa 225/CHDI/1,4-BD based PU elastomer with block ratio of 1/3/2. Numbers 1-5 represent the effect of ageing time (0-21 days) on polymers containing 5% excess

* B79 with 0.1% antioxidant

** Ciba-Geigy, Industrial Chemical Division, Manchester

CHDI and numbers 6+10 shows the effect of ageing time on polymers with 30% excess CHDI. It can be seen from the figure that as the amount of excess CHDI used increases the change of colour obviously increases. Similar results are also observed for the Capa 225/CHDI/1,4-BD+1,4-CHDM based polyurethanes (see Figure 4.16). In this figure numbers 11+15 and 31+35 represent the effect of ageing time (0-21 days) on polymers containing 0.2% and 30% excess CHDI respectively. As seen in this figure, the colour change in polymers with higher amounts of excess CHDI is more significant than polymers containing lower amounts of excess CHDI.

Figure 4.17 shows the effect of ageing time at 150°C on the Capa 225/CHDI/Polacure based PU elastomer. Numbers 41+45 represent polymer with 0.2% excess CHDI and numbers 46+50 shows the polymer with 30% excess CHDI. In this series of PU elastomers the change of colour obviously decreases with increasing percentage of excess diisocyanate. Figure 4.18 illustrates the effect of ageing time at 150°C as a comparison between diol and diamine cured polyurethane elastomers. It can be seen from this figure that the amount of excess used CHDI has differing effects on the colour stability of diol and diamine type polyurethanes. In diol extended polyurethanes (1,4-BD and 1,4-BD+1,4-CHDM based) the change of colour increases with increasing excess of the CHDI used while in diamine extended polyurethane (Polacure based) it decreases with increasing excess of CHDI. This effect might be due to greater intermolecular bonding in diamine based polymers and therefore their higher stability during ageing in respect of diol based polyurethane elastomers.

The effect of ageing time at 150°C on the soft polymer series is also shown in Figure 4.19 and represents two different polymers based on Capa 231/CHDI/Capa 305 (numbers 51+55) and Capa 225/PPDI/Dianol (22+33) +TMP (numbers 56+60) respectively. In this series of PU elastomers, as in the other series, the change in original colour increases with increase of ageing time and after 21 days of ageing at 150°C the original colourless sample changed to a black coloured sample (see Figure 4.19).

TABLE 4.26: Heat Ageing Properties of Polyurethane Elastomer Based on Capa 225/CHDI/1,4-BD with Block Ratio of 1/3/2 at 150°C

Tensile Properties	Sample No	% Excess CHDI	Unaged Value	Ageing Time							
				3 days		7 days		14 days		21 days	
				Value	% Change	Value	% Change	Value	% Change	Value	% Change
Ultimate Tensile Strength (MPa)	B84	5	32.8	18.73	-42.8	12.63	-61.5	10.86	-66.9	9.55	-70.8
	B85	10	44.46	24.95	-43.8	15.61	-64.8	13.64	-69.3	10.61	-76.1
	B86	25	55.0	29.52	-46.3	20.07	-63.5	16.54	-69.9	15.56	-71.7
	B87	30	52.73	30.38	-42.3	20.09	-61.9	19.75	-62.5	15.88	-70.0
Elongation at break (%)	B84	5	600	450	-25	270	-55	220	-63	160	-73
	B85	10	720	480	-33	310	-57	290	-59	150	-79
	B86	25	675	480	-28	340	-49	290	-57	250	-62
	B87	30	630	460	-27	460	-27	375	-40	280	-55
100% Modulus (MPa)	B84	5	10.95	10.95	-2.7	10.28	-6.1	9.55	-12.7	8.99	-17.9
	B85	10	11.80	11.70	-0.8	11.47	-2.8	10.77	-8.7	10.07	-14.6
	B86	25	14.24	14.04	-1.4	13.20	-7.3	12.36	-13.2	12.07	-15.2
	B87	30	14.38	14.29	-0.6	11.27	-7.7	12.55	-12.7	12.31	-14.4
300% Modulus (MPa)	B84	5	17.49	14.87	-14.9	-	-	-	-	-	-
	B85	10	19.18	18.03	-5.9	15.52	-19.0	-	-	-	-
	B86	25	25.41	20.52	-19.2	18.83	-25.9	-	-	-	-
	B87	30	27.39	22.62	-17.4	19.84	-27.5	17.20	-37.2	-	-

TABLE 4.27: Heat Ageing Properties of Polyurethane Elastomers Based on Capa 225/CHDI/1,4-BD+1,4-CHDM with Block Ratio of 1/3/2 at 150°C

Tensile Properties	Sample No	% Excess CHDI	Ageing Time								
			Unaged	3 days		7 days		14 days		21 days	
			Value	Value	% Change	Value	% Change	Value	% Change	Value	% Change
Ultimate Tensile Strength (MPa)	Capa 18,6	0.2	35.84	21.52	-39.9	14.37	-59.9	18.43	-62.5	-	-
	B74	5	49.27	25.70	-47.8	15.53	-68.4	15.23	-69.2	14.06	-71.4
	B75	10	56.74	30.25	-46.6	25.47	-55.1	17.94	-68.3	15.42	-72.8
	B76	15	56.91	-	-	24.80	-56.4	20.77	-63.5	18.50	-67.5
	B77	20	55.89	36.24	-35.1	26.07	-53.3	17.73	-68.2	14.35	-74.3
	B78	25	57.4	-	-	23.69	-58.7	20.70	-63.9	17.02	-70.3
	B79	30	62.45	42.26	-32.3	28.28	-54.4	21.32	-65.8	17.77	-71.5
	B79*	30	54.00	-	-	38.29	-29.0	-	-	23.03	-57.3
	B80	35	54.82	-	-	24.62	-55.0	18.68	-65.9	16.20	-70.4
	B81	40	54.46	31.17	-42.2	22.56	-58.5	19.98	-63.3	14.13	-74.0
Elongation at Break (%)	Capa 18,6	0.2	665	490	-26	390	-41	380	-42	-	-
	B74	5	790	540	-31	480	-39	470	-40	450	-43
	B75	10	705	550	-21	520	-26	400	-43	350	-50
	B76	15	715	-	-	510	-28	490	-31	450	-37
	B77	20	675	560	-17	500	-26	380	-43	330	-51
	B78	25	650	-	-	380	-41	430	-33	350	-46
	B79	30	620	560	-9	490	-20	400	-35	350	-43
	B79*	30	590	-	-	570	-3	-	-	470	-20
	B80	35	560	-	-	380	-32	280	-50	250	-55
	B81	40	515	400	-22	370	-28	350	-32	200	-61

/Continued

TABLE 4.27: continued

100% Modulus (MPa)	Capa 18,6	0.2	10.58	10.01	-5.4	9.31	-12.0	8.69	-17.8	-	-
	B74	5	12.05	10.5	-12.8	9.66	-19.8	8.75	-27.4	8.5	-29.4
	B75	10	12.45	11.22	-9.8	10.31	-17.2	9.73	-21.8	9.64	-22.5
	B76	15	12.25	-	-	11.04	-9.8	9.89	-19.2	9.68	-20.9
	B77	20	12.62	12.00	-4.9	11.11	-11.9	10.40	-17.6	9.67	-23.6
	B78	25	12.94	-	-	12.28	-5.1	10.55	-18.4	10.28	-20.5
	B79	30	14.36	13.26	-7.6	12.05	-16.0	11.06	-22.9	10.95	-23.7
	B79*	30	13.11	-	-	11.94	-8.9	-	-	10.78	-17.7
	B80	35	14.80	-	-	12.98	-12.3	12.01	-18.8	11.64	-21.3
	B81	40	16.01	13.73	-14.2	12.85	-19.7	11.91	-25.6	11.91	-25.6
300% Modulus (MPa)	Capa 18,6	0.2	15.21	14.46	-4.9	13.30	-12.5	11.66	-23.3	-	-
	B74	5	19.59	15.84	-19.1	13.80	-29.5	11.90	-39.2	11.52	-41.2
	B75	10	22.54	18.03	-20.0	15.70	-30.3	14.13	-37.3	14.07	-37.5
	B76	15	22.03	-	-	17.00	-22.8	14.63	-33.6	14.09	-36.0
	B77	20	23.34	20.16	-13.6	17.22	-26.2	15.0	-35.7	13.70	-41.3
	B78	25	24.88	-	-	19.65	-21.0	15.85	-36.3	15.42	-38.0
	B79	30	28.29	22.44	-20.6	18.72	-33.8	16.55	-41.5	16.19	-42.7
	B79*	30	25.08	-	-	20.01	-20.2	-	-	16.63	-33.7
	B80	35	28.84	-	-	20.77	-27.9	-	-	-	-
	B81	40	31.40	23.90	-23.8	20.56	-34.5	18.05	-42.5	-	-

* B79 with 0.1% Irganox

TABLE 4.28: Heat Ageing Properties of Polyurethane Elastomer Based on Capa 225/Diisocyanate/1,4-BD with block ratio 1/2/1 at 150°C

Tensile Properties	Sample No	% Excess Diisocyanate	Diisocyanate	Ageing Time								
				Unaged	3 days		7 days		14 days		21 days	
				Value	Value	% Change	Value	% Change	Value	% Change	Value	% Change
Ultimate Tensile Strength (MPa)	B62	20	CHDI	56.56	20.54	-63.6	13.33	-76.4	12.82	-77.3	11.10	-80.3
	B63	30	CHDI	60.97	20.90	-65.7	17.05	-72.0	15.17	-75.1	12.70	-79.1
	B66	45	CHDI	54.20	23.59	-56.4	18.31	-66.2	12.5	-76.9	10.51	-80.6
	B119	0.2	PPDI	54.89	46.84	-14.6	-	-	28.40	-48.2	25	-54.4
	B122	15	PPDI	50.67	35.02	-30.8	34.69	-31.5	30.23	-40.3	25.62	-49.4
	B123	20	PPDI	51.6	38.36	-25.6	36.73	-28.8	33.63	-34.8	30.76	-40.3
	B125	30	PPDI	56.59	38.21	-32.4	35.43	-37.4	30.34	-46.4	25.17	-55.5
Elongation at break (%)	B62	20	CHDI	750	570	-24.0	480	-36.0	460	-38.6	400	-46.6
	B63	30	CHDI	715	480	-32.8	460	-35.6	440	-38.4	370	-48.2
	B66	45	CHDI	580	460	-20.6	400	-31.0	280	-51.7	220	-62.0
	B119	0.2	PPDI	720	700	-2.7	-	-	690	-4.1	690	-4.1
	B122	15	PPDI	640	630	-1.5	620	-3.1	610	-4.6	600	-6.2
	B123	20	PPDI	645	640	-0.7	630	-2.3	580	-10.0	560	-13.1
	B125	30	PPDI	600	580	-3.3	570	-5.0	560	-6.6	550	-8.3
100% Modulus (MPa)	B62	20	CHDI	10.61	8.29	-21.8	7.28	-31.3	6.85	-35.4	6.34	-40.2
	B63	30	CHDI	11.52	9.06	-21.3	8.52	-26.0	7.85	-31.8	7.46	-35.2
	B66	45	CHDI	13.12	10.46	-20.2	9.77	-25.5	8.79	-33.0	8.4	-35.9
	B119	0.2	PPDI	11.06	8.76	-20.7	-	-	8.58	-22.4	8.01	-27.5
	B122	15	PPDI	10.39	8.85	-14.8	8.74	-15.8	8.60	-17.2	8.50	-18.1
	B123	20	PPDI	10.82	9.71	-10.2	9.57	-11.5	9.40	-13.1	9.11	-15.8
	B125	30	PPDI	10.19	8.58	-15.8	8.43	-17.2	8.37	-17.8	8.27	-18.8

/Continued.....

TABLE 4.28: Continued

300% Modulus (MPa)	B62	20	CHDI	18.82	12.72	-32.4	10.9	-42.0	10.12	-46.2	9.32	-50.4
	B63	30	CHDI	20.79	14.60	-29.7	12.79	-38.4	11.92	-42.6	9.50	-54.3
	B66	45	CHDI	25.57	16.71	-34.6	14.84	-41.9	-	-	-	-
	B119	0.2	PPDI	18.67	13.86	-25.7	-	-	13.21	-29.2	12.17	-34.8
	B122	15	PPDI	18.04	13.93	-22.7	14.10	-21.8	12.84	-28.8	13.17	-26.9
	B123	20	PPDI	19.52	15.34	-21.4	14.66	-24.8	13.66	-30.0	13.09	-32.9
	B125	30	PPDI	21.06	15.52	-26.3	14.11	-33.0	13.60	-35.4	12.58	-40.2

TABLE 4.29: Heat Ageing Properties of Soft Series Polyurethane Elastomer at 150°C

Tensile Properties	Sample No	Polyol	Diisocyanate	Chain Extender	Ageing Time								
					Unaged	3 days		7 days		14 days		21 days	
						Value	% Change	Value	% Change	Value	% Change	Value	% Change
Ultimate Tensile Strength (MPa)	B103	Capa 225	PPDI	Dianol (22+33)	31.61	-	-	15.66	-50.4	-	-	16.46	-47.9
	B106	"	PPDI	Dianol (22+33)	13.22	8.72	-34.0	17.59	+33.0	18.98	+43.5	21.06	+59.3
	B108	"	PPDI	+TMP	12.45	-	-	8.22	-33.9	10.14	-18.5	12.63	+1.4
	B131	Capa 240+ Capa 305	PPDI	TMP	15.56	10.21	-34.3	22.47	+44.4	22.61	+45.3	23.83	+53.1
	B155	Capa 231	CHDI	Capa 305	19.13	14.43	-24.5	14.80	-22.6	23.00	+20.2	25.00	+30.6
Elongation at Break (%)	B103	Capa 225	PPDI	Dianol (22+33)	440	-	-	500	+13.6	-	-	570	+29.5
	B106	"	PPDI	Dianol (22+33)	200	220	+10	290	+45.00	295	+47.5	330	+65.00
	B108	"	PPDI	+TMP	120	-	-	125	+4.1	140	+16.6	160	+33.3
	B131	Capa 240+ Capa 305	PPDI	TMP	165	170	+3.0	230	+39.4	250	+51.5	260	+57.5
	B155	Capa 231	CHDI	Capa 305	220	300	+36.3	350	+59.0	370	+68.1	380	+72.7

/continued....

TABLE 4.29: continued

100% Modulus (MPa)	B103	Capa 225	PPDI	Dianol (22+33)	3.04	-	-	3.01	-0.98	-	-	2.07	-31.9
	B106	"	PPDI	Dianol (22+33) +TMP	4.87	3.25	-33.4	3.53	-27.5	3.83	-21.3	3.58	-26.4
	B108	Capa 225	PPDI	TMP	8.58	-	-	6.90	-19.5	6.82	-20.5	6.48	-24.4
	B131	Capa 240+	PPDI	TMP	6.45	4.49	-30.3	4.81	-25.4	15.17	+135.2	16.04	+148.6
	B155	Capa 305 Capa 231	CHDI	Capa 305	7.56	3.60	-52.3	2.86	-62.1	2.86	-62.1	3.33	-55.9
300% Modulus (MPa)	B103	Capa 225	PPDI	Dianol (22+33)	10.86	-	-	5.59	-48.5	-	-	4.45	-59.0
	B106	"	PPDI	Dianol (22+33) +TMP	-	-	-	-	-	-	-	15.25	-
	B108	"	PPDI	TMP	-	-	-	-	-	-	-	-	-
	B131	Capa 240+	PPDI	TMP	-	-	-	-	-	-	-	-	-
	B155	Capa 305 Capa 231	CHDI	Capa 305	-	14.43	-	11.44	-	12.95	-	14.53	-

Increasing ageing time



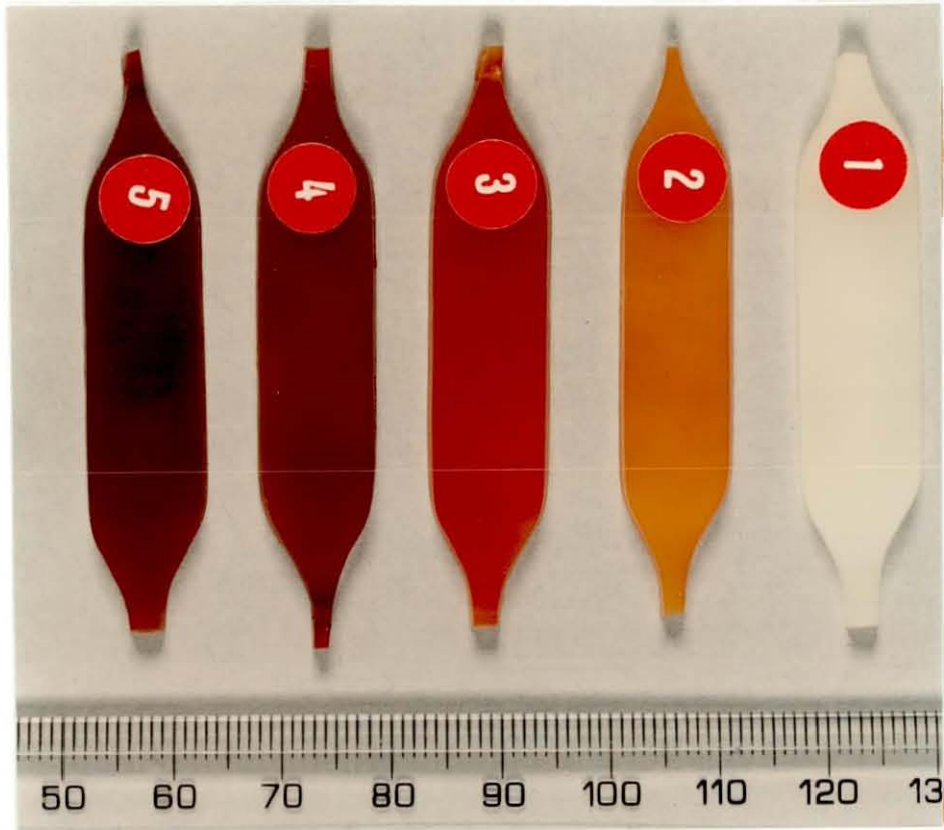
21 days

14 days

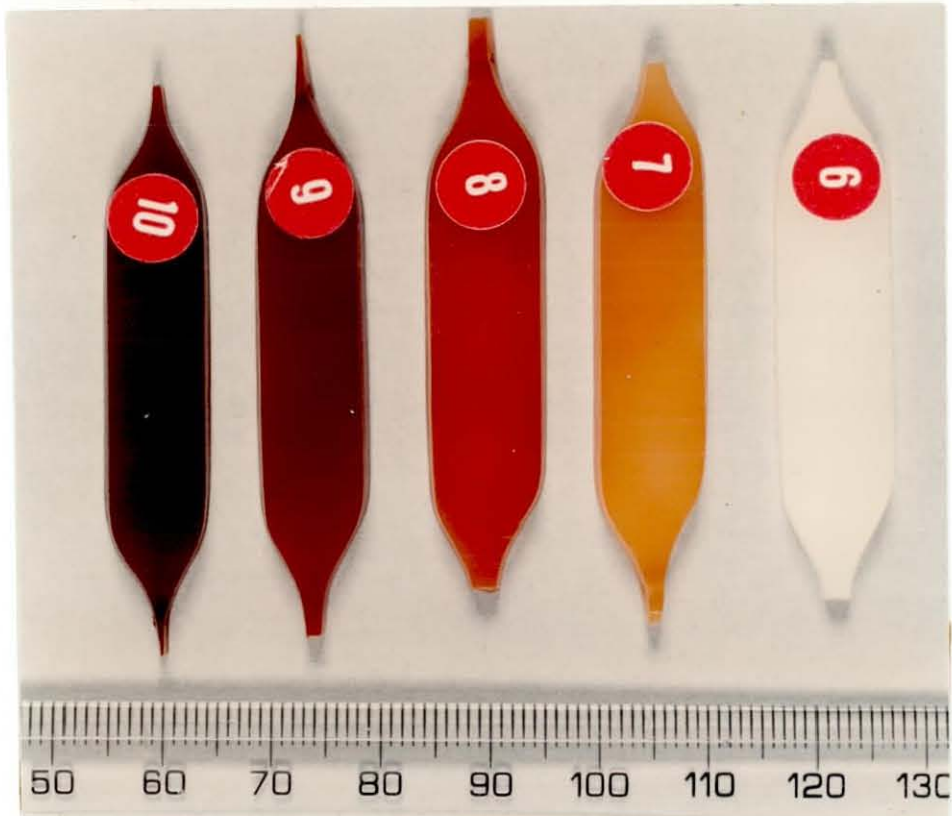
7 days

3 days

0 days

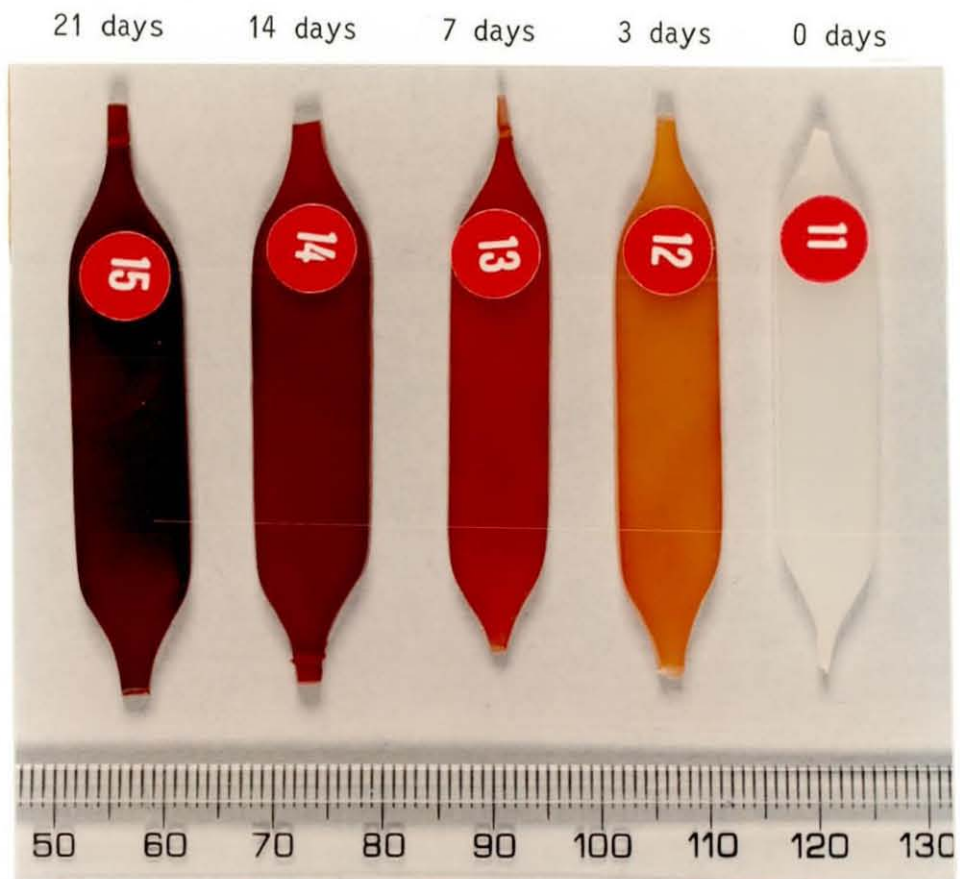


(a)

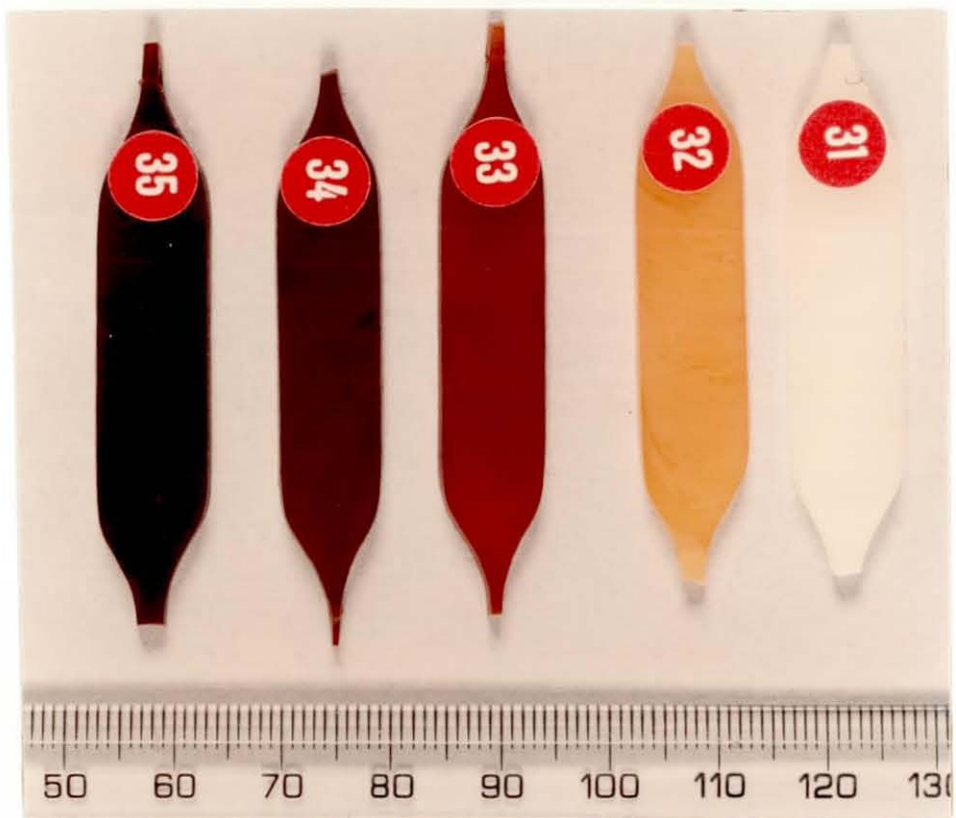


(b)

FIGURE 4.15: Effect of ageing time on 1,4-BD based PU elastomer at 150°C: (a) with 5% excess CHDI; (b) with 30% excess CHDI

Increasing ageing time
←

(a)



(b)

FIGURE 4.16: Effect of ageing time on 1,4-BD+1,4-CHDM based PU elastomer at 150°C: (a) with 0.2% excess CHDI; (b) with 30% excess CHDI

Increasing ageing time



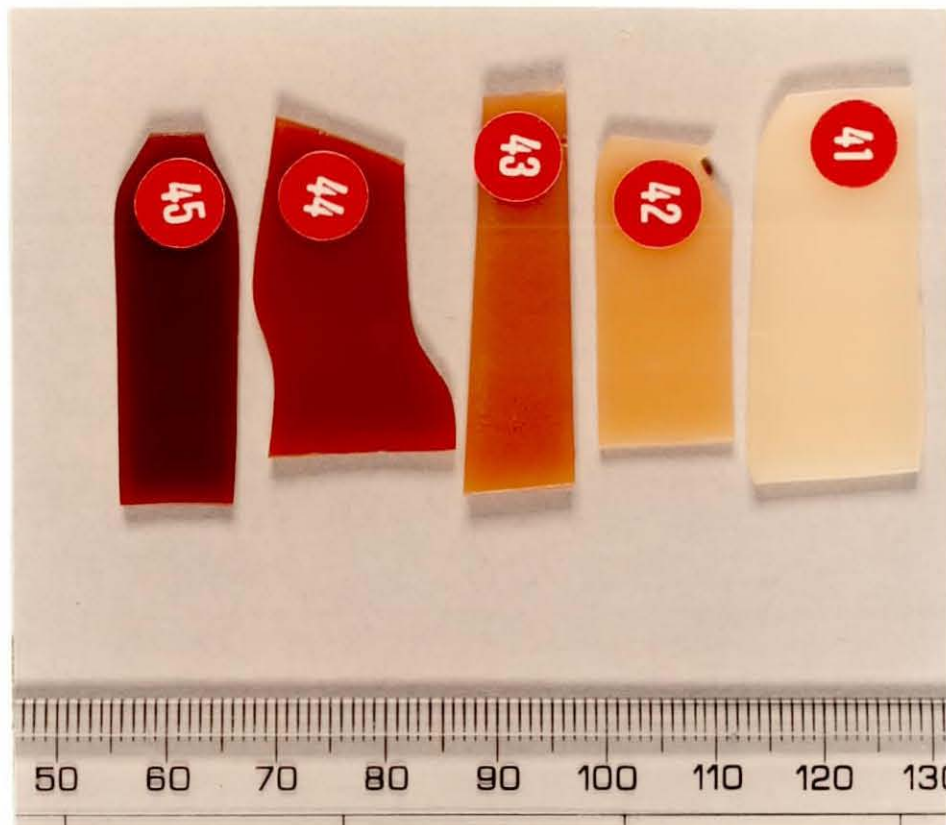
21 days

14 days

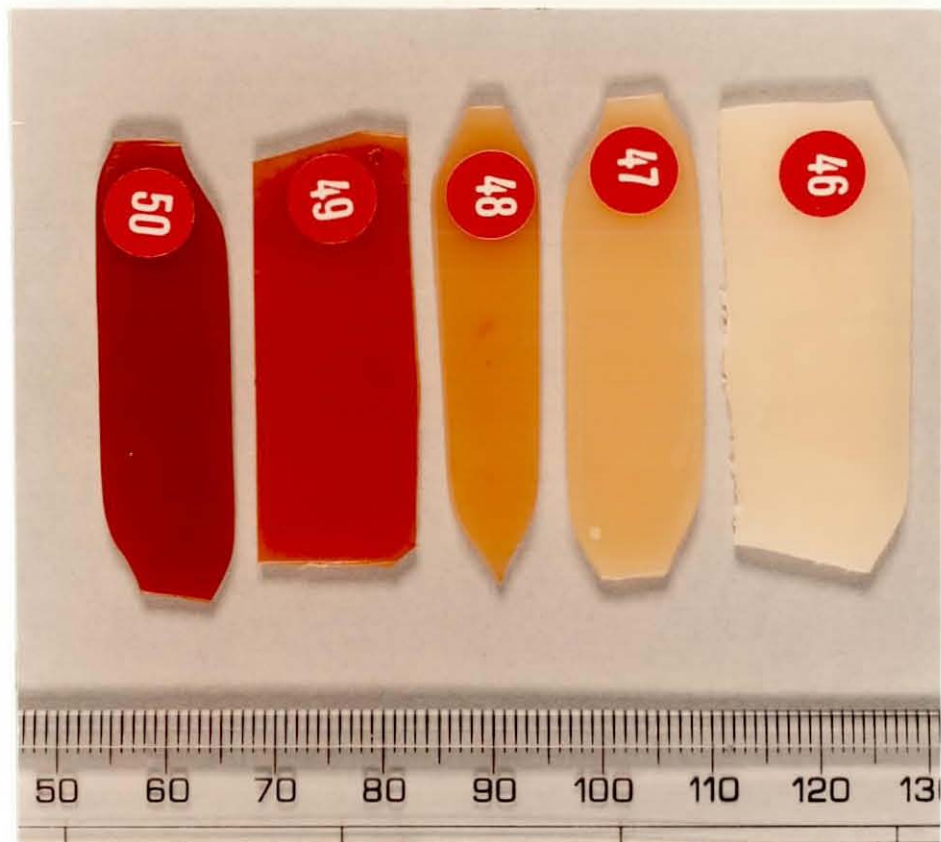
7 days

3 days

0 days



(a)



(b)

FIGURE 4.17: Effect of ageing time on Polacure based PU elastomer at 150°C: (a) with 0.2% excess CHDI; (b) with 30% excess CHDI.

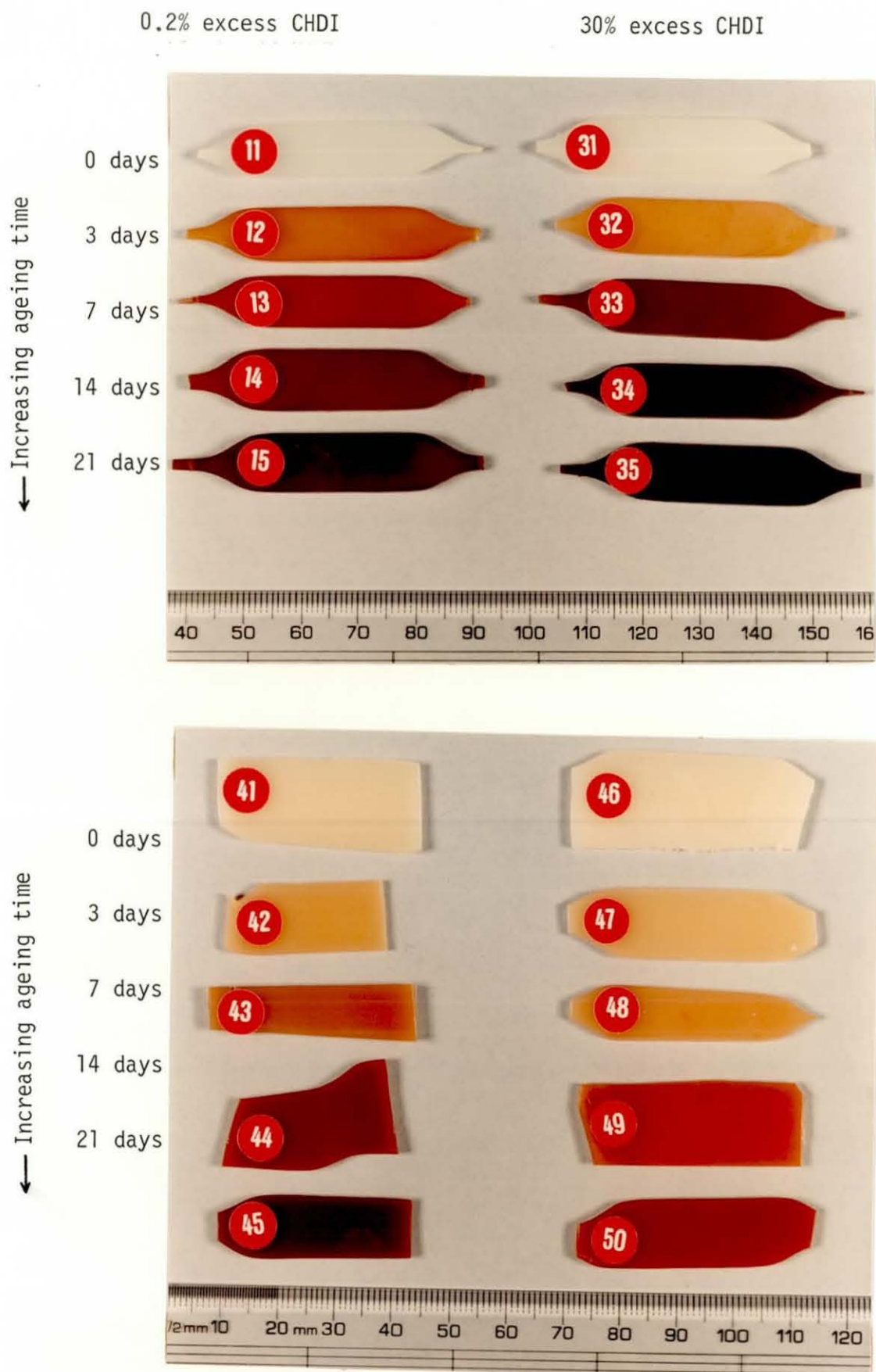


FIGURE 4.18: Comparing the effect of ageing time on diol and diamine cured polyurethanes at 150°C:
 (a) 1,4-BD+1,4-CHDM based polyurethane;
 (b) Polacure based polyurethane

Increasing ageing time



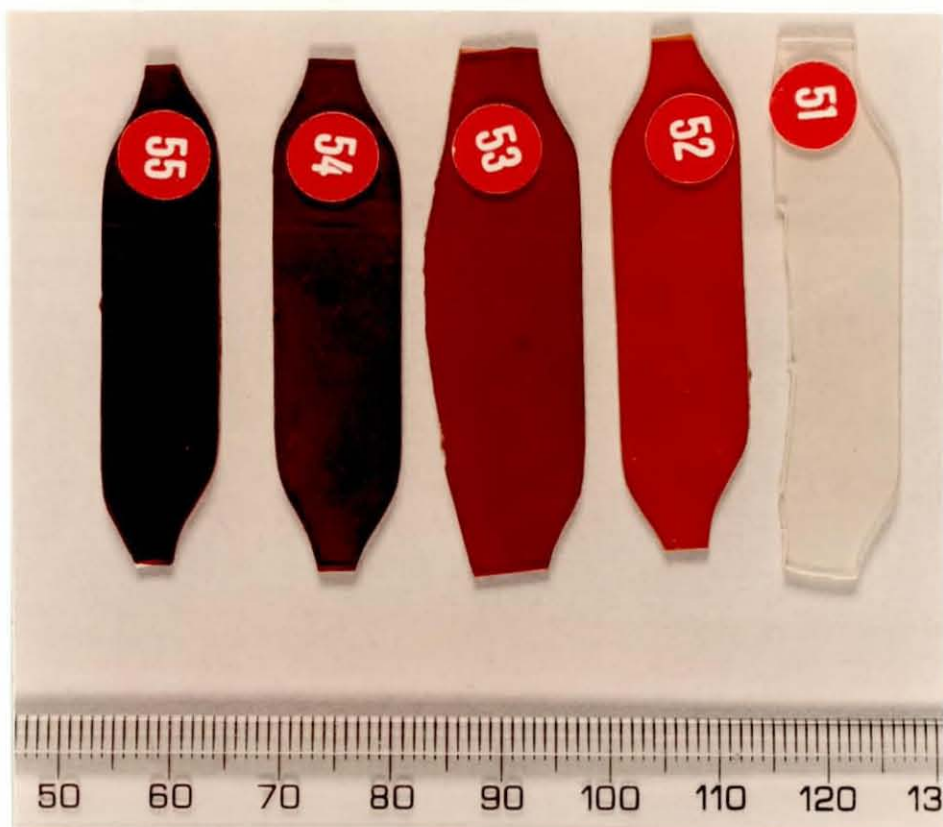
21 days

14 days

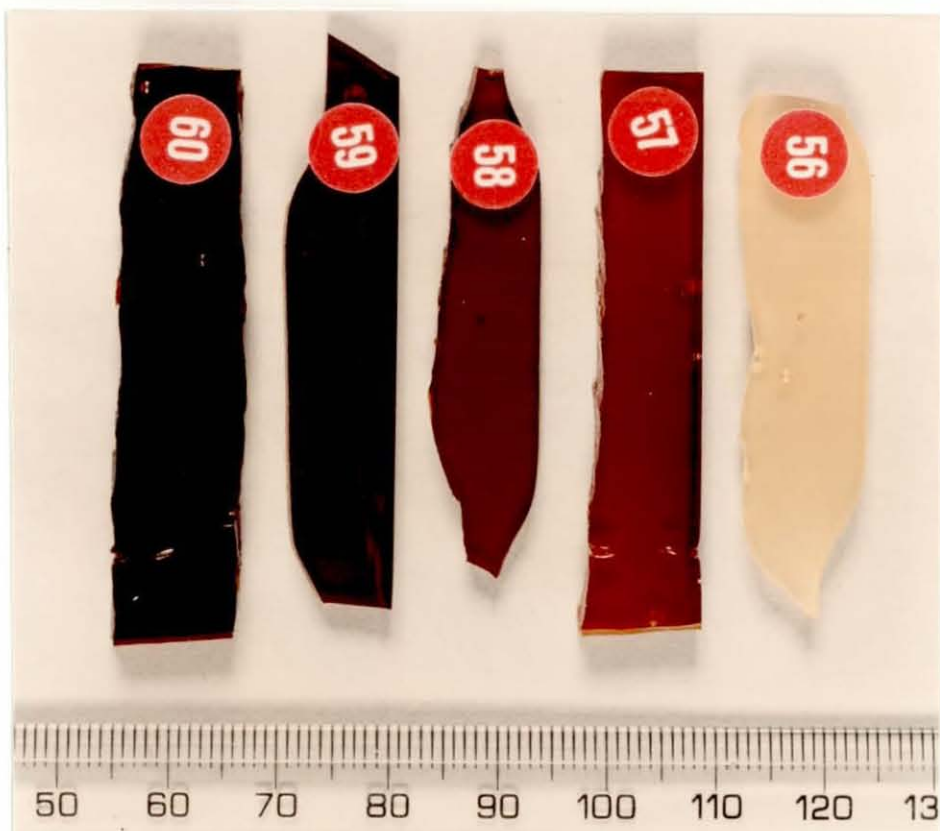
7 days

3 days

0 days



(a)



(b)

FIGURE 4.19: Effect of ageing time on soft polyurethane series at 150°C:
 (a) Capa 231/CHDI/Capa 305 based PU;
 (b) Capa 225/PPDI/TMP+Dianol (22+33) based PU

CHAPTER 5

GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

5.1 DISCUSSION AND CONCLUSIONS

The present research programme was initiated with the aim of establishing a synthesis technique for the preparation of thermally stable polyurethane elastomers, some of which could possibly be used as tyre materials. A summary of the research investigation and steps undertaken to establish this programme is given by means of a line diagram in Figure 5.2.

In a preliminary investigation different polyurethane reactants were examined but the one chosen for detailed study was based on a 2000 molecular weight polycaprolactone diol (Capa 225) and 1,4-trans cyclohexane diisocyanate (CHDI) prepolymer system. Capa polyols, in general, were found appropriate for use in such polyurethane elastomers due to their high polarity increasing the intermolecular attraction and hence improving mechanical properties.

Preliminary studies established that environmental contamination of the raw materials could be a problem and that these must be stored in air tight containers and also special precautions taken not to allow any moisture to come into contact with these materials which may lead to undesired side reactions. The quasi polymerisation method was found to be a suitable technique for the preparation of polyurethanes which involved the use of high melting point chain extenders. Using this technique it was found possible to carry out a bulk polymerisation at the normal PU reaction temperature range of 100-130°C.

All chain extenders, in general, exhibited high reactivity with the prepolymer systems investigated. The major problem faced in the synthesis of polymer was quick gelation (short pot life). This meant that

the rate of the reaction between chain extender and prepolymer was so fast that there was insufficient time for casting of the final polymer into a suitable test specimen sheet. This problem was overcome by the use of a new type of delayed action catalyst, dicarbo-butyloxy tin dichloride, T220, which extended the pot life time sufficiently for satisfactory casting of the polymers to be accomplished. The use of such a catalyst was found essential to make satisfactory CHDI based polyurethanes.

The influence of block ratio, type and structure of chain extenders and diisocyanates on thermal stability of polyurethane elastomers was investigated. An attempt was also made to investigate the role of excess diisocyanate calculated stoichiometrically on a block ratio basis on thermal stability of these PU elastomers. Through this attempt a new method of producing polyurethane elastomers resulted in materials that retained strength and elasticity at temperatures higher than was previously thought possible. In this process the initially fully formed PU contained a large excess of diisocyanate over the stoichiometric amount required to form the simple linear polyurethane. It was discovered that this excess of diisocyanate, which is apparently present in a suspended activity form in-situ in the initially formed PU, can be activated by means of a further heating cycle, or post cure, to give a PU possessing enhanced crosslinking. This both substantially increases the initial physical properties of the PU and the maximum temperature at which the elastomer will retain useful mechanical and engineering properties. A typical example of the property improvements possible is in the Capa 225/CHDI/1,4-BD PU of 1/2/1 molar ratio where the initial tensile strength (UTS) of the linear polymer is 17.02 MPa and it has lost all its strength by 120°C; using a molar ratio of 1/2.04/1 (2% excess CHDI) raises the UTS to 43.8 MPa at ambient only to completely lose its strength at 150°C. If this process is continued, then a molar ratio of 1/2.7/1 (35% excess CHDI) raises the UTS to 60.69 MPa and reasonable strength is retained until 210°C.

It is considered that these enhanced physical properties and temperature resistance are conveyed to the PU elastomer by formation of many isocyanurate crosslinks during the reaction and post-curing step. The scheme of isocyanurate modified urethane elastomer preparation is shown in Figure 5.1.

A feature possessed by these isocyanurate crosslinked PU elastomers and considered important is that the crosslinks formed are believed to be covalent and hence the resulting polymer possesses no melting point or melting point range. At elevated temperatures of 210-240°C, and above, only a general softening and lowering of modulus occurs. This is considered important for engineering applications where the sudden catastrophic failure that accompanies the melting of many thermoplastic type rubbers is unacceptable.

A number of analytical techniques were used to characterise the prepared urethanes and to study their structure and morphology. These included infrared spectroscopy, differential scanning calorimetry, dynamic mechanical thermal analysis, X-ray and scanning electron microscopy.

The hydrogen bonding in PU elastomers as measured by the IR technique was observed to lie between 50-60%. Isocyanurate crosslinking showed no marked variation in the extent of hydrogen bond formation. TMP extended polymers showed relatively lower values of hydrogen bonding, which can be explained by considering them to possess reduced intermolecular attractive forces resulting from spatial separation of chains due to the increased crosslinking that results from the use of a tri-functional polyol.

The crosslink density of polyurethanes was measured experimentally using the swelling method and it was found that the crosslink density values of the polyurethanes significantly increased with either increasing the amount of excess diisocyanate in the original polymer or the

presence of a trifunctional chain extension agent i.e. TMP. It was also found that a higher crosslink density was ~~found~~ present in diamine (Polacure) based polyurethane than in diol (1,4-BD or 1,4-BD+1,4-CHDM) based materials. Samples with higher block ratios also showed relatively higher crosslink densities.

X-ray studies showed all materials to be amorphous in the relaxed state with the presence of only a broad diffuse halo indicating the absence of crystallinity. However, on stretching the samples at approximately 300% extension, paracrystallisation of the polyester soft segment was observed. These X-ray results were found to be in agreement with the DSC results which showed no evidence of a sharp crystalline melting point.

Surface morphology of polyurethane elastomers was studied by scanning electron microscopy (SEM) and the results showed that a systematic change in morphology of these polymers occurred with increasing amount of excess CHDI. This is considered to result from increasing domain structure formation formed by aggregation of the hard segment units and their proportion gets higher as the amount of excess diisocyanate used increases.

The DSC results showed significantly higher transitions for PUs containing symmetrical ring structure type chain extenders and diisocyanates. This gave further evidence of effective hydrogen bonding and the consequently increased domain formation in such polyurethanes. In particular, CHDI based urethanes showed no evidence of short range order transitions. This suggested that in those materials the extent of hard/soft segment mixing is relatively low and that the greater hard segment formation of CHDI based PUs resulted in segregated domain structures. An increase in the transition temperature was found with increase of excess CHDI, possibly associated with the increased thermal stability of the more bulky hard segment domains. Transition temperatures were also found to increase as the block ratio increased from 1/2/1 to 1/3/2.

Thermal stability properties were measured by two complimentary methods those of tensile type measurements at elevated temperatures using a hot air environmental chamber and also the dynamic mechanical thermal analysis (DMTA) technique was used.

The DMTA technique was found to be a rapid method for measuring the change in modulus over a wide range of temperature and the following conclusions are drawn from the results which have been obtained, from the DMTA experimental work:

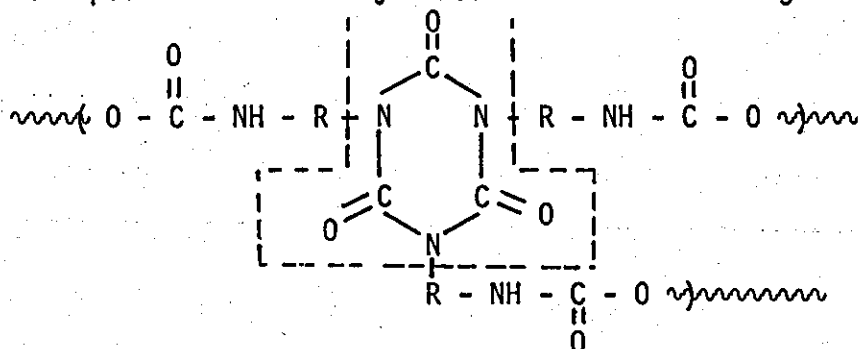
1. The effect of chemical structure of various diisocyanates on the thermal stability of the resulting polyurethane elastomers is found by comparing five different types of diisocyanates synthesised to produce PUs. CHDI based polyurethanes demonstrated relatively higher temperature stability than the other four diisocyanate based polyurethanes. It is found that the contribution to PU thermal stability of various diisocyanate falls in the following order



2. A special feature of the cyclohexane diisocyanate (CHDI) based polyurethane is the uniquely flat storage modulus (E') - temperature profile they possess showing no change in E' over a very wide temperature band from 23°C to 205°C for the BD+CHDM extended PU to the presently obtained maximum of 23°C-260°C for the Polacure extended PU.
3. It is found that thermal stability can be improved by using CHDI as a co-diisocyanate in both TDI and the H_{12}MDI based polyurethanes.
4. The structure of diol chain extenders has been shown to have a marked influence on the thermal stability of polyurethanes. It has been demonstrated that increasing symmetry in chain extenders

gives rise to progressively greater degrees of thermal stability. It is also considered that the thermal stability is higher when diamine (Polacure) chain extension is used and lower for diols.

5. It is considered that using an excess of diisocyanate enhances the thermal stability of a PU by means of isocyanurate crosslinking and an approximately linear relationship applies between the quantity of crosslinking in a PU and its thermal stability. Isocyanurate structures are well known in the polyurethane field as possessing outstanding thermal stability and also have the particular property of not melting but instead decompose and eventually char when heated to high temperatures.



The isocyanurate crosslink

6. Using an excess CHDI together with a suitable chain extension agent is considered to give higher temperature stability.
7. Thermal stability is also found to increase when TMP is used as a chain extender. This is considered to be due to the increased crosslinking in the TMP based polyurethane elastomer.

In order to measure thermal stability and strength retention, tensile properties were measured at elevated temperatures. Tensile properties, namely ultimate tensile strength, elongation at break and modulus are observed to generally decrease over the temperature range 23°C through to 240°C. This effect may be attributed to the effect of temperature on the crosslink entities present. It is especially observed that these

polyurethanes show no sharp melting point and also do not exhibit the rapid loss in dimensional stability displayed by conventional PUs when heated.

The greater degree of hard segment domain formation associated with the use of excess diisocyanate gives rise to high modulus and tensile strength values and relatively harder materials. The effect of molecular symmetry on domain formation and phase separation, and subsequently on the properties of the polyurethane elastomer have been demonstrated. Tensile strength properties are generally much improved by the use of the symmetrical diisocyanates and chain extenders, compared with asymmetrical ones, where they give a much softer material with lower tensile properties indicative of relatively poor packing of hard segments. Most of the polyurethanes showed hardnesses in the range 80-95 Shore A. Polacure based PUs exhibited higher hardness and modulus values than their diol analogues; generally however the elongation at break of the Polacure based PUs was lower. This was considered to be due to the predominance of urea linkages in the Polacure based elastomer which enhances crosslinking and hydrogen bonding formation and thus gives more rigidity to the polymer. Also found was an increase in hardness and modulus and a decrease in ultimate tensile strength and elongation at break when TMP based PUs were compared with PUs using the mixed Dianol (22+33) diol chain extender. This is considered due to more crosslinking and poor molecular ordering being present in the TMP systems and thus indicates mixing of hard with soft segments. Obviously the hard segment to soft segment ratio will have, as was observed, a significant effect on polyurethane properties.

It was observed that compression set and tension set decreases with increased hard segment content and it is generally concluded that the higher crosslinked polyurethanes showed lower set values.

It was found that both crack initiation and crack propagation resistance decrease with increasing crosslinking and the heat generation,

by flexing, of polyurethanes also increased with increasing cross-linking or applied strain.

Hysteresis loss has been found to depend on the chemical structure of the hard segment and this has been explained in terms of the reorganisation of hard segment domains. The greatest proportion of hysteresis loss occurs in the first cycle and this is primarily associated with the high degree of structural reorganisation which takes place in the first cycle. It was found polymers of higher hard segment content possess greater net energy absorption. This is considered to be due to the presence of longer domain structures being associated with the longer hard segments.

In the hot air oven ageing test series it was found that physical and mechanical properties usually decrease with increasing ageing time. The original colour of the polyurethane samples were obviously changed during the ageing cycle from an originally off-white material through the various stages of yellow to brown to dark brown to finally black. The results illustrated that the colour change in BD+CHDM systems increased with increasing amounts of excess CHDI. By contrast the Polacure based polymers exhibited a decrease in colour change with increasing percentages of excess diisocyanate. These results can be explained on the basis that urea linkages in Polacure based PU elastomers can give the possibility of higher hydrogen bond formation and hence higher thermal stability.

5.2 RECOMMENDATIONS FOR FURTHER WORK

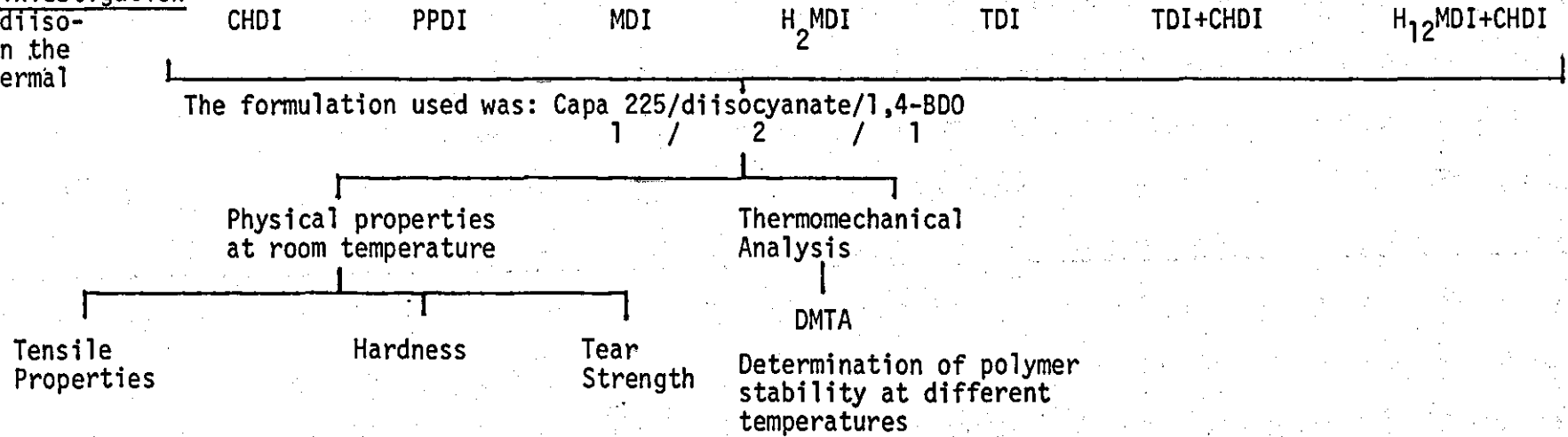
In view of the results of the investigation carried out in the present work, the following recommendations can be made:

1. Investigate the effect of various catalysts on CHDI based polyurethane elastomers as the presence of catalyst is known to control the final properties.
2. Investigate the effect of reinforcing fillers and fibres on physical and mechanical properties and thermal stability of polyurethane elastomers.
3. Comparison between two different types of polyurethanes based on polyester/CHDI and polyether/CHDI and evaluation of their role in thermal stability and general physical and mechanical properties e.g. polyether based PU elastomers generally gives the best heat build up resistance.
4. Evaluation of the effect of cyclic polyol and chain extender structures, coupled with isocyanurate crosslinking on thermal stability of PU elastomers.

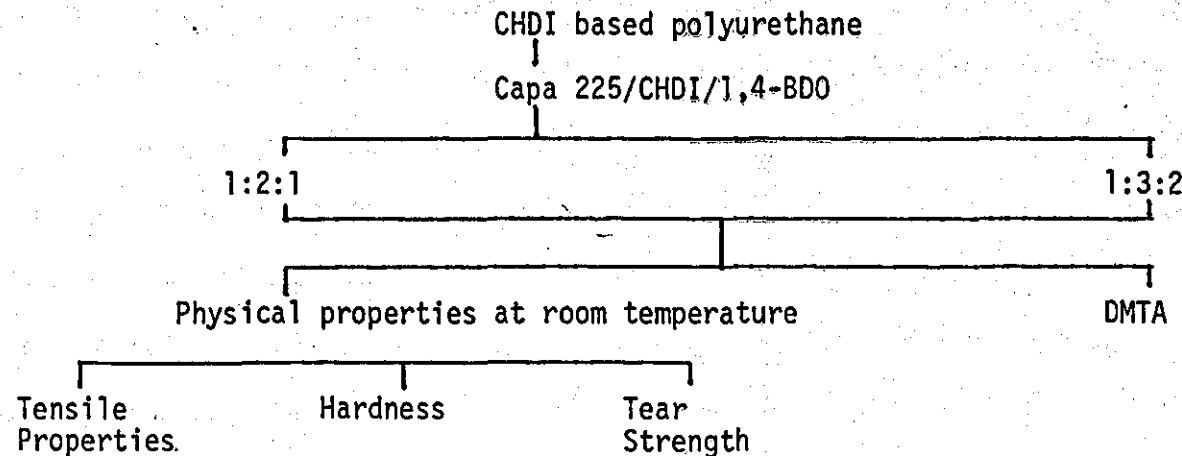
FIGURE 5.2: Summary of Research Investigation

1) Diisocyanate investigation

Influence of the diisocyanates effect on the properties and thermal stability

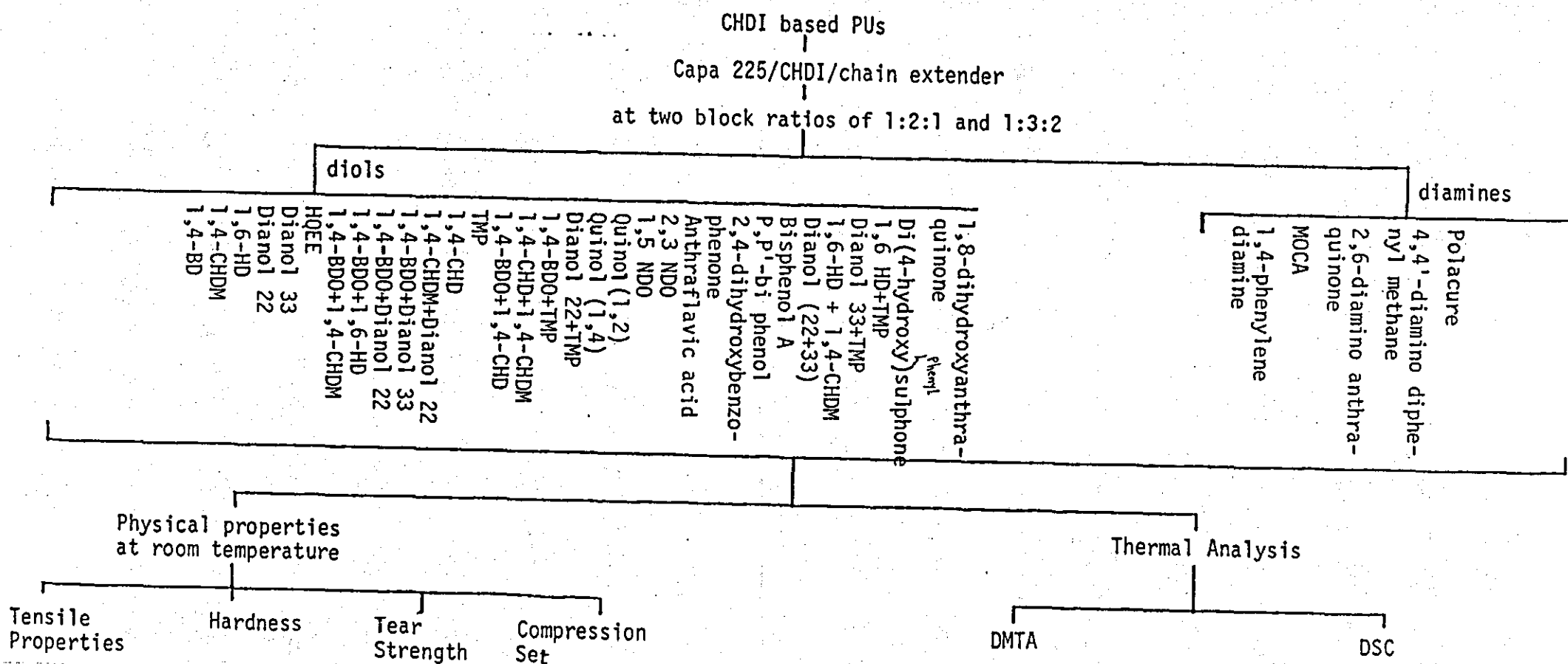


2) Block ratio investigation



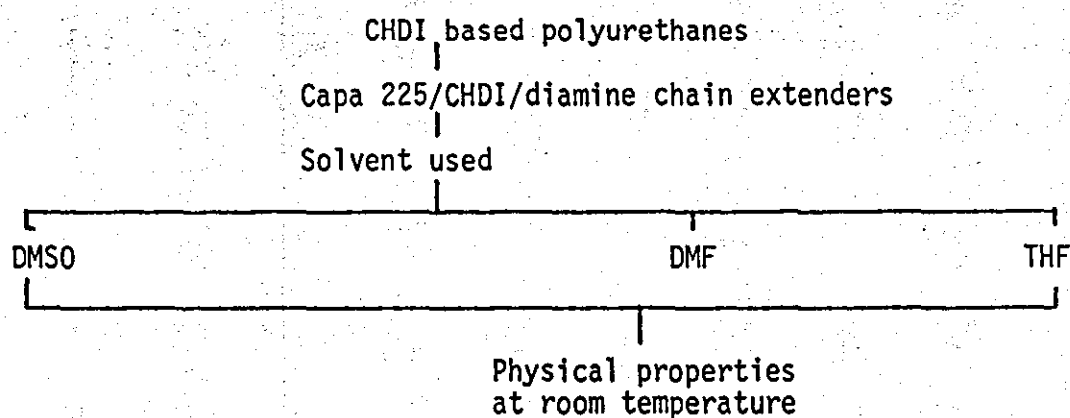
(The material became very hard at higher block ratio, so higher block ratios were not used)

3) Chain extension investigation



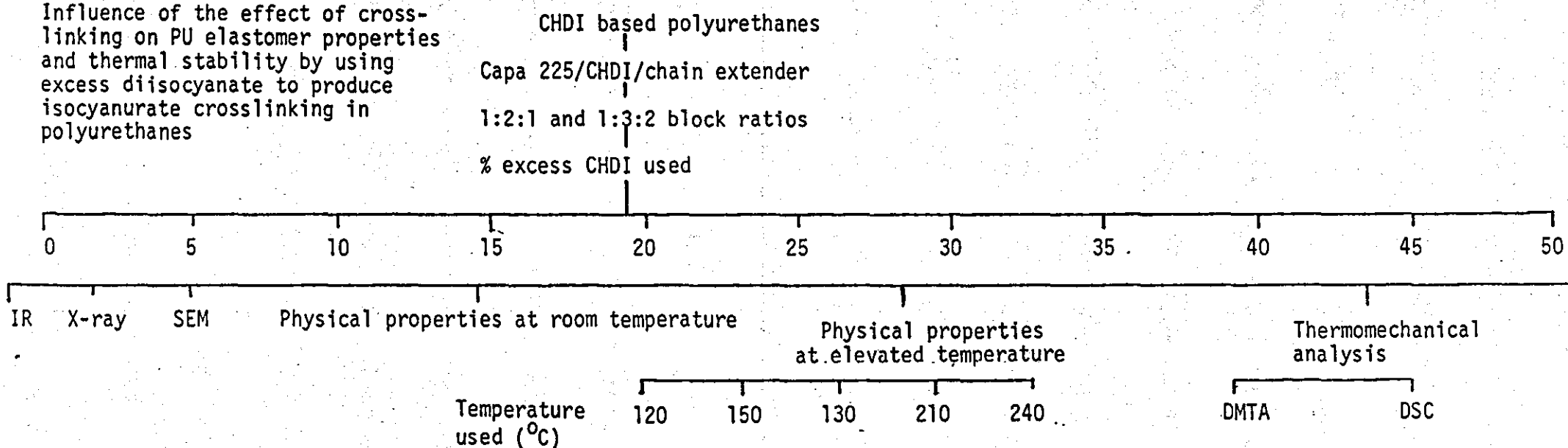
4) Polymerisation system investigation

The aim of this investigation was to reduce the reactivity of chain extender by means of solution polymerisation and improve gelling time of the polymers but the polymers were prepared by this method and demonstrated very poor physical property

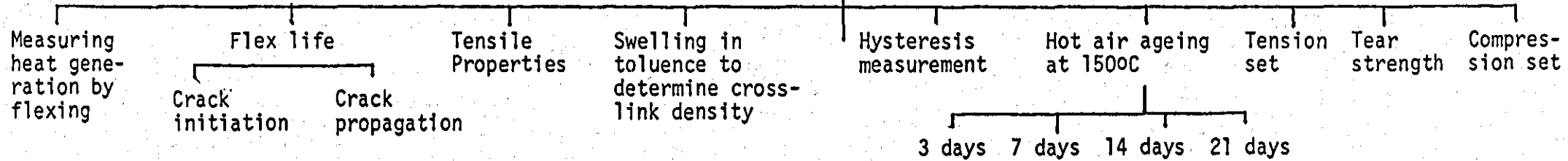


5) Crosslinking investigation

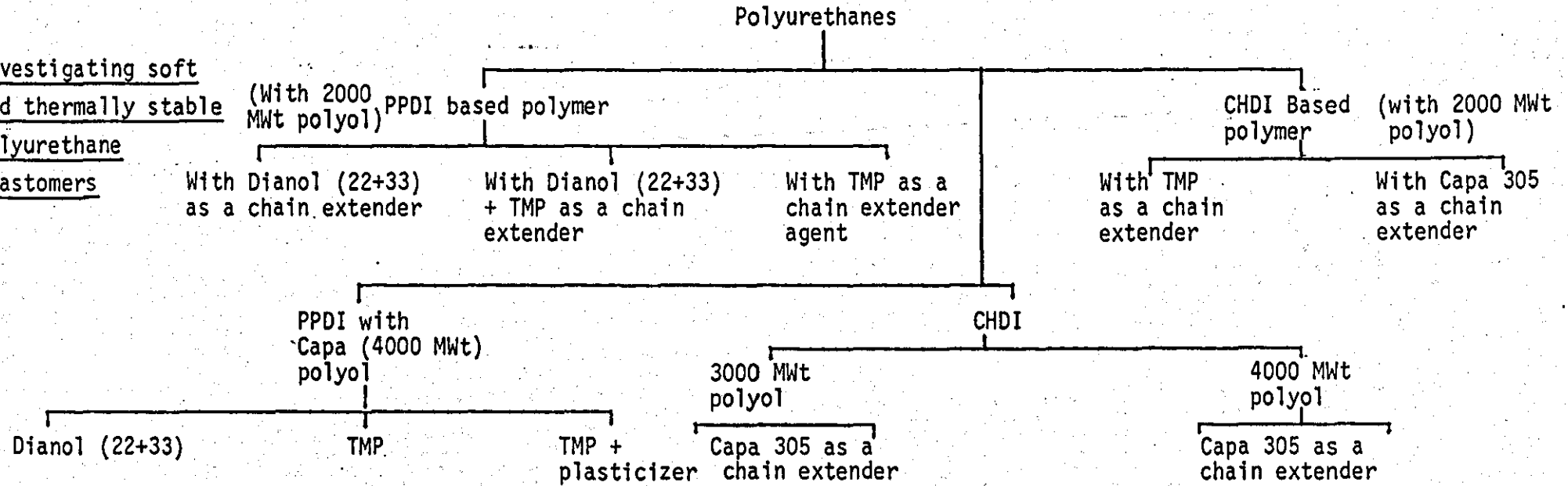
Influence of the effect of crosslinking on PU elastomer properties and thermal stability by using excess diisocyanate to produce isocyanurate crosslinking in polyurethanes



Physical properties at room temperature (continued)

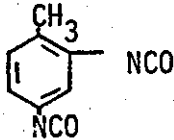
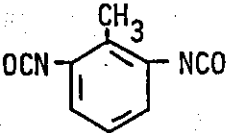
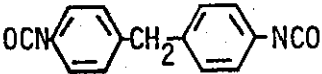
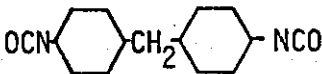
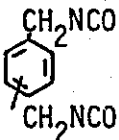

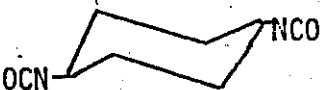


6) Investigating soft and thermally stable polyurethane elastomers

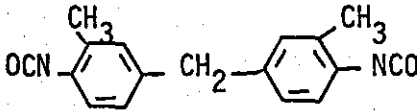
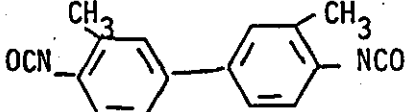
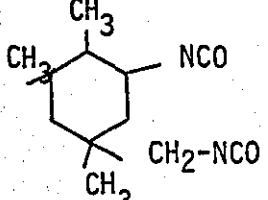
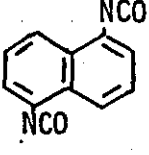


APPENDIX 1

A. STRUCTURAL FORMULA OF THE INDUSTRIALLY IMPORTANT DIISOCYANATES USED IN POLYURETHANE ELASTOMER SYNTHESIS

Name	Abbreviation	Structure
2,4-Toluene diisocyanate	TDI	
2,6-Toluene diisocyanate	TDI	
4,4'-Diphenylmethane diisocyanate	MDI	
4,4'-Dicyclohexylmethane diisocyanate	H ₁₂ MDI	
1,6-Hexamethylene diisocyanate	HDI	$\text{OCN}-(\text{CH}_2)_6-\text{NCO}$
xylylene diisocyanate	XDI	
para-phenylene diisocyanate	PPDI	
cyclohexyl diisocyanate	CHDI	

/Continued..

Name	Abbreviation	Structure
2,2,4-Trimethyl-1,6-hexamethylene diisocyanate	TMDI	$\text{OCN-CH}_2-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{NCO}$
3,3'-Dimethyl-diphenylmethane 4,4'-diisocyanate		
3,3'-Tolidene 4,4'-diisocyanate	TODI	
Isophorone diisocyanate	IPDI	
1,5-Naphthalene diisocyanate	NDI	

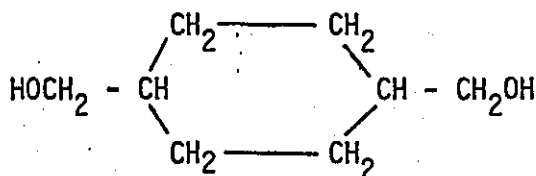
B. PHYSICAL PROPERTIES OF CHDI AND PPDI

Physical Properties	CHDI	PPDI
Form	White flaked solid	Colourless flaked solid
Purity	99 ± 1%	99 ± 1%
Molecular weight	166.18	160.13
NCO content	50.57% by weight	52.5%
Isocyanate equivalent	83.1	80.06
Trans stereoisomer	≥99.0%	-
Total chlorine	100 ppm max	100 ppm max
Hydrostable chloride	20 ppm max	20 ppm max
Specific gravity	1.116 at 70°C	1.170 at 100°C
Melting point	62-64°C	94-95°C
Boiling point	260°C at 760 mm Hg 143°C at 25 mm Hg	260°C at 760 mm Hg 110-112°C at 25 mm Hg
Viscosity, Brookfield	≈13 Cp at 65°C (#2 spindle at 20 rpm)	1.114 Cp at 100°C (#2 spindle at 20 rpm)
Solubility	Soluble in aliphatic hydrocarbons at elevated temperatures, soluble in inert organic solvents at room temperature	Soluble in most inert organic solvent at elevated temperature
Flash point	>210°F (Pensky-Martens) -	
Ames test for mutagenicity	Negative	Negative
Toxicity LD ₅₀ (oral)	Similar to TDI	Similar to TDI
Vapour pressure	Similar to TDI	Similar to TDI
Storage stability	Stable at room temperature in closed containers up to 6 months	Stable at room temperature in closed containers for up to 6 months

C. NAME, FORMULA AND BASIC TECHNICAL INFORMATION OF THE CHAIN EXTENDERS USED IN POLYURETHANE ELASTOMERS

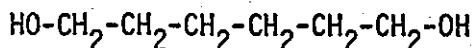
- I) 1,4-BD = 1,4-Butane diol (liquid), $C_4H_{10}O_2$, M.W. = 90.12,
Eq. W = 45.06, Fl.p = $134^{\circ}C$, m.p. = $16^{\circ}C$, b.p. = $227.230^{\circ}C$,
 $HO-CH_2-CH_2-CH_2-CH_2-OH$
Supplier: GAF (Great Britain) Co Ltd.

- II) 1,4-CHDM = 1,4-cyclohexane dimethanol (cis, trans-1,4-bis-(hydroxymethyl)-cyclohexane (solid), $C_6H_{10}(CH_2OH)_2$, M.W. = 144.21,
Eq. W. = 72.10, m.p. = $56^{\circ}C$, b.p. = $283^{\circ}C$

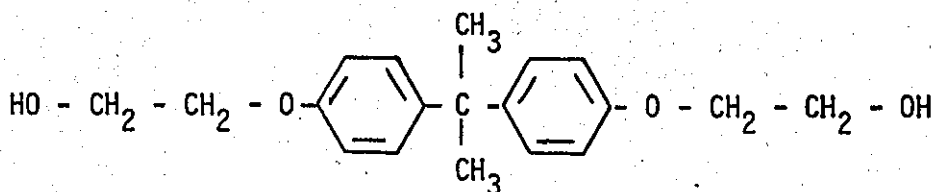


Supplier: Aldrich Chemical Co Ltd.

- III) 1,6-HD = 1,6-Hexane diol (hexamethylene glycol), (solid), $C_6H_{14}O_2$,
M.W. = 118.18, Eq. W = 59.09, Fl.p. = $98-100^{\circ}C$, m.p. = $40.42^{\circ}C$,
b.p. = $250^{\circ}C$

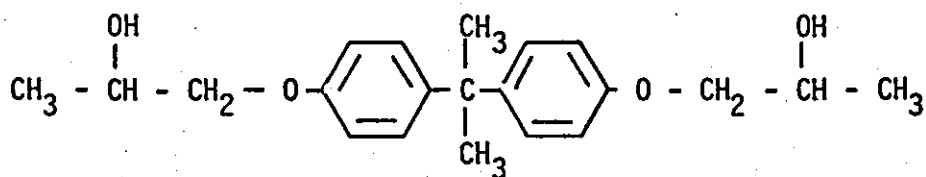


- IV) Dianol 22 = [1,1'-Isopropylidene-bis-(p-phenylene-oxy), di- β -ethanol],
(solid), M.W. = 316, Eq. W = 158,



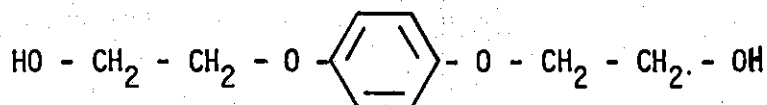
Supplier: Akzo Chemie UK Ltd

V) Dianol 33 = [1,1'-isopropylidene-bis-(p-phenylene-oxy)di-w-propanol-2],
(solid), M.W. = 344, Eq. W = 172, m.p. = 70-80°C,



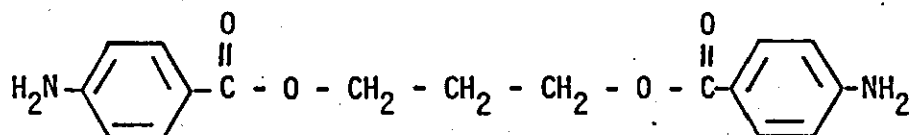
Supplier: Akzo Chemie, UK Ltd.

VI) HQEE = Hydroquinone-bis-hydroxyethyl ether (solid), $C_{10}H_{14}O_4$
M.W. = 198, Eq. W = 99, m.p. = 100°C,



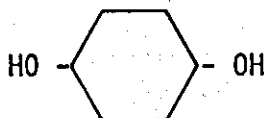
Supplier: Eastman Chemicals USA and Aldrich Chemical Co Ltd.

VII) Polacure 740M = Trimethylene glycol Di-p-aminobenzoate (solid),
 $C_{17}H_{18}N_2O_4$, M.W. = 314, Eq. W = 157, m.p. = 125-128°C,



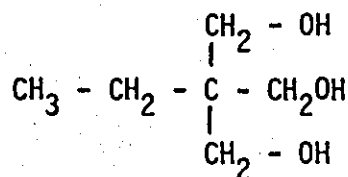
Supplier: Polaroid Corporation, USA.

VIII) 1,4-CHD = cis, trans-1,4-cyclohexane diol (solid), $C_6H_{12}O_2$,
M.W. = 116.16, Eq. W = 58.08, m.p. 98-100°C, b.p. = 150°C/20 mm Hg



Supplier: Koch-Light Ltd.

IX) TMP = Trimethylol propane (2-ethyl-2-hydroxymethyl propanediol),
(solid), $C_6H_{14}O_3$, M.W. = 134.18, Eq. W = 44.73, m.p. = 56-58°C,



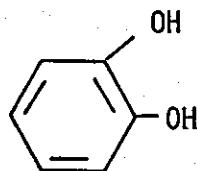
Supplier: BDH Chemicals Ltd.

X) Quinol = Hydroquinone (solid), $C_6H_6O_2$, M.W. = 110.11, Eq. W = 55.05,
m.p. = 170-174°C



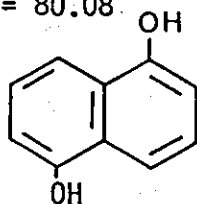
Supplier: BDH Chemicals Ltd.

XI) Catechol = 1,2-Dihydroxy phenylene (solid) $C_6H_6O_2$, M.W. = 110.11,
Eq. W = 55.05



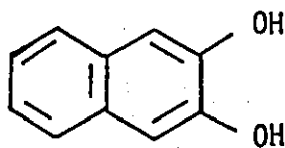
Supplier: Ralph N Emanuel Ltd.

XII) 1,6-ND = 1,5-Naphthalene diol (solid), $C_{10}H_8O_2$, M.W. = 160.17,
m.p. = 260-262°C, Eq. W = 80.08



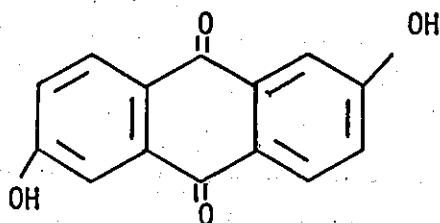
Supplier: Ralph N Emanuel Ltd.

- XIII) 2,3-ND = 2,3-Naphthalene (2,3-Dihydroxynaphthalene), (solid),
 $C_{10}H_8O_2$, M.W. = 160.17, Eq. W = 80.08, m.p. = 162-164°C,



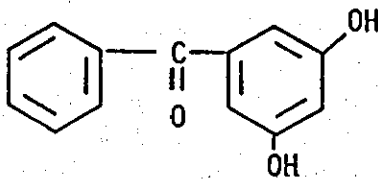
Supplier: Ralph N Emanuel Ltd.

- XIV) Anthraflavic acid = 2,6-Dihydroxyanthraquinone (solid),
 $C_{14}H_8O_4$, M.W. = 240.21, Eq. W = 120.1, m.p. > 320°C



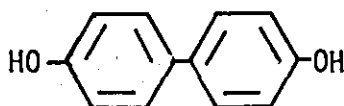
Supplier: Ralph N Emanuel Ltd.

- XV) 2,4-DB = 2,4-Dihydroxybenzophenone (solid), $C_{13}H_{10}O_3$, M.W. = 214.22
 Eq. W = 157.11, m.p. = 144.5-147°C,



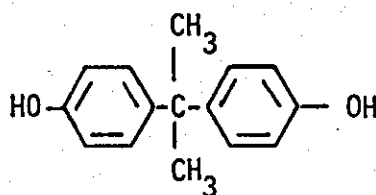
Supplier: Koch-Light Laboratories Ltd.

XVI) p,p'Biphenol (solid), $C_{12}H_{10}O_2$, M.W. = 186.21, Eq. W = 93.1, m.p. = 278°C



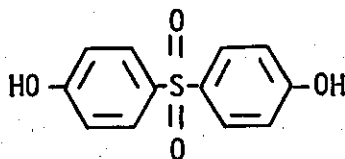
Supplier: Aldrich Chemical Co Ltd.

XVII) Bisphenol A = 2,2'Di(4-hydroxyphenyl)-propane, (solid), $C_{15}H_{16}O_2$, M.W. = 228.29, Eq. W = 114.14, m.p. = 153-156°C,



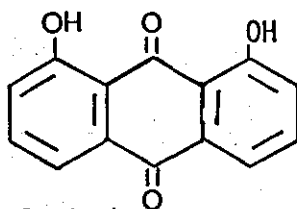
Supplier: BDH Chemicals Ltd.

XVIII) Di(4-hydroxyphenyl) sulphone (solid), $C_{12}H_{10}O_4S$, M.W. = 250.27, Eq. W = 125.13, m.p. = 238-242°C



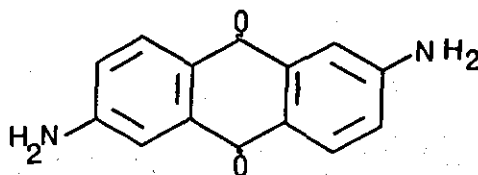
Supplier: BDH Chemical Co Ltd.

XIX) 1,8-Dihydroxyanthraquinone (solid), $[CO.C_6H_3(OH)_2]$, M.W. = 240.21, Eq. W = 120.10, m.p. = 190-193°C



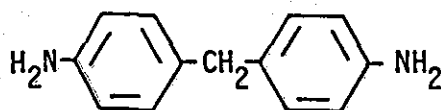
Supplier: BDH Chemicals Ltd.

XX) 2,6-Diaminoanthraquinone (solid), $C_{14}H_{10}O_2N_2$, M.W. = 238.25,
Eq. W = 119.1, m.p. > 325°C,



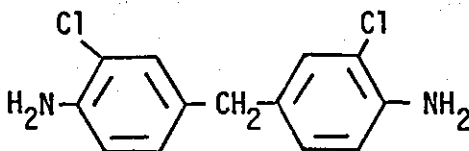
Supplier: Ralph N Emanuel Ltd.

XXI) 4,4'-DMA = 4,4'-Diaminodiphenyl methane (solid), $C_{13}H_{14}N_2$,
M.W. = 198.27, Eq. W = 99.1,



Supplier: BASF.

XXII) MOCA = 4,4'-Methylene bis-0-chloroaniline (solid), $C_{13}H_{12}N_2Cl_2$,
M.W. = 267, Eq. W = 133.5, m.p. = 110°C



Supplier: Hickson and Welch Ltd.

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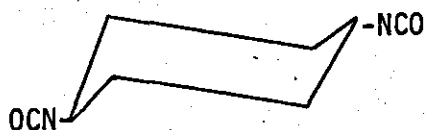
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LIST OF THE DIISOCYANATES AND POLYOLS USED WITH THEIR STRUCTURE AND RELEVANT TECHNICAL INFORMATION:

a) *Diisocyanates:*

- I) CHDI = 1,4-trans cyclohexane diisocyanate (solid), M.W. = 166.16, Eq. W = 83.09, m.p. = 60-64°C, b.p. = 260°C and 760 mm Hg



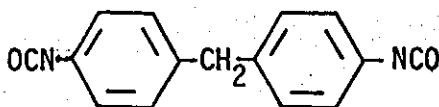
Supplier: Akzo Chemie and Armak Co.

- II) PPDI = p-phenylene diisocyanate (solid), M.W. = 160, Eq. W = 80, m.p. = 93-94°C, b.p. = 260°C at 760 mm Hg



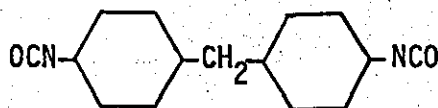
Supplier: Akzo Chemie and Armak Co.

- III) MDI = 4,4'-methylene-bis-phenyl diisocyanate, M.W. = 250, Eq. W = 125, m.p. = 38°C,



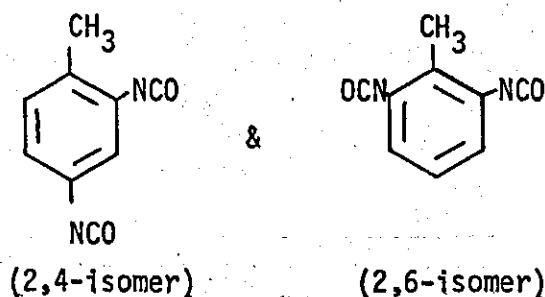
Supplier: Bayer Ltd.

IV) H₁₂MDI (Des. W) = 4,4'-methylene-bis-cyclohexyl diisocyanate
(liquid), M.W. = 262, Ew. W = 131,



Supplier: Bayer Ltd.

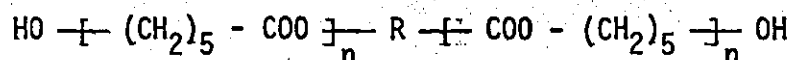
V) TDI = Toluene diisocyanate (80/20 of 2,6 and 2,4 isomers),
(liquid), M.W. = 174, Eq. W = 87, F.P. = 127, b.p. = 246-247°C



Supplier: Bayer Ltd.

b) Polyols

I) Capa 225 = (hydroxyl terminated poly(caprolactone) (solid),
M.W. = 2000, Eq. W = 1000, m.p. = ~60°C.
Hydroxyl value mg KOH/g = 56



R = polymerization initiator

Supplier: Laporte Industries, Interlox Chemicals Ltd, Luton,
Bedfordshire.

II) Capa 305 = (hydroxyl terminated polycaprolactone triol) (liquid)

M.W. = 540, Eq. W = 180, OH value mg KOH/g = 310.

Supplier: Laporte Industries, Interlox Chemicals Ltd, Luton,
Bedfordshire.

APPENDIX 2

PRECAUTIONS NECESSARY IN THE HANDLING OF RAW MATERIALS

a) DIISOCYANATES

All isocyanates are potentially hazardous chemicals and because they are used as raw materials on a very large scale in the manufacture of polyurethanes, great care must be taken in handling these materials. Due to their high vapour pressure they are strong lachrymators and may cause asthma after repeated inhalation¹⁶⁰. However, the general hazards to health associated with isocyanates may be summarized as follows: isocyanates are strong irritants to the skin, eyes, gastrointestinal tract and the respiratory systems¹⁶. In particular, mild to severe asthmatic attacks will result in the majority of people exposed to inhalation of isocyanate vapour and this must be recognised as an acute hazard.

As a result of experiments based on animal and clinical analysis, a threshold limit value (TLV) of each isocyanate has been recognised. It means the maximum average atmospheric concentration of an isocyanate to which one may be exposed for an eight hours working day. TLV is expressed in concentration as 'part per million' (ppm) which is the parts of vapour per million parts of contaminated air by volume at 25°C and 760 mm Hg pressure. Threshold limit values (TLV) for some commonly used diisocyanates are given in Table A2.1. It is important to realise that isocyanates are usually not detected by odour until their concentration reaches 10-20 times their TLV.

TABLE A2.1: Threshold Limit Values (TLV) for Some Commonly Used Diisocyanates

Diisocyanate	TLV (ppm)
Toluene diisocyanate (TDI)	0.02
Diphenylmethane diisocyanate (MDI)	0.02
Isophorone diisocyanate (IPDI)	0.01
1,6-hexamethylene diisocyanate (HDI)	0.01

The probability of an isocyanate vapour becoming harmful is increased if it is used above its TLV. One should always wear rubber gloves and safety spectacles or respirator while handling isocyanates and ensure proper ventilation. In the case of any spillage, a decontaminant should be used to neutralise the reaction of isocyanate. A suitable decontaminant fluid has the following composition (by volume): industrial methylated spirits or isopropyl alcohol (50 parts) water (45 parts), concentrated ammonia solution (5 parts). Empty isocyanate drums should be decontaminated before disposal by filling them with sodium carbonate solution and leaving them to stand for 24 hours with the bungs removed to allow carbon dioxide to escape. Care should be taken to avoid the inhalation of the isocyanate vapour displaced from the drum during filling.

b) DIAMINES

In view of the toxic nature of these chemicals special precautions are necessary in the handling of them. Diamines seriously damage the eyes and in certain cases cause serious burns on contact with skin¹⁶. Some diamines are undoubtedly active cancer promoting agents, for example, one technically and commercially important diamine has acquired the reputation of a potential carcinogen over later years which is 4,4' methylene bis o-chloro-aniline (MOCA) and particular hygiene precautions are required in its use.

c) POLYOLS AND GLYCOLS

Polyols and glycols are generally regarded as non-hazardous and no special precautions are necessary. They do not vaporise at ambient temperatures and hence do not constitute an inhalation hazard.

APPENDIX 3FORMULATION OF RUBBER USED THROUGHOUT THE
COMPRESSION SET, TEAR AND SKID RESISTANCE INVESTIGATION

Material	phr
NR (SMR-20)	30.00
SBR 1500	70.00
Zinc oxide	4.00
Sulphur	2.00
CBS	0.25
Santocure MOR	0.25
Flectol-H	0.75
Permanax B	2.00
Microcrystalline wax	3.00
Stearic acid	2.00
Carbon black FEF	51.00
Processing oil	7.50

$t_{90} = 16.5$ minutes

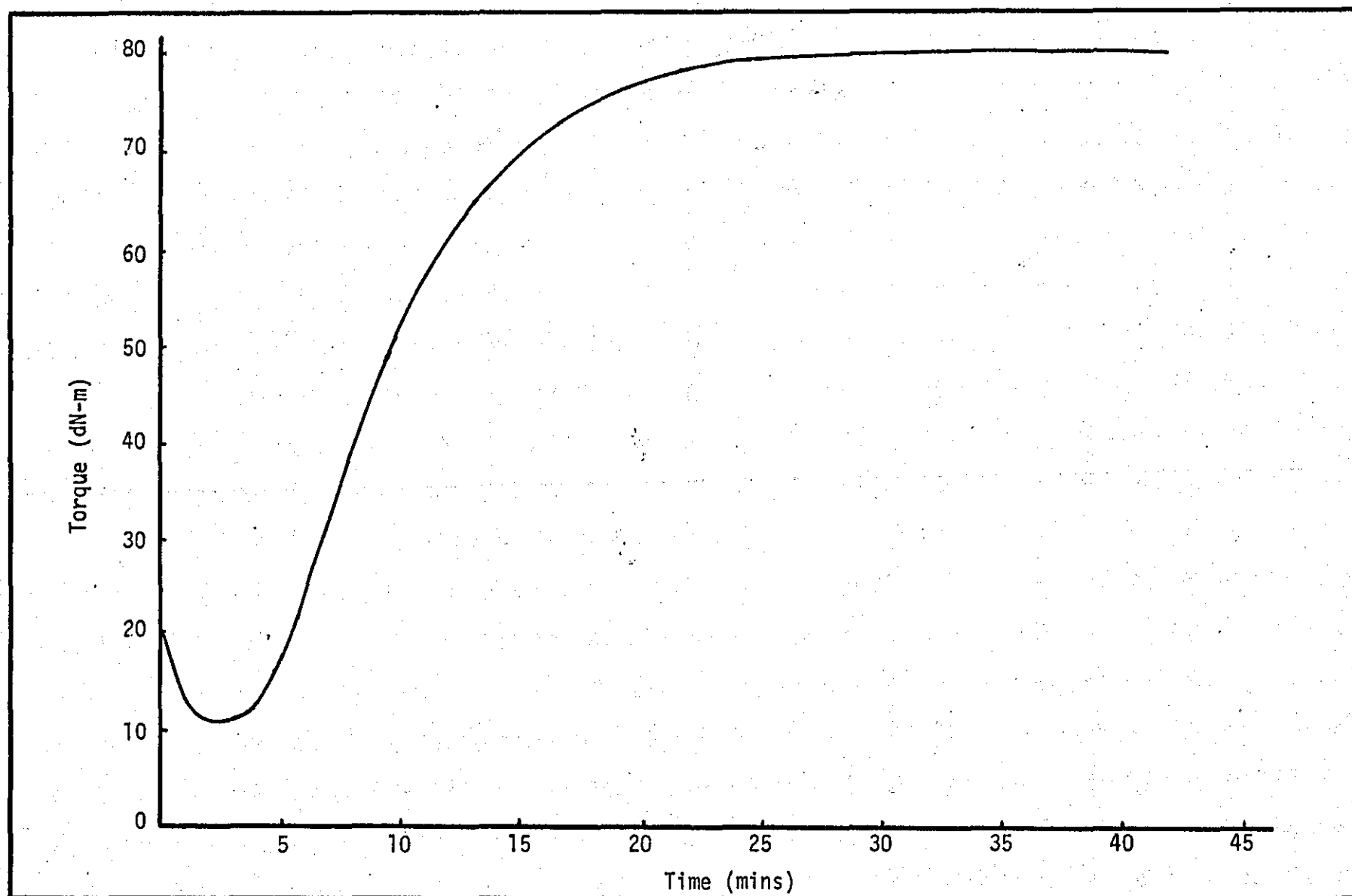


FIGURE A3.1: Curing Behaviour of NR/SBR Compound

APPENDIX 4

PL DYNAMIC MECHANICAL THERMAL ANALYSER

The Dynamic Mechanical Thermal Analyser is made up of four main parts: dynamic analyser, temperature programmer, measuring mechanical head and plotter.

The dynamic analyser computes the dynamic storage moduli (E') and damping ($\tan \delta$). The geometry constant for the sample is dialled into the front panel to give absolute moduli and on board microprocessors adjust the drive current to hold the strain at pre-selected levels and analyse signal amplitudes and phase. The driven frequency technique allows measurement at a number of fixed frequencies from 0.033 Hz to 90 Hz. Analogue outputs for $\tan \delta$, $\log E'$ and temperature are available from the rear panel.

The temperature programmer provides versatile programmed heating, cooling or isotherming of the sample from -150°C to $+300^{\circ}\text{C}$ (500°C high temperature option). Normally scanning rates for good measurement accuracy are $<5^{\circ}\text{C}/\text{min}$.

The measuring mechanical head houses the sample in a temperature enclosure, where it is subjected to small amplitude sinusoidal oscillation. In normal operation a bar sample is clamped rigidly at both ends and its central point vibrated sinusoidally by the drive clamp. The stress experienced by the sample, via the ceramic drive shaft, is proportional to the current supplied to the vibrator. The strain in the sample is proportional to the sample displacement and is monitored by the non-loading eddy current transducer and the metal target on the drive shaft. The drive shaft is supported on the light metal diaphragms which allow longitudinal but not lateral motion.

The environment is completely controllable in the temperature enclosure as nitrogen coolant circulates in an enclosed jacket with electrical heating providing the temperature control. An inert gas or controlled humidity air can be introduced from pipes in the rear bulkhead. Temperature is sensed and controlled to within 0.2°C by a platinum resistance thermometer lying immediately behind the sample. A schematic view of the mechanical head is shown in Figure 3.23.

REFERENCES

1. SAUNDERS, J.H. and FRISCH, K.C.
"Polyurethanes: chemistry and technology", Vols I and II, Interscience, New York, London (1962).
2. WURTZ, A.
Ann. 71, 326 (1849).
3. BAYER, O.
Angew. Chem., A59, 257 (1947).
4. BAYER Plastics,
Farbenfabriken Bayer, Leverkusen (2nd edition), p23 (1959).
5. BAYER, O.
German Patent 728, 981.
6. DOMBROW, B.A.
"Polyurethanes", Second edition (1965).
7. BAYER, O., MULLER, E., PETERSEN, S., PIEPENBRINK, H. and WINDEMUTH, E.
Rubb. Chem. Tech., 23, 812 (1950).
8. MULLER, E., BAYER, O., PETERSEN, S., PIEPENBRINK, H., SCHMIDT, F.
and WEINBRENNER, E.
Rubb. Chem. Tech., 26, 493 (1953).
9. BUIST, J.M.
Design engineering series (Rubber Handbook), 157 (1969).
10. DOYLE, E.N.
"The development and use of polyurethane products", McGraw-Hill, New York (1971).

11. WRIGHT, P. and CUMMING, A.P.C.
"Solid polyurethane elastomers", Maclaren and Sons, London, (1969).
12. WOODS, G.
"Flexible polyurethane foams, chemistry and technology", Applied Science, London and New Jersey (1982).
13. BRUINS, P.F.
"Polyurethane technology", Interscience (1969).
14. SHASHOUA, V.E.
J. Am. Chem. Soc., 81, 3156 (1959).
15. LYMAN, D.J.
Reviews in macromolecular chemistry, 1(1), 217 (1966).
16. HEPBURN, C.
"Polyurethane elastomers", Applied Science, London (1982).
17. KOGON, I.C.
J. Am. Chem. Soc., 78, 4911 (1956).
18. BUIST, J.M. and GUDGEON, H.
"Advances in polyurethane technology", Maclaren and Sons Ltd., London (1968).
19. SAUNDERS, J.H. and FRISCH, K.C.
"Polyurethanes: chemistry and technology", Vol. I, Interscience, New York, London (1962).
20. SMITH, P.A.S.
The Curtius reaction in organic reactions, Vol. 3, Eds. Addams, R., Bachmann, W.E., Fieser, P.F., Jorgenson, J.R., and Snyder, H.R. John Wiley and Sons, New York (1946).

21. BAYER AKTLENGENSELL SCHAFT,
"Bayer polyurethanes", Germany (1979).
22. HEPBURN, C.
"Polyurethane elastomers", Chap. 1, Applied Science, London,
(1982).
23. RYAN, J.D.
"MOCA, a diamine curing agent for isocyanate containing polymers",
Elastomers Bulletin, No 3C, August 1971 (Du Pont).
24. KIRK, O.
Encyclopaedia of Chemical Technology, Vol. 10, 2nd Edition, John
Wiley and Sons, New York, 1966.
25. SYED, E.A.
*"The effect of diols as chain extension agents on the properties
of polyurethane elastomers"*, MSc Thesis, Loughborough University
of Technology, UK (1978).
26. SAUNDERS, K.J.
"Organic polymer chemistry", Chapman and Hall, London (1973).
27. BAKER, J.W., DAVIES, M.M. and GAUNT, J.
J. Chem. Soc., 24 (1949).
28. BAKER, J.W. and HOLDSWORTH, J.B.
J. Chem. Soc., 713 (1947).
29. BAKER, J.W. and GAUNT, J.
J. Chem. Soc., 9, 19, 27 (1949).
30. BRECKER, L.R.
Plast. Eng., 33 (3), 39 (1977).

31. BRITAIN, J.W. and HENEINHARDT, P.G.
J. Appl. Pol. Sci., 4, 207 (1960).
32. SMITH, H.A.
J. Appl. Pol. Sci., 7, 85 (1963).
33. HEPBURN, C.
"Polyurethane elastomers", Chap. 2, Applied Science, London, (1982).
34. SYED, E.A.
"The chemistry and technology of transparent flexible polyurethanes", PhD Thesis, Loughborough University of Technology, UK (1982).
35. HARGET, D.C.
"Influence of chain extension agents on the properties of polyether based urethane elastomers at elevated temperatures", PhD Thesis, Loughborough University of Technology, UK (1977).
36. NISCHK, G.
(To Farbenfariken Bayer A.G.), DBP.924751 (1955).
37. BUIST, J.M. and LOWE, A.
Trans. J. Plastics Inst., 67, 13 (1959).
38. WRIGHT, P. and CUMMING, A.P.C.
"Solid polyurethane elastomers", Chap. 7, MacLaren and Sons, London (1969).
39. WOLKENBREIT, S.
"Handbook of thermoplastic elastomers", Van Nostrand Reinhold Company, 216 (1974).
40. CLOUGH, S.B. and SCHNEIDER, N.S.
J. Macromol. Sci. Phys., B2, 553 (1968).

41. CLOUGH, S.B., SCHNEIDER, N.S. and KING, A.O.
J. Macromol. Sci. Phys., B2, 641 (1968).
42. ESTES, G.M., COOPER, S.L. and TOBOLSKY, A.V.
J. Macromol Sci., Rev. Macromol. Chem., 4, 313 (1970).
43. AGGARWAL, S.L. (Ed),
"Block polymers", Plenum Press, New York (1970).
44. NOSHAY, A. and McGRATH, J.E. (Eds),
"Block copolymers", Wiley, New York (1973).
45. COOPER, S.L. and ESTES, G.M. (Eds),
"Multiphase polymers", Adv. Chem. Ser. 176, American Chemical Society, Washington, DC (1979).
46. SEYMOUR, R.W., ESTES, G.M. and COOPER, S.L.
Macromol., 3, 579 (1970).
47. ESTES, G.M., COOPER, S.L. and TOBOLSKY, A.V.
J. Macromol Sci., Rev. Macromol Chem., 4, 167 (1970).
48. BUIST, J.M.
"Development in polyurethanes - 1", Applied Science, London (1978).
49. PAIKSUNG, C.S. and SCHNEIDER, N.S.
Macromol, 8, 68, (1975).
50. ISHIHARA, M., KIMURA, I., SAITO, K. and ONO, M.J.
Macromol Sci., Phys., 10, 591, (1974).
51. ALLPORT, D.C. and MOHAJER, A.A.
In Block Copolymers, D.C. Allport and W.H. James (Eds), Applied Science, London, Ch. 8C, (1973).

52. BOYARCHUK, YU M., RAPPOPORT, L. YA, NIKITIN, V.N. and APUKHTINA, N.P.
Polym. Sci., USSR, 7, 859 (1965).
53. MILLER, G.W. and SAUNDERS, J.H.
J. Appl. Pol. Sci., 13, 1277 (1969).
54. MILLER, G.W. and SAUNDERS, J.H.
J. Pol. Sci., (A-1), 8, 1923 (1970).
55. VROUENRAETS, C.M.F.
Polym. Prepr., 13, 529 (1972).
56. SEYMOUR, R.W. and COOPER, S.L.
Macromol., 6, 48 (1973).
57. MACKNIGHT, W.J., YANG, M. and KAJIYAMA, T.
Polym. Prepr., 9, 860 (1968).
58. BONART, R., MORBITZER, L. and HENTZE, G.
J. Macromol. Sci., Phys., B3(2), 337 (1969).
59. KOUTSKY, J.
Polym. Letters, 8, 353 (1970).
60. SAMUELS, S.L. and WILKES, G.L.
J. Polym. Sci. (C), 43, 149, (1973).
61. CHANG, Y.P. and WILKES, G.L.
J. Polym. Sci. Phys., 13, 455 (1975).
62. SLOWIKOWSKA, J. and DAVISON, S.
J. Polym. Sci., Poly. Symp., 53, 187 (1975).
63. COOPER, S.L., WEST, J.C. and SEYMOUR, R.W.
Encyclopaedia of Polymer Science and Technology, Supplement Vol. 1,
(1976).

64. BISHOP, E.T. and DAVISON, S.
J. Polym. Sci. Part C, Poly. Symp., 26, 59 (1969).
65. COOPER, S.L. and TOBOLSKY, A.V.
Rubb. Chem. Tech., 40, 1105 (1967).
66. PUETT, D.
J. Poly. Sci., (A2), 5, 839 (1967).
67. BEECHER, J.F., MARKER, L., BRADFORD, R.D. and AGGARWAL, S.L.
J. Polym. Sci., (C), 26, 117 (1969).
68. FISHER, E. and HENDERSON, J.F.
Polym. Sci., (C), 26, 149 (1969).
69. SMITH, T.L. and DICKIE, R.A.
J. Polym. Sci., (C), 26, 163 (1969).
70. FULCHER, K.U. and CORBETT, G.G.
Br. Pol. J., 7, 225 (1975).
71. SCHOLLENBERGER, C.S.
"Polyurethane thermoplastics", Chap. 10, of Polyurethane Technology, edited by P.F. Brian, Wiley Interscience, New York (1969).
72. FERRARI, R.J.
Rubber Age, 53, (Feb. 1967).
73. PIGOTT, K.A., FRYE, B.F., ALLEN, K.R., STEINGISER, S., DARR, W.C.
and SAUNDERS, J.H.
J. Chem. Eng. Data, 5 (3), 391 (1960).
74. B.F. GOODRICH CO.,
British Patent 1,025,970 (1966).

75. SEEFRIED, C.G., KOLESKE, J.V. and CRITCHFIELD, F.E.
J. Appl. Polym. Sci., 19, 2493 (1975).
- 75a. SAUNDERS, J.H.
Rubb. Chem. Tech., 33 (5), 1259 (1960).
76. AITKEN, R.R. and JEFFS, G.M.F.
Polymer 18, 197 (1977).
77. SAMSON, A.J. and BLAICH, C.F.
Rubber Age, 89, 263 (1961).
78. NG, H.N., ALLEGREZZA, A.E., SEYMOUR, R.W. and COOPER, S.L.
Polymer, 14, 255 (1973).
79. HARRELL, L.L.
J. Macromol. 2, 607 (1969).
80. AXELROOD, S.L. and FRISCH, K.C.
Rubber Age, 88 (3), 465 (1960).
81. LITTLE, R.J. and GREGG, B.A.
Rubb. Chem. Tech., 39 (4), 1089 (1966).
82. SMITH, T.L. and MAGNUSSON, A.B.
J. Polym. Sci., 42, 391 (1960).
83. SMITH, T.L. and MAGNUSSON, A.B.
J. Appl. Polym. Sci., 5, 218 (1961).
84. PIGOTT, K.A., COTE, R.J., ELLENGAST, K., FRYE, B.F., MUELLER, E.,
ARCHER, W., ALLEN, K.R. and SAUNDERS, J.H.
Rubber Age, 91 (4), 629 (1962).

85. HAVLIK, R.J. and SMITH, T.L.
J. Polym. Sci., A-2, 539 (1964).
86. SASAKI, N., YOKOYAMA, T. and TANAKA, T.
J. Polym. Sci., (A1), 11, 1765 (1973).
87. FRAZER, A.H.
High Temperature Resistant Polymers, Interscience, Publ. New York (1968).
88. CRITCHLEY, J.P., KNIGHT, G.J. and WRIGHT, W.W.
"Heat resistant polymers", Plenum Press. New York, (1983).
89. CASSIDY, P.E.
"Thermally stable polymers", Marcel Dekker, New York (1980).
90. TILLEY, P.N., NADEAU, H.G., REYMORE, H.E., WASZECIAK, P.H. and SAYIGH, A.A.R.
J. Cell. Pl. 4(2), 56 (1968); 4(1), 22 (1968).
91. FRISCH, K.C., REEGEN, S.L. and ROBERTSON, E.J.
J. Cell Pl., page 75, (April 1966).
92. SAUNDERS, J.H.
J. Cell Plast., page 123, (April 1966).
93. BACKUS, J.K., BERNARD, D.L., DARR, W.C. and SAUNDERS, J.H.
J. Appl. Pol. Sci., 12, 1053 (1968).
94. SHEEHAN, D., BENTZ, A.P. and PETROPOULOS, J.C.
J. Appl. Pol. Sci., 5 (19), 47 (1962).
95. FABRIS, H.J.
"Thermal and oxidative stability of urethanes", in Advances in Urethane Science and Technology, K.C. Frisch and S.L. Reegan (Eds), Technomic, Westport, Conn., Vol. 4, 89, (1976).

96. HESKETH, T.R., BOGART, W.C. and COOPER, S.L.
Polym. Eng. Sci., 20 (3), 190 (1980).
97. MASIULANIS, B.
J. Appl. Polym. Sci., 29, 681 (1984).
98. BRITAIN, J.W.
"The Polymer Chemistry of Synthetic Elastomers", J.H. Saunders.
Chap. VII-A, J.P. Kennedy and Tornquist, ed. Interscience (1969).
99. BAYER, O.
In *Kunststoffhandbuch*, Vol. VII, Polyurethanes, p.8; R. Viehweg
and Hochtlen, Ed., Carl Hanser Verlag, Munich, (1966).
100. MATUSZAK, M.L. and FRISCH, K.C.
J. Polym. Sci., A11, 637 (1974).
101. CONLEY, T.
Thermal stability of polymers, Vol. 1, 12, Marcel Dekker Inc.,
New York, (1970).
102. TOBOLSKY, A.V., YU, H. and THACK, R.J.
Appl. Polym. Sci., 6, 544 (1962).
103. TARAKANOV, O.G., NEVSKJI, L.V. and BELJAKIV, V.K.
J. Polym. Sci., C-23, 117 (1968).
104. TARAKANOV, O.G., NEVSKJI, L.V. and BELJAKIV, V.K.
J. Polym. Sci., C-23, 193 (1968).
105. SAUNDERS, J.H.
J. Inst. Rubb. Ind., 2 (2), 21 (1968).
106. KOGON, I.C.
J. Org. Chem., 23, 1594 (1958).

107. NICHOLAS, L. and GMITTER, G.T.
J. Cell. Plast., 1, 85 (1965).
108. BALL, G.W., HAGGIS, G.A., HURD, R. and WOOD, J.F.
J. Cell. Plast., 6, 248, (1968).
109. SANDLER, S.R.
J. Appl. Polym. Sci., 11 (6), 811 (1967).
110. ARGABRIGHT, P.A., SINKEY, V.J. and PHILLIPS, B.L.
US Patent 3458,448 (July 1969).
111. HOFMANN, A.W.
Jahresber., 349 (1858).
112. IDRIS, J. and SAVILL, N.G.
J. Chem. Soc., 4392 (1957).
113. LYMAN, D.J.
J. Polym. Sci., 45, 49 (1960).
114. KING, C.
J. Org. Chem., 25, 352 (1960).
115. SORENSON, W.R.
J. Org. Chem., 24, 978 (1959).
116. LAPORTE INDUSTRIES, Interlox Chemicals Ltd., Luton, Bedfordshire, UK.
117. AKZO CHEMIE BV, PO Box 247, 3800 AE Amersfoort, The Netherlands.
118. ARMAK COMPANY, 300 South Wacker Drive, Chicago, Illinois 60606, USA.

119. HEPBURN, C.
European Rubb. Journals, Feb. 59 (1982).
120. GAF (Great Britain Co Ltd.
Chemical and Industrial Products, Tilso Road, Roundthorne
Wythenshawe, Manchester.
121. ALDRICH CHEMICAL CO, LTD.
Gilligham, Dorset, England.
122. POLAROID CORPORATION.
Chemical Commercial Development Department, 730 Main Street-1A,
Cambridge, Massachusetts, USA.
123. HUH, D.S. and COOPER, S.L.
Polym. Eng. and Sci., Vol. 11, No. 5, (1971).
124. ILLINGER, J.L., SCHNEIDER, N.S. and KARASZ, F.E.
Polym. Eng. Sci., Vol. 12, No. 1 (1972).
125. BRUNETTE, C.M., HSU, S.L., ROSSMAN, M., MacKNIGHT, W.J. and
SCHNEIDER, N.S.
Polym. Eng. Sci., Vol. 21, No. 11 (1981).
126. MAYER, J.S. and CASSEL, R.B.
Elastomerics, (Feb. 1981).
127. SEYMOUR, R.W. and COOPER, S.L.
J. Polym. Sci., B(9), 689 (1971).
128. SCHNEIDER, N.S., PAIKSUNG, C.S., MATTON, R.W. and ILLINGER, J.L.
Macromolecules, Vol. 8, No. 1 (1975).
129. SCHNEIDER, N.S. and PAIKSUNG, C.S.
Polym. Eng. Sci., Vol. 17, No. 2 (1977).

130. PAIKSUNG, C.S., HU, C.B. and WU, c.s.
Macromolecules, 13, 111 (1980).
131. TANAKA, T. and YOKOYAMA, T.
J. Polym. Sci., C, 23, 865 (1968).
132. TRIFAN, D.S. and TERENCE, J.F.
J. Polym. Sci., 28, 443 (1958).
133. TANAKA, T., YOKOYAMA, T. and YAMAGUCHI, Y.
J. Polym. Sci., (A1) 6, 2153 (1968).
134. NAKAYAMA, Y., INO, T. and MITSUBARA, I.
J. Macromol. Sci. Chem., (A) 3, 1005 (1969).
135. SEYMOUR, R.W., ESTES, G.M. and COOPER, S.L.
Macromolecules, 3, 579, (1970).
136. TANAKA, T., YOKOYAMA, T. and YAMAGUCHI, Y.
J. Polym. Sci., (A1) 6, 2137 (1968).
137. PAIK SUNG, C.S., SMITH, T.W. and SUNG, N.H.
Macromolecules, 13, 117 (1980).
138. BONART, R.
J. Macromol. Sci., Physics, B(2), 115 (1968).
139. BONART, R. and MULLER, E.
J. Macromol Sci., B(10), 177, 345 (1975).
140. BONART, R., MORBITZER, L. and MULLER, E.
J. Macromol. Sci., B(9), 447 (1974).

141. WILKES, C.E. and YUSEK, C.S.
J. Macromol Sci. Phys., B7(1), 157 (1973).
142. MINOURA, Y., YAMASHITA, S., OKAMOTO, H., MATSUO, T., IZAWA, M.
and KOHMOTO, S.I.
J. Appl. Polym. Sci., Vol. 22, 1817, 3110 (1978).
143. KOUTSKY, J.A., HIEN, N.V. and COOPER, S.L.
J. Polym. Sci., B8, 353 (1970).
144. WILKES, G.L., SAMUELS, S.L. and CRYSTAL, R.
J. Macromol. Sci. Phys., B10 (2), 203 (1974).
145. ILLERS, K.H.
Macromol. Chem., 38, 168 (1960).
146. JACOBS, J. and JENCKEL, E.
Macromol Chem., 42, 132 (1961).
147. HUH, D.S. and COOPER, S.L.
Polym. Eng. Sci., 11(5) 369 (1971).
148. KAJIYAMA, T. and MacKNIGHT, W.J.
Macromol. 2, 254 (1969).
149. SCHATZKY, T.F.
T. Polym. Sci., 57, 496 (1962) and Polym. Preprints 6, 646 (1965).
150. CRAVER, C.D.
"Polymer Characterization", Advances in Chemistry Series, American
Chemical Society, (1983).
151. ELLIOTT, A.
"Infrared spectra and structure of organic long-chain polymers",
Edward Arnold Ltd., London, p.18 (1969).

152. ZICHY, V.J.
"Laboratory methods in infrared spectroscopy", (Eds. R. Miller and B. Stace), Heyden, p.51 (1972).
153. ABOUZAHR, S., WILKES, G.L. and OPHIR, Z.
Polymer, Vol. 23, 1077 (1982).
154. BOONSTRA, B.B.S.T. and DANNENBERG, E.M.
Swelling behaviour of rubbers compounded with reinforcing pigments, Rubber Chem. Technol. 32, 836 (1959).
155. FLORY, P.J.
J. Chem. Phys., 18, 108 (1950).
156. BRISTOW, G.M. and WATSON, W.F.
Trans. Faraday Soc., 54, 1731 (1958).
157. BRANDRUP, J. and IMMERGUT, E.H.
"Polymer Handbook", Interscience, New York, pages IV-345 and IV-366, (1967).
158. BLOW, C.M. and HEPBURN, C.
"Rubber Technology and Manufacture", Second Edition, Butterworth Scientific, London, (1982).
159. HEPBURN, C.
"Polyurethane Elastomers", Chap. 7, Applied Science, London (1982).
160. FRISCH, K.C.
"Recent Advances in the Chemistry of Polyurethanes", Rubb. Chem. and Technol., Vol. 45 (1972).

161. SCHOLLENBERGER, C.S. and STEWART, F.D.
'Thermoplastic urethane structure and ultraviolet stability'
in *Advances in Urethane Science and Technology*, K.C. Frisch and
S.L. Reegan, Vol. 2, 71 (1973).
162. HATAM, E.A.
*'Studies of the oxidative degradation of butyl rubber in tyre
inner tubes'*. PhD Thesis, Loughborough University of Technology,
UK (1984).
163. FILIP, Z.
'Microbial degradation of polyurethanes', *Biodeterioration and
Biodegradation of Plastics and Polymers*, Biodeterioration Society,
Occasional Publication No. 1, 1985.
164. IDRIS JONES, J. and SAVILL, N.G.
'The polymerisation of aromatic isocyanates', *J. Chem. Soc.*
4392 (1957).

