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**WATERBORNE POLYURETHANE IONOMERS: STRUCTURE- PROPERTY
RELATIONSHIPS OF ELASTOMERIC POLYURETHANE UREAS AND
POLYURETHANE IONOMERS.**

BY

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ABSTRACT

Two groups of water-borne polyurethane ionomers were synthesised using well known methods of synthesis in order to determine the type of elastomers that may be obtained from each method. To begin with, the conventional methods of synthesis for water-borne polyurethane dispersions (WPUDs) in which the process of chain extension occurs in the presence of water was evaluated. This method is restricted to the use of diamines as chain extenders. It was demonstrated that the use of diamines, whether they are primary such as ethylene diamine, or tertiary such as NN'-dimethyl ethylene diamine lead to the formation of polyurethane-urea ionomers that are known for their higher modulus, strength, and lower elongation at break (EAB). The copoly(urethane-urea) ionomers indicated a decreased rate of stress relaxation (RSR).

The alternative method of synthesis evaluated was the bulk method of synthesis in which the chain extension process takes place in the bulk. This method allowed the use of diols as chain extenders and resulted in softer elastomers. The polyurethane ionomers obtained by the bulk method of synthesis indicated a high rate of stress relaxation, and, a rapid reduction of load immediately after the application due to their weaker inter-segmental hydrogen bonding interaction.

The research also demonstrated that both methods result in the formation of stable dispersions when an optimum level of ionic moiety is used. Using a Brookfield viscometer and a Malvern Zeta sizer, it was found that the dispersion particle size, its distribution, as well as the dispersion viscosity were influenced by the concentration of the ionic moiety.

The presence of the ionic moiety was found to influence the development of molecular weight of the polyurethane and poly (urethane-urea) ionomers. This was demonstrated by using gel permeation chromatography (GPC) to measure the molecular weights of the final films. As higher levels of ionic moiety were introduced in both types of materials, the GPC chromatogram changed from mono-to a clear bimodal distribution indicating the development of various size polymeric species. These species were suggested to influence the degree of phase separation in both types of materials.

The relationship between structure and properties of the polyurethanes were investigated by using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), tensile stress-strain and stress relaxation measurements.

DSC measurements showed a distinct glass transition temperature associated with polyester, or polyether, soft segments. Although no T_g for the hard segment was detected, several endotherms arising from the dissociation of hard blocks were shown. In cases where a polyester polyol was used as the soft segment the T_g were much higher than the isolated soft segment indicating that the phase separation was incomplete in these materials. The DMTA results provided further evidence to support the existence of a partially phase separated morphology in both types of materials. In most cases, a rubbery plateau on the modulus-temperature curves and secondary relaxation peaks on the damping curves were detected.

Typical stress-strain curves for both types of materials were obtained, and the results of physical properties obtained reflected the type of chemical structures present in the respective domains and related to the degree of phase separation achieved by each material.

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Background

Thermoplastic polyurethane elastomers (TPUs) are widely used in the manufacture of soft elastic articles for medical device applications. These polyurethane materials, that owe their elastomeric properties to their block copolymer and two phase morphology, are solvent dipped to form the required product such as gloves and condoms. The use of organic volatiles as a processing solvent, as well as being harmful to the environment, renders the manufacture of products from TPUs, rather costly and unattractive.

Recently it has become desirable to develop products such as gloves from waterborne polyurethane dispersions (WPUDs). WPUDs have been commercially available for many years and are extensively used as high quality coatings and adhesives. WPUDs are predominantly copoly(urethane-ureas) and their use as soft elastomers is relatively unknown. Several attempts have been made to dip gloves or condoms from commercially available waterborne polyurethane dispersions with little or no success. This is because commercially available WPUDs do not exhibit the physical properties that are required in a glove material. For an elastomer to function as a stand-alone film a certain level of tensile strength and a degree of elasticity is required. The elastomer also needs to be soft to provide the necessary comfort during wear. Typical physical properties desirable in glove materials are indicated to be: tensile strength $\geq 25\text{-}30\text{MPa}$, modulus at 100% extension (S_{100}) ≤ 1.5 to 2.0MPa and elongation at break (EAB) $\geq 500\%$, with a minimum degree of relaxation.

Although it is possible to obtain polyurethane dispersions of high tensile strength with acceptable elasticity, these dispersions often also show high hardness (high S_{100} modulus) which make them unsuitable for the manufacture gloves and similar products. Therefore, a fundamental understanding of the chemical structure-properties relationships and the morphology of polyurethane dispersions have become necessary. Additionally it is also important to identify the chemical or morphological features that restrict the development of soft elastomeric polyurethane dispersions, while at the same time to explore the feasibility of identifying alternative routes to synthesising polyurethane dispersions of the desirable physical properties.

1. Literature review

1.1 Introduction to Block Copolymers

Block copolymers are formed by joining blocks of two chemically dissimilar segments along the polymer backbone. At the service temperatures, one of the components is in a viscous or rubbery state i.e. soft segment while the other is in a glassy, or semi-crystalline, state i.e. hard segment. The two phases are bonded to each other by covalent chemical bonds and, depending on the chemical nature of the blocks, phase segregation arises from thermodynamic incompatibility of the two blocks since their solubility parameters (δ) differ significantly.

Styrenics, polyurethanes, copoly(ester-polyamide) thermoplastic elastomers are examples of block copolymers. These materials are often referred to as (A-B)_n block copolymers. The morphology of an (A-B)_n block copolymer (i.e. a linear multiblock polymer of alternating A and B blocks), with one monomer unit in preponderance, will consist of blocks with the minor component dispersed as spheres in the continuous phase blocks of the major components monomer units. As the proportions of the two monomers approaches equivalence, the morphology changes from dispersed spheres to dispersed cylinders, to lamellae at approximately equal amounts ^[1,2]. Thus, the morphology can range from spheres of hard segments in a continuous phase of soft or rubbery segments, to spheres of soft segments in a continuous hard segment phase.

Block copolymers exhibit a number of properties as a result of morphological features which are unique to such systems. These features are the result of phase separation of the incompatible block components, being restricted to a microscopic scale size defined by the block length. The existence of some form of phase separation between block components, is expected since the dissimilar block components, as homopolymers are typically incompatible as a result of a positive heat of mixing, or as a result of crystallisation of one, or both components. When two incompatible homopolymers are mixed, they have a tendency to macrophase separate. Their mixture, however, becomes thermodynamically stable, since contact between the two is limited to their interfacial contact. Incompatibility still exists when such homopolymers are joined to form a block copolymer and each would like to segregate from the other. However, the fact that they are joined together restricts segregation to microscopic dimensions, i.e. to microphases having dimensions of the order of the molecular blocks. At equilibrium, these microphases consist of highly organised structures whose morphology is dependent on structural parameters such as:

- (i) the copolymer sequence distribution, the length and number of the blocks;

- (ii) the chemical nature of the blocks;
- (iii) the copolymer composition, the average molecular weight and the molecular weight distribution of blocks and of the copolymer.

In practice, however, the phase separation is incomplete and the properties of the final bulk polymer are determined by the degree of phase separation^[2].

1.2 Thermodynamics of Microphase Separation

The thermodynamic considerations of phase behaviour are dealt with in terms of the balance between the enthalpic, ΔH_m , and the entropic, ΔS_m , contributions to the free energy of mixing and are often limited to the qualitative consideration that the Gibbs free energy of mixing, ΔG_m must be positive for (micro) phase separation to occur. Thus,

$$\Delta G_m = \Delta H_m - T\Delta S_m > 0 \quad (1.1)$$

and the boundary between the stable and the unstable state is determined by the condition $\Delta G_m = 0$. In fact, ΔG_m being positive is not a sufficient criterion for (micro) phase separation, as the second derivative of free energy being zero defines the stability limit in terms of free energy curve. Thus two conditions must be fulfilled for (micro) phase separation to occur. These are $\Delta G_m > 0$ and where ϕ is the volume fraction:

$$\left[\frac{\delta^2 \Delta G_m}{\delta \phi^2} \right]_{T,P} \leq 0 \quad (1.2)$$

The second differential of the Gibbs free energy of mixing with respect to volume fraction defines the spinodal curve. In most cases, a critical value of the Flory-Huggins interaction parameter is used to characterise phase separation processes and this may be readily obtained from the Flory-Huggins equation derived for polymer solutions^[3,4].

$$\Delta G_m = RT (N_1 \ln \phi_1 + N_2 \ln \phi_2 + N_1 \phi_2 \chi_{12}) \quad (1.3)$$

where N and ϕ are the polymerisation index and volume fraction, respectively, and the subscripts 1 and 2 refer to the different chain segments. χ_{12} is the temperature-dependent Flory-Huggins interaction parameter. In the case of polymers, it is the product χN which is the critical molecular parameter ($N=N_1+N_2$) [4].

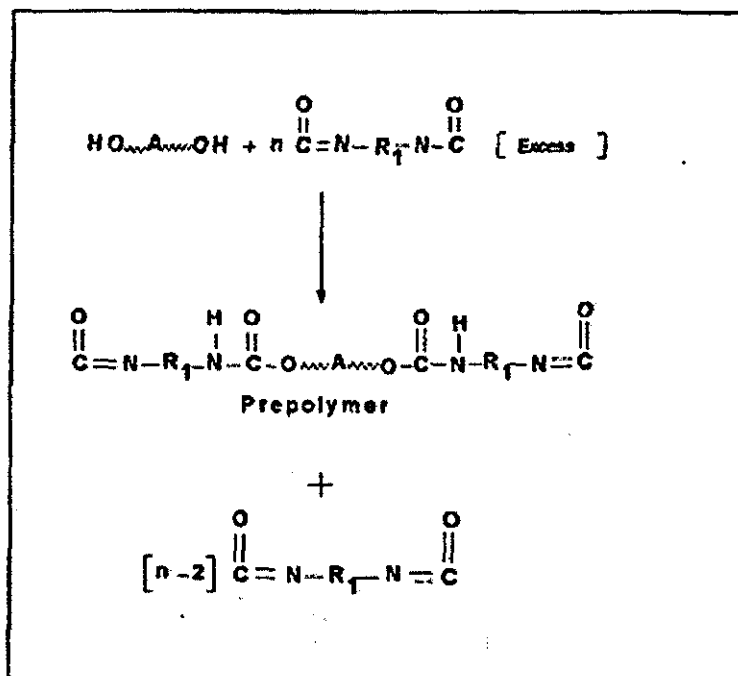
1.3 Polyurethane materials

Polyurethane materials constitute an important class of block copolymers because of their highly diverse chemistry. These materials have found applications in many areas of everyday life. Polyurethanes have been used extensively in industry for several decades. The diversity of their chemistry allows the development of many materials from foams, to coatings, sealants, and adhesives, but more importantly as far as this study is concerned, high performance elastomers. Polyurethane materials can be processed from the bulk via melt processing. They can be solvent processed and more significantly they may also be processed from water.

Their use as thermoplastic elastomers goes back many years. The following sections provide a brief overview of their basic chemistry, which is then followed by an in depth discussion of the development as well as the chemistry of waterborne polyurethanes.

1.3.1 Thermoplastic polyurethanes (TPUs)

Thermoplastic polyurethane elastomers [5,6] (TPUs) have a general $(AB)_n$ structure where the soft segment is usually made from a polyester or polyether macro glycol of molecular weight between 600 and 3000. In common commercial synthesis, the hard segment is formed by chain extending a macro glycol with a diisocyanate and a low molecular weight aliphatic diol or diamine such as 1,4-butanediol or ethylene diamine, to produce, respectively, a polyurethane or polyurea segmented copolymer. The polyether or polyester terminal hydroxyl groups are usually reacted with an excess of isocyanate to form an isocyanate - terminated prepolymer mixed with excess diisocyanate according to the reaction shown below in Scheme 1.1. This prepolymer mixture is then reacted with a chain extender (diol or diamine) to give a block copolymer composed of highly polar urethane or urea hard segments alternating with the polyester or polyether $-OAO-$ (soft segment) residues, where A is the ether or ester repeat unit. Scheme 1.2 illustrates the reactions involved.



Scheme 1.1 Prepolymer formation^[7]

Alternatively, the three reactants may be mixed together in the correct molar ratios in a one shot bulk polymerisation and the polymer is allowed to grow freely to maturity in a controlled environment. Commercial development of polyurethanes arose from the work of Bayer^[6] and his team of chemists who were able to produce fibre-forming polymers by reacting many hydroxyl compounds with diisocyanates.

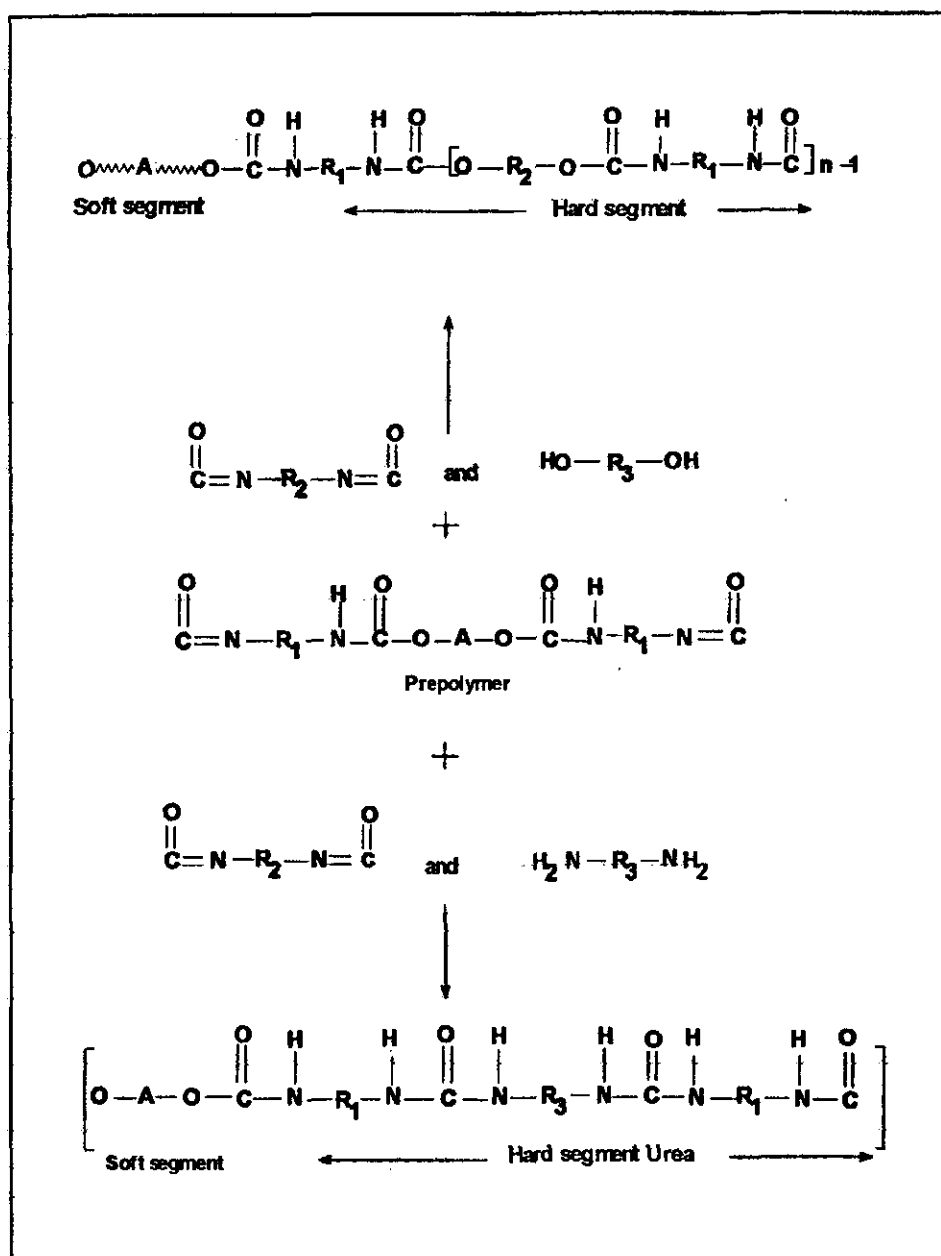
The first rubbers were prepared by Pinten^[9] in about 1940. These were known as I. Gummi and were produced by reacting a polyester with a diisocyanate. The product had high tensile strength and abrasion resistance, but low tear strength and poor low temperature properties. Subsequently, the variables in the formulation were systematically examined by Bayer and Müller^[6] and this led to the advent of the Vulkalon rubbers. The starting point in the preparation of these rubbers is a polyester which was reacted with a bulky diisocyanate such

as 1,5-naphthalene diisocyanate. The resulting prepolymer is then chain extended by water, a glycol, or a diamine by linking across the terminal isocyanate groups.

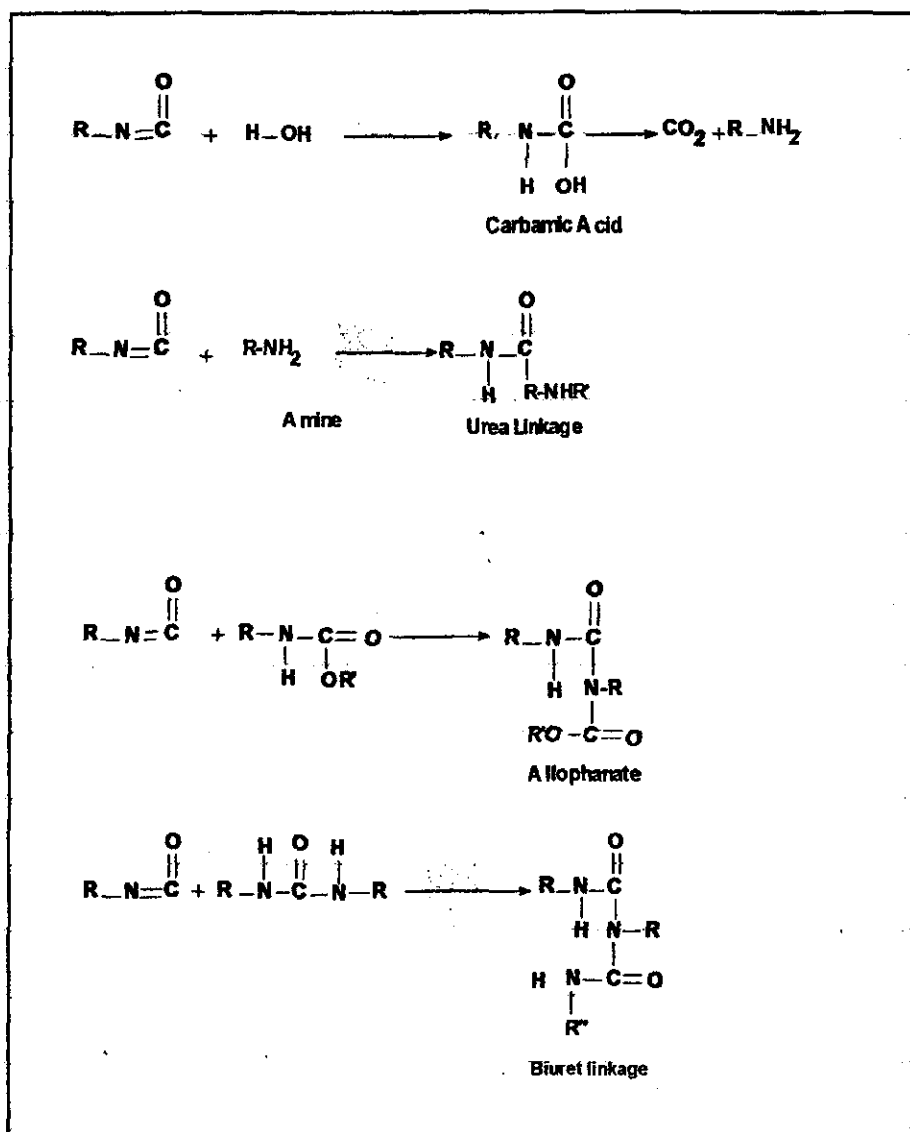
The reaction with water gives rise to carbon dioxide (scheme 1.3) which can be used as a blowing agent in the manufacture of foams. If the overall molar proportion of hydroxyl groups and isocyanate are equivalent, a high molecular weight linear polyurethane elastomer will be produced. A material of this type was first described by Schollenberger and co-workers in 1958 ^[8] as polyurethane VC, a "virtually" cross linked elastomer, in which the crosslinking was due to secondary and to primary valence forces. An example of this type of elastomer may be prepared by reacting 4,4-diphenylmethane diisocyanate with a polyester such as poly(tetramethylene adipate) and 1,4-butane diol as the chain extender. These elastomers are completely soluble in dimethylformamide and can be processed by conventional thermoplastic fabrication techniques, such as extrusion and injection moulding.

Isocyanates are highly reactive compounds^[9] and enter into a number of reactions with groups containing active hydrogen substituents. This is because of the highly positive nature of the carbon atom in the double bond to nitrogen and oxygen. Reactions of importance in the formation of polyurethanes are given in scheme 1.3. The initial reaction product of isocyanate with water is a carbamic acid, which breaks down to give carbon dioxide and an amino group which can then react with isocyanate to give a substituted urea. These primary reaction products still contain active hydrogen atoms that can react further with isocyanate groups to give secondary reaction products such as allophanates or biurets. Although these secondary reactions occur less readily, they may contribute significantly to the structure of many polyurethanes and cause branching, or cross-linking, in otherwise linear polymer systems.

The relative reactivity of active hydrogen compounds towards an isocyanate has been shown to be very dependent upon the solvent used for the reactants, the isocyanate, the nature of the active hydrogen compound and especially upon catalytic substances ^[6-9]. The order of reactivity of active hydrogen compounds towards an aromatic isocyanate is aliphatic amine > aromatic amine > primary hydroxyl > secondary hydroxyl > water > carboxylic acid = urea > urethane. Most isocyanate reactions are very susceptible to catalysis, particularly by tertiary amines and by certain metal compounds, notably those of mercury, tin and lead ^[6-9]. The influence of many of these catalysts is so profound in that their effects can outweigh constraints of reaction medium, and steric hindrance in the reaction system. Moreover, they do not affect all isocyanate reactions to the same extent, and it is therefore possible to favour a desired reaction in a particular system.



Scheme 1.2 Polyurethane and polyurea formation^[7]



Scheme 1.3 Reactions of isocyanates ^[7]

1.3. 2 Structure- property relationship in polyurethane.

The chemical structure of the individual blocks of a polyurethane determine the type of properties of the ultimate polyurethane. The soft segment often is a polyether, such as poly(propylene glycol) (PPG), poly(tetramethylene glycol) (PTMG) or polyesters such as polyadipates, or polycaprolactones ^[10].

The hard segment is normally an aromatic diisocyanate that has been chain extended with a low molecular weight diol, or diamine, to form an oligomeric aromatic urethane or urethane urea segment of molecular weight in the range of 300 to 3000. The macroglycol and the chain extended diisocyanate combine to form an $(AB)_n$ - type block copolymer.

A broad spectrum of physical properties can exist, ranging from hard and glassy or tough and leathery polymers to soft and gum-like materials. It is the polymer microstructure that is responsible for the novel, and some times unique, properties of these materials. Much work has been done recently in an attempt to define more quantitatively the actual microstructure of these systems. Methods such as electron microscopy, small angle x-ray scattering (SAXS), infrared dichroism, dynamic mechanical analysis, differential scanning calorimetry, and stress - strain testing have been used to investigate polymer morphology^[11, 12, 13].

Bogart^[11] first detected the presence of phase separation in these materials by using SAXS. It is generally agreed that the hard segments separate into glassy, or semi-crystalline, domains in a rubbery matrix and that the hard domains serve both as multifunctional cross links and as a reinforcing filler, thus increasing the material's strength. Since urethane groups are capable of forming inter-urethane hydrogen bonds, they enhance the driving force for phase separation. Other factors influencing the formation of a two phase system include segment polarity, segment length, crystallisation of either segments, overall composition¹, method of preparation, and the mechanical and thermal history^[13-15].

1.3.3 Effect of molecular structure on properties

1.3.3.1 Hard block structure

The hard blocks in polyurethane elastomers formed by the reaction of a diisocyanate with a glycol or a diamine are essentially low molecular weight polyurethanes or polyureas. The chemical nature and the proportion of hard blocks determine the degree of interchain interactions in the elastomer, and, thus, determine the network "structure", where the hard blocks effectively act as cross linking sites which give the material its elastomeric properties.

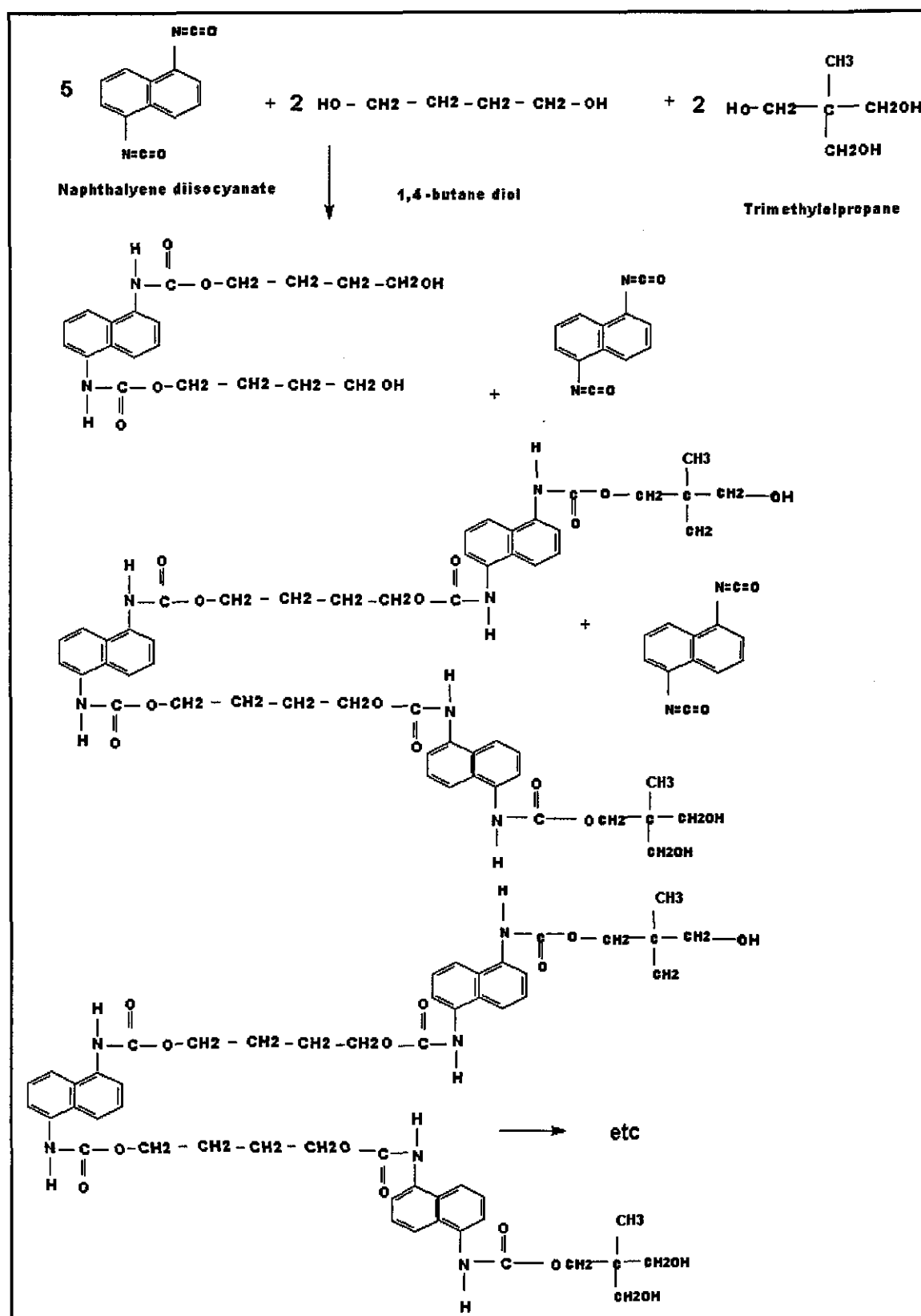
Bayer and co-workers^[6, 16] have shown that elastomers having excellent properties are obtained if diisocyanates with large molecular bulk are used in the hard segment since this gives rise to interchain steric hindrance. Furthermore, Bayer^[17] showed that polyurethanes with the highest levels of modulus, tear and tensile strengths are obtained by the use of the most rigid, bulky and symmetrical diisocyanates. Thus, the reduced symmetry of toluene diisocyanate (TDI), compared with 1,4-phenylene diisocyanate causes a significant reduction

in the level of physical properties obtained. A 1,3-diisocyanate substitution pattern on a benzene residue gives a lower modulus product than a 1,4-substitution and substitution of the benzene ring by a methyl group, as in 2,4-toluene diisocyanate (TDI) lowers the modulus even further. The diisocyanate component in polyurethanes influences the ability of the polymer chains to align themselves and hence affects the development of interchain structure by hydrogen bonding.

The choice of chain extender also influences the elastomeric properties considerably. When a diamine is employed as an extender, better physical properties relative to a diol extended polyurethane are obtained ^[17-19] probably due to the introduction of urea linkages which enter into strong hydrogen bonded interactions. The tensile strength and elongation at break are higher when the diamine has an odd number of carbon atoms in the chain^[20], whilst at 300% elongation, the modulus and the hard block softening temperature are highest for diamines having an even number of carbon atoms. This is because a hard segment based on an odd number of carbon atoms forms weaker crystallite networks ^[20] than those based on reactants with an even number of carbon atoms. The weaker packing of the hard segment causes a somewhat higher proportion of the hard segments to be dissolved in the soft segment matrix, and, consequently, less is present in the hard domains. The combination of a weaker network and a lower quality of hard domains results in reducing the modulus, which will then lead to greater elongation at break, which in turn allows further stress crystallisation of the flexible segment with consequent development of a higher tensile strength.

The diol chain extended systems are softer and weaker than the corresponding diamine extended compositions. The commonly used diphenylmethane (MDI) and naphthalene diisocyanate based polymers are frequently chain extended with a glycol, but it is usually desirable to introduce additional cross-linking into diol chain extended elastomers by the use of a proportion of triol such as trimethylolpropane. Scheme 1.4 gives an example of a system containing a triol as a cross-linker.

As the level of diisocyanate and the chain extender increases, so does the size of the hard blocks. In an elastomer made from a polyester, diphenylmethane diisocyanate(MDI) and butanediol, as the size of the hard block increases, the hardness, modulus and flow temperature increases, whilst the elongation at break decreases^[17].



Scheme 1.4 Example of a system containing a triol as a cross-linker ^[18]

1.3.3.2 Soft blocks structure

Aliphatic polyesters and polyethers ^[5,16,21] are the most common commercially used soft blocks in elastomeric polyurethanes. Those of importance have glass transition temperatures below room temperature, and usually have a low melting point or are amorphous, and the molecular weight can range from about 600 to 3000, depending upon the property requirements of the final polyurethane composition^[17]. The most common polyesters used are polyethylene and tetramethylene adipates, and polycaprolactone. In general the higher molecular weight polyesters produce materials with better tensile properties, but an increasing tendency to cold harden, a phenomenon which is due to slow crystallization of the flexible blocks on storage.

The higher the molecular weight of the polyester the greater the rate of cold hardening. The main consequence of an increase in the molecular weight of the soft block for a given overall ratio of soft block to isocyanate plus extender is a fall in modulus and an increase in the elongation at break. The undesirable tendency of some polyesters to crystallise and produce a cold hardening effect can be avoided by the use of co-polyesters which possess structural irregularity in their composition, such as 1,2-propylene glycol. Another option is to use polycaprolactone polyesters as the soft segment as they do not cold crystallise. The ability of polyurethane with polyester soft segments to crystallise on extension, is a desirable feature, which gives them superior physical properties compared to those based upon polyethers. When using a higher molecular weight polyester soft segment, a compromise between the level of physical properties required and the acceptable degree of cold hardening is often necessary. Weisfeld et. al^[22] have shown that certain copolyesters undergo stress crystallisation upon extension. As the regularity of the polyester backbone influences the tensile stress, the presence of an irregularity e.g. the presence of a methyl group in the side chain would result in a lower tensile strength. This is a reflection of the side chain hindering crystallisation upon extension. Elastomers from polyesters which are symmetrical and which contain rigid ring structures produce harder elastomers due to reduced soft segment chain flexibility. For example for an elastomers prepared from MDI, various polyesters and 1,4-butane diol, a much harder elastomer was obtained when the adipate polyester of 1,4-bis (hydroxymethyl) cyclohexane replaced that of ethylene glycol ^[17].

Among polyethers, poly(propylene glycol) PPG, poly(tetramethylene glycol) PTMG and poly(ethylene Glycol) PEG, are most commonly used as soft blocks. Polyethers have weaker interchain attractive forces than polyesters and generally give elastomers with somewhat inferior physical properties, except, at low temperatures due to their lower T_g. PEO is normally used in the form of a copolymer due to its water solubility and moisture sensitivity.

Use of PPG to produce polyurethane elastomers leads to lower mechanical properties and to compensate for this a diamine is often used as the chain extender. Among the polyethers PTMG gives elastomers having good physical properties ^[17,23-24], a fact which is due in part to its regular chain structure and hence its ability to crystallise upon extension.

Elastomers based on polyethers show much better resistance to hydrolysis than the corresponding polyester-based materials, a feature that reflects the hydrolytic stability of ether groups over esters ^[25].

1.4 Methods of Characterisation.

1.4.1 Infra-Red Spectroscopy Analysis

Spectroscopic methods commonly employed for studying polymers are dispersive infra red (IR) with recent emphasis on Fourier transform (FTIR), and attenuated total reflectance IR (ATR), proton ¹H and carbon ¹³C nuclear magnetic resonance (NMR) spectroscopy, ultra violet/visible spectroscopy and scattering techniques such as X-ray, electron and neutron scattering.

Both types, dispersive as well as FTIR spectroscopy, have been used to obtain qualitative identification of polyurethanes based on the functional groups present. It is possible to obtain information on variation in stereochemistries, or monomer sequence distribution because such differences usually give rise to different spectra. ATR-FTIR spectroscopy can probe detailed changes in the structure and chemical composition of polyurethane elastomers in the bulk or at the surface of the material by monitoring specific infra-red bands assigned to various chemical moieties.

FTIR spectroscopy can be used to determine the degree of phase separation in block copolymers ^[26-28] provided bands sensitive to mixed and phase separated states are present. The typical polyurethane is extensively hydrogen bonded, the donor being the NH groups of the urethane linkages. The hydrogen acceptor may be either the hard urethane segments (carbonyl of the urethane groups) or the soft segment (ester carbonyls or ether oxygens). Using IR spectroscopy, Wang and Cooper ^[26] studied the effect of soft segment composition on the degree of phase separation and suggested a greater degree of phase mixing poly(ester-urethane) to phase mixing due to greater susceptibility of the ester carbonyl to hydrogen bond with the urethane carbonyl group.

The role of hydrogen bonding in polyurethanes has been widely studied using infra-red spectroscopy. Lee and Wang ^[27] studied a well defined model polyurethane which they

subjected to thermal treatment in a modified purge-box that allowed slow heating followed by rapid cooling to encourage mixing of hard and soft phase and formation of a random copolymer of polyurethane. For polyurethanes, it is generally accepted that two NH stretching vibrations are apparent: the 3300 cm^{-1} region is the absorption most sensitive to hydrogen bonding distribution: the "free" NH component is usually observed at 3450 cm^{-1} . Similarly, in the 1700 cm^{-1} region, two clearly resolved bonds may be observed, one at 1735 cm^{-1} associated with the free C=O stretching vibration and the other at 1705 cm^{-1} associated with the hydrogen bonded C=O stretch vibration. In their experiments, Lee and Wang^[27] used a special set up to heat the sample beam area to 130°C , held for 10 minutes and then rapidly cooled to -100°C within a few seconds. This gave a fully phase mixed polymer, i.e. a quenched mixed sample. The spectrum of a quenched sample usually exhibits the free NH stretching vibration at 3450 cm^{-1} . When the sample temperature is raised, the NH bond diminishes in intensity and is replaced by the 3330 cm^{-1} bond associated with the NH bonded to carbonyl group.

However, quantitative analysis of the hydrogen bonds formed by using the NH stretching bond is complicated by the significant bond overlap, perhaps due to large difference in the ambient extinction coefficient as a function of the hydrogen bond strength. The carbonyl stretch vibration responds in a similar manner, but due to less overlap, its behaviour can be used to monitor phase separation quantitatively. If the sample temperature is allowed to rise, a decrease of the 1735 cm^{-1} component occurs with a corresponding increase in the 1705 cm^{-1} component as a function of time. If the quenched sample is assumed to represent a phase mixed, state, then most NH groups are bonded to the ether/ester oxygen as expected from sample composition. Some carbonyl groups, however, will remain unbonded even in the quenched sample before phase separation commences. The overall integral intensity of the two components is independent of time at a given temperature. The inter-conversion between the two principal components is considerable and can be analysed. Thus, the C=O stretching vibration is a suitable bond for estimating the amount of hydrogen bonding present at a given time and for following the phase separation kinetics because its inherent extinction coefficient remains relatively constant.

1.4.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

Another spectroscopic technique which is widely used to obtain valuable information on structural units is NMR spectroscopy. Using ^{13}C and ^1H NMR spectra of polymer solutions, structural units of polymers are identified from a combination of chemical shift data and spin-spin splitting. It has been found that linear polyurethanes give good quality high resolution NMR spectra in polar solvents such as dimethyl formamide or pyridine, and as a result model

compounds have been prepared by many investigators and their NMR spectra examined^[29-32]. The results of NMR spectroscopy from model compounds have then been used to analyse either commercially available or in-house prepared linear polyurethanes. Particular attention has been paid so that the model compounds include those partial structures which are likely to be formed in the linear polyurethanes, including all the side reactions which can arise as a consequence of the presence of impurities such as water (carbamic acid and its amine breakdown products). Compounds containing typical diisocyanates such as toluene diisocyanate (TDI), diphenyl methane diisocyanate (MDI), and hexamethylene diisocyanate (HDI) combined with polyols such as, poly(propylene glycol) (PPG), poly(ethylene glycol) (PEG), poly(ethylene and poly(tetramethylene adipate) (PEA and PTMA), simple diols like 1,4 butane diol (BD), ethane diol (ED) and diamines such as ethylene diamine (EDA) which are commonly used as starting materials in polyurethane elastomers, have been made, and their NMR spectra obtained. A model compound based on PEA-MDI-BD, gave two NH proton resonances, one at 9.63 ppm and the other at 9.55 ppm. The former is attributed to the urethane NH derived from the primary terminal hydroxyl in PEA, and the latter to the NH derived from the primary hydroxyl of BD. In addition, for the CH₂ proton resonance, a set of peaks at 1.67, 2.35 and 4.36 ppm indicates the presence of PEA while the BD moiety gives a signal at 1.67 ppm and this is always accompanied by a peak at 4.14 ppm.

The MDI moiety is identified by the CH₂ peak at 3.89ppm and characteristic aromatic ring protons centred at 7.30 ppm. Similarly, in another model compound comprised of PEA-MDI-ED, the presence of ED can be determined from the CH₂-proton resonance at 4.48 ppm. Consequently, the elucidation of the presence of ED in a PU from PEA-MDI-ED can be ascertained by the examination of the NMR spectrum in the region of the NH and CH₂-protons. This means that every component in polyurethanes, including the diisocyanates, polyols, and the chain extender, can be identified from their NMR spectra provided the chemical shift characteristics of those components are investigated and determined via their model compounds.

Molecular weight determination of linear polymers by NMR spectroscopy, requires the quantification of the end group distribution relative to the internal polymer units^[33]. NMR analysis offers the advantage of direct number average molecular weight (M_n) determination, in addition to its capability in identification of various end groups structures when competing synthesis and/or cleavage processes are present. Various approaches have been introduced to overcome limitations of sensitivity and resolution in NMR end group analysis^[33].

²H NMR spectroscopy has been used to determine the hard segment content in thermoplastic polyurethanes (TPUs) from the intensity of selected ²HNMR spectra signals^[34].

The hard segment content of TPU was obtained by using two characteristic signals, (one exclusive for hard and another for soft segments), in the ^1H NMR spectra ^[34].

In recent years, ^{13}C NMR analysis has become more straightforward because of the introduction of Fourier transform methods and increasing magnetic field strengths. This provides more information about the composition of polyurethane starting materials such as polyether polyols, with respect to the type of hydroxyl group, i.e. whether primary/secondary, as well as the overall purity of the polyether ^[35].

^{13}C and ^2H NMR spectroscopy are frequently used to determine end group types as well as degree of purity, e.g. level of monols in polyether polyols such as propylene oxide, which make up an important class of polyurethane foam precursors^[35-36]. Le Master et al. used multi-dimensional NMR to analyse end groups of a series of polyether urethanes and determine the hydrolysis kinetics of commercially available TPUs after storage at 70°C ^[33]. Using a sensitivity enhanced NMR spectrometer equipped with a $\{^1\text{H}, ^{13}\text{C}, ^{15}\text{N}\}$ triple-resonance, triple axis gradient probe ^[33] reliably estimated polymer end group concentrations at a high sensitivity. It was found ^[33] the approach was particularly robust for differential measurement of the same cross-peak as a function of synthesis when variations in relaxation behaviour can potentially be minimised. In the more general case of comparing intensities of groups with significantly differing relaxation behaviour, correction for the differential relaxation effects can be determined. They concluded that the ability to establish extensive ^1H , ^{13}C spin coupling corrections at natural abundance to the level of 1-2 sites per 40 kDa should markedly facilitate characterisation of minor structural variations in polymers arising via either synthesis or degradation. The natural abundance of ^{13}C enrichment can be used to break local symmetries and thus provide an effective means of overcoming resonance assignment problems arising from spectral degeneracy^[33].

Trezvora et al.^[37] studied the effects of the order of monomer addition during the process of synthesising polyurethanes on the morphology, molecular mass and properties of the final polymer using ^{13}C NMR spectroscopy. Four methods of synthesis were examined that differed in that the polyurethane blocks were formed at different stages of the process. Using several parameters such as molar ratio between the diisocyanate and the chain extender, the triad of isocyanate-chain extender-isocyanate and fragments of isocyanate not linked to the polymer chain in ^{13}C NMR spectroscopy, they determine the synthesis procedure that was more likely to produce high molecular weight polyurethane was the one single-stage process in which the polyols, isocyanate and chain extender are added in one step.

1.4.3 X-Ray Scattering

X-ray scattering is used to obtain information about the size and shape of molecular assemblies. The spatial extent of the scattering pattern is inversely related to the size of the scattering object. X-rays scattered or diffracted at high angles can provide information about the detailed structure of the molecules or crystals at resolutions where it may be possible to distinguish individual atoms.

Small-angle X-ray scattering (SAXS), however, provides information on the overall shape and size of the scattering object, its density, orientation, and packing with other objects.

Since X-ray scattering arises from electron density fluctuations in the specimen, a scattering object can be any inhomogeneity – a molecule in solution, a small crystal, a part of a large molecule, a solid or a liquid particle, a rubber particle in a glassy polymer matrix etc. SAXS allows measurement of scattering angles^[38] corresponding to spacings between 150nm and 2nm. Therefore it may be possible to interpret the small angle scattering data or the system in a variety of states and to follow dynamically the changes in a structure as a function of temperature, stress, pH, ionic strength.

The information obtainable from small-angle X-ray scattering, particularly from disorientated systems, is often very limited and the interpretation ambiguous. But SAXS, when used in conjunction with other methods, can be extremely powerful. This is particularly the case when sufficient information is available elsewhere to provide a starting point for the analysis.

To follow rapid structural changes in a scattering pattern, the data need to be collected quickly. This requires a high photon flux on the sample. To follow such changes in large molecules it is necessary to make measurements at small angles. An X-ray beam of small area and small angular divergence is therefore required. Taken together, these requirements imply the use of a bright X-ray source, where brightness is defined as the number of monochromatic photons per unit area per unit solid angle per second. Thus, a synchrotron radiation source is extremely useful for these types of experiments. With suitable focusing optics, it is possible to resolve scattering angles of typically 0.05 degrees from the direct beam. Normally, X-rays of approximately 1.5\AA wavelength are used. It might appear that longer wavelength X-rays would be better, because the scattering pattern would enlarge and the requirements for a well collimated beam would be relaxed. However, absorption problems become severe at longer wavelengths and, in addition, the monochromators and detectors are less well developed for softer X-rays.

SAXS is extensively used to study the size and shape of crystallites in semi-crystalline polymers. It can also be applied to solutions to measure molecular dimensions, and to amorphous bulk polymers where electron density fluctuations exist due to phase separation, such as in polymer blends or block or graft copolymers. The two most common structural forms in semi-crystalline polymers are lamellar and fibrillar structure, the first occurring in solution-grown single crystals and melt-grown spherulites (spherical aggregate crystallites), the second in oriented systems such as spun or drawn fibres. The lamellae, in conventional synthetic polymers, consist of a crystal core through which straight molecular stems cross perpendicularly (or nearly perpendicularly), and of less ordered layers containing chain folds, entanglements, etc.

Time-resolved SAXS studies of structure development during the early stages of isothermal crystallisation, as well as crystal annealing above the crystallisation temperature, have been used to follow morphological changes within polymers. Also, reorientation of lamellar crystals accompanying rapid stretching has been monitored in situ ^[39].

The initial stages of micro-crack formation, the so-called "crazing" effect, involves the creation of voids which may be studied by SAXS. The progress of phase separation has also been investigated in amorphous polymer blends. Synchrotron radiation is particularly useful in liquid crystal polymer research to investigate the kinetics of temperature, flow, or field-induced relaxation processes involving molecular orientation and phase transition.

Clough and Schneider^[11] used SAXS to study microphase separation in segmented polyurethanes. Stress crystallisation of the soft segments has also been examined by SAXS, and the results show that stress crystallisation occurs at extensions of 180% and 150% for elastomers based upon polytetramethylene glycol (PTMG) or polytetramethylene adipate (PTMA) with 4,4'-diphenyl methane diisocyanate (MDI) and 1,4 butane diol (BD) as the hard segments. Bonart ^[40] examined poly(urethane-ureas) based on MDI, with polyester or polyether soft segment, and a chain extender diamine or hydrazine. On elongation, the polyester based samples gave a paracrystalline arrangement of soft segments, while the polyether, by contrast, crystallised upon extension of the elastomer beyond 150%, presumably reflecting its greater structural regularity compared to the polyester. At 200% elongation of the polyurethane specimen, strain-induced crystallisation of the soft segment occurs, with hard segment bundles arranged in a disorientated manner transverse to the stretching direction.

The arrangement of the soft and hard segments and their interactions in some 1,4-butane diol extended elastomers prepared from diphenyl methane diisocyanate and polyethylene adipate of molecular weight 2000 has been studied by Bonart and co-workers ^[40-41]. Crystal

reflections were found even in the unstretched state and were due to crystalline or paracrystalline associations of hard segments. The paracrystalline ordering of the hard segments was due to their densely packed arrangements which while not sufficiently well ordered to form crystallite to diffract x-ray, on suitable heat treatment, produced true crystallisation by the reorganisation of the hard block domains. The crystalline and paracrystalline domains could be identified both by their X-ray scattering and diffraction behaviour, and also by their thermal transitions in DSC.

1.4. 4 Thermal Analysis

1.4.4.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) have been widely used to study ^[2,5, 42-48] segmented copolymers, and has been important to the understanding of the morphology and intermolecular bonding in such segmented copolymers. In some polyurethane samples as many as five transitions can be observed in a DSC trace. These include the glass transition temperature of each phase which appear as baseline shifts, a short-range order endotherm of the hard segment attributable to storage or annealing effects, and endotherms associated with the long range order of crystalline portions of either segments. The origin of the three hard segment endotherms has been the subject of extensive study by several workers. Early studies ^[48-49] assumed that these endotherms were attributable to hard segment hydrogen bonding dissociation.

Cooper et al.^[12,44] studied the temperature dependence of hydrogen bonding in MDI-based segmented polyurethane elastomers using IR spectroscopy and DSC. They concluded that the regions of endothermic activity observed in the DSC traces for polyurethane elastomers may be ascribed to morphological effects. These effects can be broadly divided into loss of short- and, long-range order, (Figure 1.1). The short-range order (Figure 1.1A) may be continuously improved by annealing which would result in the short-range order merging with the long-order region (Figure 1.1.B) and producing a single endotherm only. It is possible to improve the short- and long- range order into a microcrystalline structure by severe annealing provided the average hard segment length is sufficiently great as indicated in Figure 1.1.C.

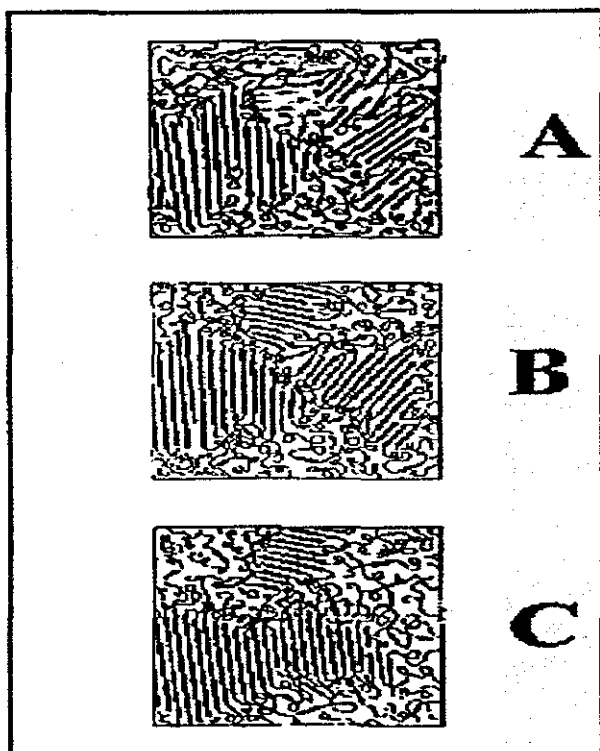


Figure 1.1 Schematic representation of degrees of hard segment domain order. (Broad line, hard segment; thin line, soft segment. (A) Lesser ordered, non-crystalline hard segment domains (B) greater ordered, non-crystalline hard segment domains; (C) microcrystalline hard segment domains^[50].

In addition, a plot of the normalised NH infra red absorbance peak area versus temperature shows a reduction in the slope at about 75-100°C. Seymour and Cooper^[49] ascribed the slope change to the onset of hydrogen bond dissociation occurring at the hard segment T_g . Furthermore, by comparing the DSC results of samples of different thermal history, they revealed that the dissociation of hydrogen bonding is insensitive to the degree of order present in samples and is accelerated at temperatures above the glass transition temperature of the hard segments. Cooper and Seymour^[44, 49] finally concluded that molecular mobility was not controlled by hydrogen bonding, but rather it is the rapid increase in molecular mobility which accompanies the T_g which allows the hydrogen bonds to dissociate. The hydrogen bonding, therefore, should not be held responsible for controlling any of these transitions, enhancing mechanical properties of these polymers or acting as tie down points in the polymer structure, and, that the multiple endotherms observed in the DSC traces of polyurethane elastomers must be of a morphological origin.

The variations of T_g of the soft blocks in segmented polyurethanes as a function of composition, or segmental chemical structure have been monitored and used as an indicator of

the degree of phase separation. Cooper and Hesketh et al.^[44] studied the effect of chemical structure, annealing and quenching on the morphology of a series of segmented elastomers. Samples were selected to be representative of the variety of chemical structures and solid state morphologies common to segmented elastomers. The hard/soft segment ratio in all cases was approximately the same, but their solid state characteristics varied from non-crystalline with hydrogen bonding to highly crystalline and non-hydrogen bonding. The polymer soft segments were based either on poly(tetramethylene adipate) (PTMA) or poly(tetramethylene glycol) (PTMG), while the hard segments were either 4,4'-diphenyl methane diisocyanate (MDI) and 1,4-butanediol (BD) chain extender or piperazine coupled with 1,4-butanediol bischloroformate. The latter hard segment is incapable of hydrogen bonding, since the nitrogens are incorporated in the piperazine ring. The effect of chemical nature and thermal treatment on these polymers can be summarised as below.

a) T_g Region: soft segment glass transition temperature

In general, poly(ether-urethanes) showed a lower soft segment T_g than their equivalent poly(ester-urethanes). The presence of hard segments dispersed in the soft segment domain, raises the T_g . This is more likely in polyester-urethanes due to greater compatibility of ester groups with the urethane hard segments^[45-46]. Annealing and quench mixing raises the T_g and, higher annealing temperatures favour more mixing and hence result in higher soft segment T_g . Polymers with highly crystalline hard segments did not exhibit increased phase mixing upon annealing. It was suggested that crystalline hard segments are less likely to be mixed into the soft domains during annealing below their melting temperature and the crystallisation driving force following quenching most likely leads to rapid demixing. The T_g , however, shifts back towards lower temperatures with time after quench if sample was conditioned at ambient temperature for a prolonged period of time.

b) The melting (T_m) Region: soft segment melting

Hesketh and Cooper^[44] reported soft segment melting endotherm only in polyurethanes with a sufficiently highly molecular weight soft segment, e.g. soft segments of number average molecular weight (M_n) of 2000 and higher. The soft segment melting (T_{ms}) was also found to shift to higher temperatures with annealing temperature T_a . This also shifts back to lower temperatures with time after quenching. This is because the soft segment is in its melt state at room temperature. Upon cooling, the system is then quenched to an amorphous glassy state which, when heated in the DSC cell, it passes through its T_g and then melts, and, therefore the crystallite disappears.

c) Region I: short-range ordered hard segment domain

This endotherm T_I which arises from the disruption of short range ordered hard segment domains, i.e. clusters of short hard segment, perhaps of only one MDI unit, was found to be absent from the DSC traces taken immediately after quenching from the annealing temperature, but reappeared at long times and was observed to grow larger in size, indicating the achievement of better short range order due to mixing/demixing.

d) Region II: long-range ordered hard segment domains

These intermediate temperature endotherms, T_{II} , are associated with long range order in the hard segment domain. In general, annealing moves this endotherm to higher temperatures^[44-45,50]. This is due to increased order. During annealing, hard segments arising from aggregates are disrupted by the annealing conditions and are formed into long-range ordered domains which dissociate at a temperature just above the anneal temperature. The size of this endotherm depends on the amount of hard segment which dissociates at temperatures below the annealing temperature^[49].

e) Region III: microcrystalline hard segment melting.

Crystallisation requires an exact packing of the hard segments into a lattice structure, and, thus, has a well defined temperature associated with its melting although annealing may be expected to alter the size or the shape of crystalline melting peak, it will not change its position unless significant changes are made in crystallite sizes or perfection^[44]. In general, crystalline hard segments are much less susceptible to disordering by stresses imposed upon them by the soft segment matrix upon demixing. Annealing, however, has been shown to improve and merge short- and long- range endotherms, T_I and T_{II} respectively into a single endotherm without affecting any long range order present in the polymer^[2, 42,44-47, 50].

Recently, Hourston et al. have proposed a new signal to indicate the differential of heat capacity with temperature, dC_p/dT , signal from modulated- temperature differential scanning calorimetry (M-TDSC). For the study of polymer-polymer miscibility, a basic limitation of the utility of glass transition determination remains. For the study of polymer-polymer miscibility, a basic limitation of the utility of glass transition determination exists with blends composed of components which have similar ($<15^\circ\text{C}$ difference) glass transition temperatures, where resolution of the T_g s by conventional DSC and dynamic mechanical thermal analysis is impossible^[51-52]. Furthermore, for small concentrations (less than 10%) the weak transition signal is difficult to resolve^[51-52]. This limitation is reduced when M-TDSC is used.

Hourston et al.^[53] have shown that when the difference in T_g is about 10°C , the dC_p/dT with temperature signal given by M-TDSC may be used to characterise polymer-polymer miscibility with high resolution.

Multi-component polymeric materials exhibit phase separation. A common feature across the spectrum of such multiphase polymer materials is the presence of large regions of interface. The interfaces are invariably important in controlling the properties of the composite and the ability to understand and optimise the interface is recognized as a key feature in developing improved materials^[54]. The majority of polymer-polymer blends are two-phase and their morphologies depend on the type of molecular interaction present, the rheology of the components and the processing history. Models used to describe multiphase materials show that properties of these materials can be correlated with the interface volume fraction. Many techniques have been used to determine the fraction of materials contained in the mixed regions between micro-phases. Small angle x-ray, and neutron scattering data can be used to estimate the thickness of the interface. Dynamic mechanical data can be modelled by assuming large interfacial profiles, but the methods require large interface volume fractions. A technique that yields both interfacial thickness and composition gradient across the interface is transmission electron microscopy. Results from highly ordered systems have been obtained that are in good agreement with small-angle X-ray, dynamic mechanical measurements, but preparation of appropriately ordered samples can be difficult. Hourston et al. studied the changes in the heat capacity and dC_p/dT vs. temperature signal for a (50:50 by mass) blend of polybutadiene and a natural rubber prepared by melt blending and for a physical mixture of the two samples. A characteristic behaviour in the decrease of increment of heat capacity, ΔC_p , at the glass transition temperature of both polymers was observed by Hourston et al.^[55]. The value of ΔC_p for a component was found to be proportional to its mass fraction in the system under investigation. They concluded that the heat capacity vs. temperature signal cannot provide information about that inter-phase glass transition or its composition distribution. However, the dC_p/dT vs. temperature signal can provide that information.

The M-TDSC dC_p/dT vs. temperature signal is a useful tool for characterising the morphology of multi-component polymers. Calibrated dC_p/dT vs. temperature signal can be used quantitatively to analyse inter-phases in terms of mass fraction and component composition in multi-component polymer materials. Although inter-phases do not exhibit separate glass transition temperatures, they occur continuously between the glass transition temperatures of the two constituent polymers^[55].

Pang et al.^[39] used M-TDSC to characterise the interfacial contents of both kinds of blends with different compatibilising extents. In their analysis, Pang et al.^[39] discovered that although no change in the melting temperature (T_m) of PP was seen on addition of compatibilisers, the enthalpy of melting (ΔH_m) of blends containing compatibilisers was lower than pure polypropylene (PP). Pang et al.^[39] concluded that the reduction in ΔH_m is an

indicator of compatibilisation and the change in the inter-phase composition as the weight fraction of PP in the inter-phase is reduced by further addition of the compatibiliser.

Similar effects in the behaviour of T_g and ΔH_m of polypropylene and poly(ethylene terephthalate) (PET) were observed by Pang et al.^[39]. They showed that M-TDSC was superior to conventional DSC in determining the glass transition. In M-TDSC thermograms, the T_g is displayed as a peak when the differential signal of heat capacity versus temperature is plotted. This means the peak plus the onset and final temperatures of the glass transition can be precisely determined. The increment of heat capacity at the glass transition (ΔC_p) can also be obtained precisely from the integration below.

$$\Delta C_p = \int_{T_1}^{T_2} (dC_p/dT) dT = \int_{T_1}^{T_2} dC_p$$

This is because ΔC_p is the peak area of the glass transition region. T_1 and T_2 are the onset and final temperatures of the glass transition region, respectively. It is well known^[39] that the heat capacity of matter is a characteristic constant at a given temperature and pressure. The ΔC_p of a pure material is also a specific constant under fixed conditions of determination, whether it is in the bulk state or dispersed in another medium. This feature provided an effective way to investigate interfacial contents of polymer blends. That is, the ΔC_p of the i th component in a fully phase-separated blend must be exactly the product of that in its pure state multiplied by its weight fraction in the blend^[39].

In a partially miscible system, however, a portion of the i th component is not in the equivalent phase, but mixes with a portion of other components to form interfaces, so the ΔC_p of the i th component becomes smaller because of this net reduction of the component in the blend. Therefore, the change of ΔC_p values before and after blending provides a criterion to estimate compatibility of the blend.

$$\begin{aligned} d\Delta C_p &= \omega \Delta C_p^\circ - \Delta C_p \\ &= 0, \text{ the blend is fully incompatible} \\ &= \omega \Delta C_p^\circ, \text{ the blend is fully compatible} \\ &> 0 < \omega \Delta C_p^\circ, \text{ the blend is partially compatible} \end{aligned}$$

ΔC_p and ΔC_p° are heat capacity increments in the blend and pure state, respectively, and ω is the weight fraction of the i th component in the blend.

1.4.4.2 Wide Angle X-ray Scattering/DSC

Koberstein et al.^[45-47] investigated the nature and the origin of the multiple endotherms exhibited in DSC traces of MDI/BDO/PPG polyurethanes. Using DSC-synchrotron X-ray scattering experiments they demonstrated that the melting behaviour of these polymers is highly dependent on the procedure used for the sample preparation as well as the subsequent thermal conditioning. Having confirmed the three regions of endothermal activities observed by Seymour and Cooper^[12,44] (figure 1.2), they characterised these melting endotherms into two categories: low temperature endotherms which relate closely to the annealing temperature, T_a usually melting at about 10-20°C higher than the temperature at which they form; and the higher temperature endotherm which exhibit the behaviour of conventional crystallisable homopolymers in which T_m increases linearly with T_a .

Figure 1.2 illustrates typical melting behaviour of MDI/BD polyurethanes crystallised from the homogenous melt by quenching to T_a . At low crystallisation temperatures near the hard segment glass transition (region I), a non-crystalline microphase structure predominates. The high temperature endotherm in this region (peak 1) is associated with a microphase separation transition (MST) to the disordered state (i.e. dissolution of the microphase structure). Thermal conditioning in region II promotes crystallisation and the appearance of two high temperature endotherms. Partial disordering of the microdomain structure occurs during the first high temperature endotherm (peak IIB) and is followed by complete disordering during the second endotherm (peak IIA)^[47]. Isothermal crystallisation at temperatures exceeding MST did not produce detectable levels of microphase separation and/or crystallisation.

Koberstein et al.^[45] then used WAXD-DSC techniques to examine the multiple endotherm phenomenon in identical polyurethanes (PPG/MDI/BD), prepared by two independent procedures, compression moulded and crystallised from the homogenous melt. They summarised their conclusions as follows. In melt crystallised specimens, multiple endotherms are associated with distinct crystal populations with different melting points, but with the indistinguishable diffraction patterns consistent with hard segment crystals of contracted form.

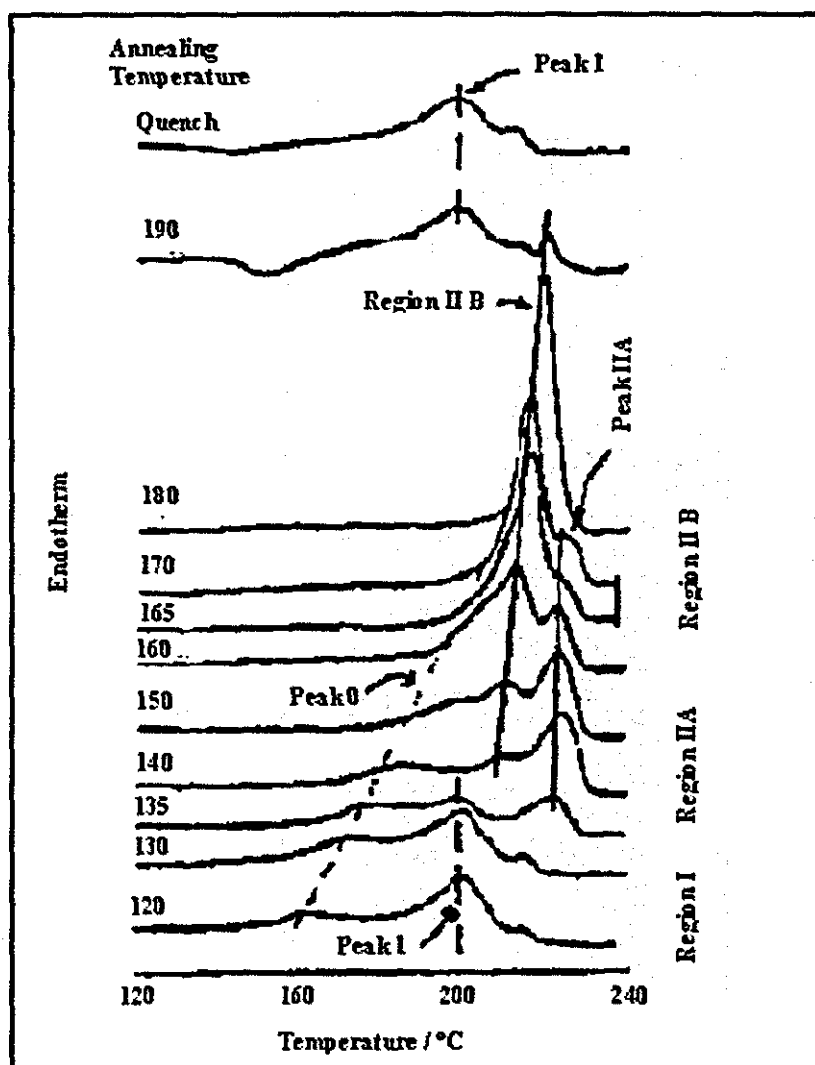


Figure 1.2 DSC thermograms of PPG/MDI/BD, after crystallisation at the indicated temperatures. The specimen contained 60% by weight hard segment^[45].

During each endotherm, the hard segment material that melts spontaneously mixes with the soft segment microphase, since this temperature exceeds the microphase order-disorder temperature (ODT). Multiple melting endotherms in compression moulded specimens, however, result from a recrystallization process rather than a crystal-crystal transformation. As the extended crystal form melts, the resultant nuclei reside in a supercooled melt. They then crystallise in similar fashion to the melt-recrystallised specimen and, therefore, exhibit a contracted type crystallisation pattern. The rate of type II recrystallization is a strong function of the supercooling.

1.4.4.3 Dynamic Mechanical Thermal Analysis

Dynamic mechanical properties provide information about first and second order transitions (T_m and T_g respectively), phase separation and mechanical behaviour of polymers^[17]. Below the T_g , the glassy state prevails, while a rapid decrease in modulus is seen as the temperature is increased through the glass transition region. A linear amorphous polymer shows a rubbery plateau region followed by a continued rapid drop in modulus, cross linking causes the modulus to stabilise with increasing temperature at about three decades below that of the glassy state^[25]. Dynamic mechanical properties of elastomers are important because they influence the performance of the elastomers. Using dynamic mechanical analysers, it is possible to determine the storage modulus E' , (elastic behaviour), loss modulus E'' (energy dissipation), $\tan\delta$ and glass transition temperature values.

In block copolymers, an enhanced rubbery region appears where modulus changes little with increasing temperature, followed by another rapid drop in modulus which occurs when the temperature is increased to the hard segment transition point^[10,48,50,56]. In contrast, a semi-crystalline polymer maintains a high modulus through the glass transition and up to the crystalline melting point where the structural integrity of the crystallites is destroyed. Figure 1.3 shows typical modulus/ temperature behaviour exhibited by various polymeric systems.

In general for elastomeric block copolyurethanes, the storage modulus quantitatively measures the materials' elastic properties and also qualitatively determines elastomer stiffness and hardness. In $(AB)_n$ type block copolymers, such as a polyurethane, two distinct transitions are indicated by the sharp drops in storage modulus and the corresponding presence of two loss peaks. Ideally, for block copolymers, these transitions are located at the T_m or T_g of the corresponding component homopolymers, but, sample composition, segmental length, inherent inter-segment solubility, and methods of sample preparation have been found to influence the degree of phase separation and thereby the shape and temperature location of the dynamic mechanical transition points^[2,10,17,48, 50,56].

Component mixing between domains is indicated by a decreased slope on the storage-modulus transitions and by broadened loss peaks. Since the hardness of a polyurethane elastomer is related to the weight percent hard block content, the storage modulus tend to increase as the level of hard block is increased and decreased where the amount of high molecular weight soft segment diol being the major component within the material^[23,48].

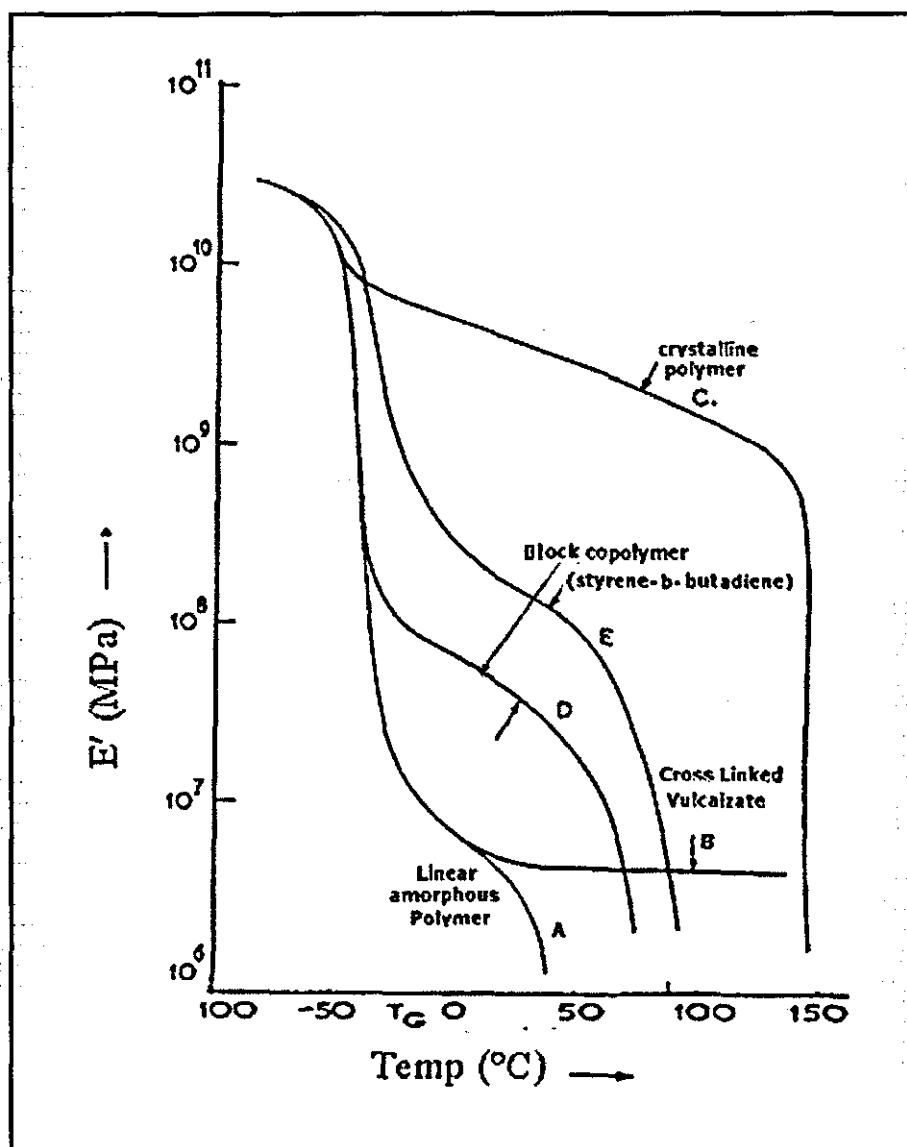


Figure 1.3 Modulus temperature behaviour of various polymer types ^[25].

Figure 1.4 illustrates the dependence of the elastic modulus- temperature curves on the block copolymer morphology: for case (a), the two blocks i.e. soft and hard blocks are quite compatible, giving a one-phase system. Case (b) of figure 1.4, however, indicates an example where there is bundling of hard and soft blocks without achieving phase separation. Case (c) is an example of a phase separated block copolymer with diffuse phase boundaries consisting of mixed hard and soft block, and case(d) is an example of a well phase separated copolymer with sharp boundaries between phases.

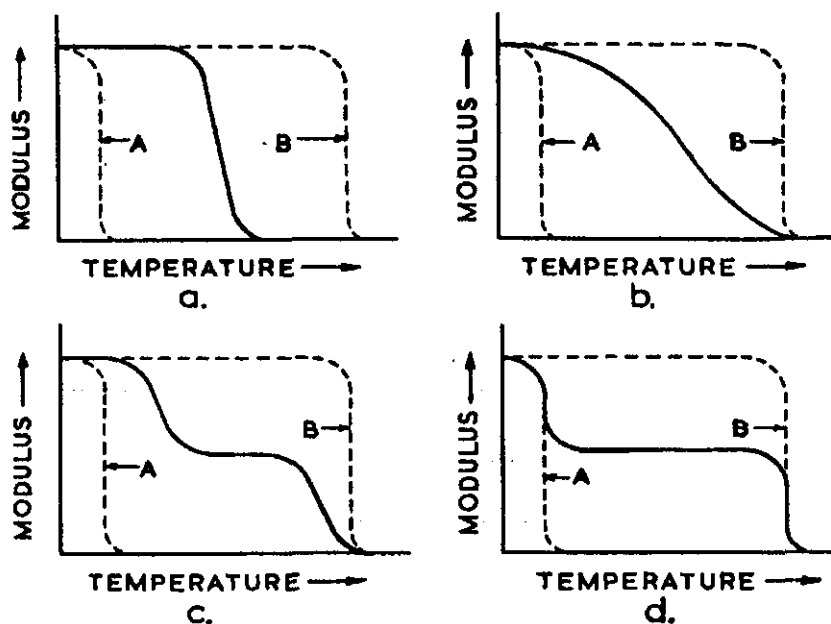


Figure 1.4 Dependence of modulus-temperature curves on block copolymer morphology. Curves A, & B correspond to the modulus curves for the pure homopolymers ^[25].

In the case of block copolymers exhibiting phase separation, figure 1.4 (c and d) two transitions are observed where the modulus changes markedly over a narrow temperature range. Between these two transitions a plateau region of lesser change of modulus with temperature is observed. When this behaviour is obtained, the block copolymer exhibits distinctive mechanical properties characteristics of thermoplastic elastomers and elastomeric fibres^[25].

The loss modulus, E'' , is a qualitative measure of energy dissipation in the elastomer^[23]. Low values of E'' are indicative of low energy dissipation, low hysteresis, and consequently, low heat build up. The loss modulus values are high at low temperature, but decrease as the temperature is increased. Dynamic mechanical investigations can be used to demonstrate the existence of a two-phase structure. The $\tan\delta$ plot as a function of temperature for a well phase separated block copolymer may show several peaks. These are structural relaxations that correspond to a soft segment T_g , (δ_s), soft segment crystalline melting (α_c), hard segment T_g , δ_h and hard segment melting α_h ^[48]. The measure of $\tan\delta$ is a qualitative tool to determine the hysteresis, (heat build up), in an elastomer during dynamic flex conditions. For a plot of $\tan\delta$ as a function of temperature, as the hard segment is decreased the $\tan\delta$ peak height is increased indicating higher hysteresis of the elastomer associated with the high amounts of

high molecular weight diols. The peak widths are also observed to increase corresponding to the decrease in the hard block content of an elastomer.

Extensive dynamic mechanical property studies have been carried out on hydrogen bonded polyurethanes^[48] and several secondary relaxations were found in addition to the major hard and soft segment transitions and a molecular mechanism can be assigned to each of these. A low temperature transition (γ) is attributed to localised motion of methylene groups in polyether or polyester sequences. Similar transitions have been found in other block copolymers^[17]. In polyurethanes with long soft segments ($M_n \approx 2000$ to 5000), a soft segment melting transition was also detectable and the T_g loss peak occurred at lower temperatures when soft segment length was increased^[2]. The longer segments are expected to produce better ordered and larger domains where the soft segments can exist in regions well removed from the domain interface and hard domain interactions so that their motion can be relatively unrestricted by the hard domains^[50]. There is also better microphase separation in these systems, and therefore, less hard segment material dissolved in the soft segment phase. Crystallisation of the hard segments in samples also serves as an additional driving force in the microphase separation. Soft segment T_g values were lower in non-hydrogen bonded materials than in hydrogen bonded samples with an equivalent hard segment content which is attributable to the influence of hydrogen bonding interactions of urethane groups with the soft segments.

Dynamic mechanical investigations by Huh and Cooper^[48] demonstrated the existence of a two phase structure in polyurethanes based on 4,4' diphenyl methane diisocyanate (MDI), and examined the effects of composition, soft segment molecular weight, and thermal history upon the relaxation mechanisms of these copolymers. Relaxations corresponding to a soft segment T_g (α_a), soft segment crystalline melting (α_c), a hard segment T_g (δ) and hard segment melting were observed in the polyurethanes studied. It was concluded that the α_a and δ relaxations were influenced by the degree of crystallinity and the nature of the domain structure, while the magnitudes of the α_c , δ and δ' (hard segment melting) relaxations were found to be related to the size of the domain structures present.

Systematic studies on MDI-based polyurethanes with polycaprolactone soft segments over a wide range of soft segment molecular weight and hard segment concentration have been carried out by Seerfried, Koleske and Critchfield^[10,56]. The glass transition was observed to shift to lower temperatures as the soft segment chain length increased, and soft segment crystallisation was found to occur for the highest molecular weight. The T_g of lower molecular weight, soft segment samples increased as the hard segment content increases, while the T_g values of polyurethanes containing higher molecular weight soft segments were

unchanged until extreme amounts of hard segment were introduced. This behaviour was attributed to a high degree of phase separation between blocks. The behaviour of polyurethanes, and poly(urethane-ureas) having MDI and toluene diisocyanates, TDI, hard segments has been compared over a limited compositional range and the effects of different chain extenders on TDI polyurethanes was also examined [2,48,50,57-58]. All TDI-containing polyurethanes displayed little or no phase separation. Schneider, Sung and co-workers [59-60] carried out an extensive study of polyurethanes prepared from the two isomers of TDI. The glass transition temperature of 2,4-TDI based polyurethanes with a polyether soft segment of about 1000 M_n , showed a strong dependence on composition, and extensive hard and soft segment mixing was postulated in these materials. Similar polyurethanes based on the 2,6-TDI-structural isomer displayed a highly ordered domain structure, indicated by a T_g independent of concentration and a strong high temperature transition attributed to the melting of the easily crystallisable hard segment. An increase in the soft segment molecular weight from 1000 to 2000 induced phase separation in the 2,4-TDI series and improved phase separation of the 2,6-TDI series to the point that the soft segment exhibited crystallization. The T_g of the soft segment was found to be a sensitive measure of the degree of phase separation in these materials. It was concluded that the structure of the diisocyanate moiety has a significant effect on the hard and the soft segment dynamic mechanical response, which is also reflected in the properties of the block polyurethane studied. An asymmetric 2,4-TDI hard segment displays only an amorphous δ relaxation, while a symmetric 2,6-TDI hard segment has a broadened glass transition relaxation and is capable of crystallization, retaining a high modulus up to the hard segment melting temperature, about 212°C [61].

1.4.5 Stress-strain behaviour of polyurethane elastomers

The fracture process can be represented by three steps: initiation of micro-cracks or cavitations, slow crack propagation and catastrophic failure [15,62]. Dispersed phases tend to interfere with the crack propagation step, redistributing energy that would otherwise cause a crack to reach a catastrophic size [18]. Thus, a two-phase morphology is essential to the achievement of high strength in elastomers, since growing cracks can be deflected at phase boundaries. Upon deformation, the hard phase particles are thought to absorb the applied stress and redistribute it over a greater surface area thereby inhibiting the growth of cavities, and those cavities which do form can be limited to small sizes, stabilised by surface energy effects. The high modulus hard phase can also relieve stress concentrations by undergoing deformation or internal structural reorganisation. In addition, at lower temperatures strength can be raised because of the greater domain yield stresses, increasing matrix viscosity or strain-induced crystallization effects [2]. Although the relative importance of each process is difficult to assess, it has been shown that only two-phase elastomers exhibit [50,62,63] toughness

over extended ranges of temperature and time or strain rate. A dispersed phase must either be present initially or result from strain-induced crystallisation.

In polyurethane elastomers, the morphology of the hard segment is not always well established, as the morphology depends upon the thermal history. This was demonstrated by Wilkes ^[64] and Ophir et al. ^[65], who studied the effect of solvent and heat treatment on the morphology of polyurethane elastomers. Furthermore, the hard and soft domain morphology is subject to changes while a specimen is being stretched, as shown by the SAXS/DSC performed by Clough and Schneider^[11].

Smith studied ^[50, 62-63] two polyether urethanes based on PTMG/MDI/BD of approximately 50% by weight hard segment content each to demonstrate the effect of differences in domain size. At low strains, infrared dichroism results ^[2,50] showing that hard segments in ET-38-2 (PTMG 2000 molecular weight as soft segment with 38% hard block) orient transverse to the direction of stress, with parallel orientation being achieved at higher stress levels.

For ET-38-1 (PTMG 1000 molecular weight soft segment with 38% hard block) having half the block length than that of ET-38-2. However, the orientation of the hard segments is always parallel with the stretch direction and much less relaxation is observed. Because of their shorter lengths, the hard segment domains in ET-38-1 are non-crystalline whereas, those for ET-38-2 are crystalline, which results in the differences observed ^[62-63]. ET-38-1 domains can be deformed readily and disrupted quickly, allowing rapid relaxation and parallel orientation, unlike the crystalline ET-38-2 which tends to oppose domain disruption and reorientation. Stress-strain curves for ET-38-2 were found to be higher than those for ET-38-1 by virtue of a greater degree of phase segregation, and the moduli at a fixed strain for these samples decreased with increasing temperature, a characteristic attributed to their thermoplastic nature.

Smith ^[50] also studied both strain and true stress at break as a function of temperature for four segmented elastomers all with PTMO as soft segments. Comparing ET-38-1 with ET-38-2, the former was superior in strength and elongation. The smaller, more numerous domains in ET-38-1 were apparently more efficient at stopping catastrophic crack growth than those for ET-38-2, (both had approximately the same hard segment content), resulting in a larger tensile strength. Furthermore, the more readily deformable domains in ET-38-1 permitted higher elongation, which increased with increasing temperature before fracture. ET-24-2 (24% hard block – 2000 molecular weight soft block), exhibited a drastic change in properties near 40°C. Below 40°C, the soft segment of molecular weight 2000 was found to have partially crystallised and so strengthened the specimen. Above 40°C, however, the soft segments were no longer crystalline, and the hard segment domains could not retard crack

growth because of their insufficient cohesive strength at these temperatures. If another hard segment characterised by high cohesive energy was used, however, as in the case of a poly(urea-urethane) specimen (similar to ET-24-2, except for the nature of the hard segments), higher tensile strengths would be observed ^[19].

Wang and Cooper ^[19] investigated the effect of variation of soft segment molecular weight and hard segment content on a series of polyether based poly(urethane-ureas) (PEUU) synthesised from PTMG of 1000 or 2000 Mwt, MDI and with ethylene diamine as chain extender. The mechanical properties were observed to depend primarily on hard segment content and especially on the concentration of urea linkages. This suggested an improvement of hard domain cohesion and an enhanced filler effect through the formation of three dimensional urea hydrogen bonds in the PEUU material. All the PEUUs showed superior high temperature performance over comparable poly(ether-urethane) chain extended with butane diol. For all samples, an increase of either the hard segment content (at constant soft segment molecular weight) or the block length (at constant hard segment content) lead to higher Young's moduli, and to higher secant moduli. In addition, it has been shown that in a multi-phase system ^[66-67], the stress hysteresis behaviour is closely related to domain morphology and phase composition. A high level of hysteresis at small strains can result from plastic deformation of semi-crystalline or glassy structure within the material and/or the disruption of interconnected hard segment domains. For polyether based poly(urethane- urea) samples, Wang and Cooper ^[19] showed that a combination of hard domain interconnectivity and the higher degree of order in the hard domains causes the plastic deformation to occur at lower strains and to a greater extent compared to samples of lower hard segment content. Samples of smaller molecular weight soft segment and lower hard segment content showed more rubbery behaviour with relatively high recovery, suggesting a morphology consisting of isolated hard domains dispersed in an amorphous soft segment matrix. Upon decreasing the hard segment content, a transition of morphology from interconnecting hard and soft segment domains to isolated hard segment domains in a soft segment matrix was observed.

1.4.6 Stress relaxation in elastomeric polyurethane

One of the most important physical properties of elastomers, and in particular for soft elastomers which are the concern of this study, is stress relaxation. The elastomeric behaviour of block copolymers is highly dependent on hard and soft domain chemistry as well as the overall morphology of the block copolymer which itself is dependent on the microstructure of each domain and the interaction between them. However, before the stress relaxation behaviour of polyurethane is discussed, an overall understanding of this phenomenon and various methods used to determine different relaxation behaviours must be given.

1.4.6.1 Stress relaxation in elastomers

The elastic limit of many crystalline and glassy solids is substantially less than 1% ^[68,69]. Natural and synthetic rubbers, however, can often be reversibly stretched several hundred percent. In rubbery materials, the stress at constant elongation is proportional to the absolute temperature in the region of rubbery behaviour. All rubbers, including natural rubber (NR), have a common molecular morphology. They are formed from long, flexible chain like molecules, occasionally cross-linked to form a three dimensional network. In a typical rubber of good properties, there is approximately one cross-link to every few hundred chain atoms. Linear polymers of significantly high molecular weight also show rubbery properties in a suitable temperature interval. In these cases, the entanglements between the chains act as transient cross-links, but linear polymers will flow at sufficiently high temperatures. For example, unvulcanised natural rubber is a linear polymer, which though rubbery at room temperature, has only limited uses because it flows at high temperatures. This is why in order to make useful products, NR is reacted with vulcanising agents such as sulphur or in the presence of peroxide. The reactions with sulphur or peroxide yield chemical cross- links in the rubber that form a three dimensional network ^[71]. In effect, these permanent entanglements, or cross-links that are created as a result of covalent bonding between the rubber chains, act as anchors and prevent chain slipping of interlinked polymer molecules capable of maintaining an equilibrium tension. The combination of chemical cross-links, the transient 'cross-links' formed by chain entanglement, or tiny crystallites, as well as in some cases presence of strong secondary valences results in rubbery behaviour ^[25]. In the unstretched state, the network chain, (the portion of the molecular chain between contiguous cross-links), is randomly coiled, and in fact is rapidly changing from one conformation to another, all, however, consistent with the fixed distance between the cross links ^[72]. When the rubber is stretched, the average distance between the cross-links increases, and the number of possible conformations of the flexible chain between its fixed end points is reduced. This is associated with an entropy change that has been calculated by many workers ^[69].

One of the recognised techniques used to determine elasticity or rubbery behaviour in polymeric materials is the measurement of stress relaxation. The stress relaxation in an elastomer provides a convenient means of following changes induced in the network structure. It also provides an insight into the processes, i.e.chemical such as oxidation, or physical such as chain slippage and viscous flow, that are responsible for the observed stress decay ^[73, 74]. In a simple stress relaxation experiment, the sample is subjected to a constant strain ϵ , and the decay of stress $\sigma(t)$ is observed. A stress relaxation modulus is then expressed as ^[75],

$$G(t) = \sigma(t) / \epsilon$$

In stress relaxation, the presence of viscous flow will affect the limiting value of stress. Where viscous flow occurs the stress can decay to zero at sufficiently long times, but where there is no viscous flow the stress decays to a finite value, and an equilibrium, or relaxed modulus, $G(t)$, at infinite time is obtained.

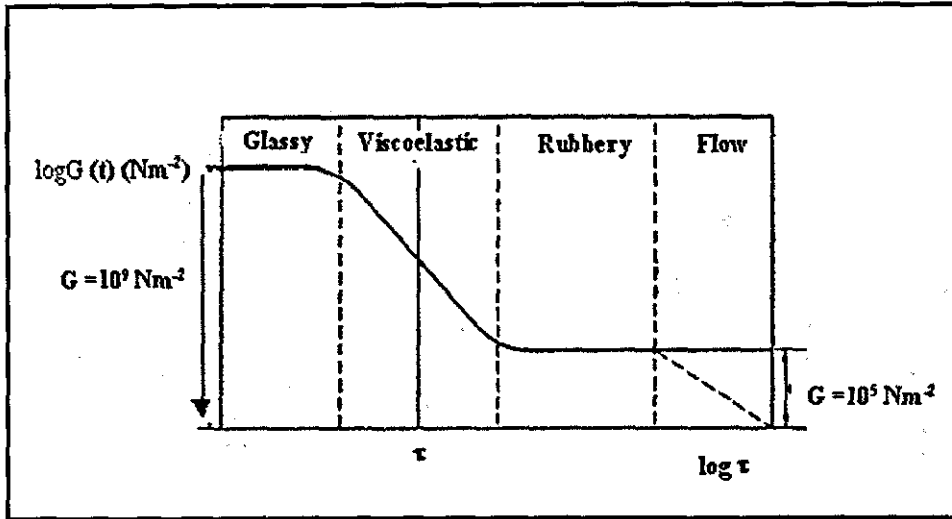


Figure 1.5 The stress relaxation modulus $G(t)$, as a function of \log time t_0 and τ is the characteristic time ^[75].

A plot of stress relaxation modulus as a function of time is shown in Figure 1.5 ^[75]. The transition defined characterises the time scale of the viscoelastic behaviour. At constant strain and temperature, the stress at any time should be proportional to the number of network chains maintaining stress per unit volume. The link between the mechanical behaviour of a cross-linked polymer and its chemical constituents is given by the fundamental equation of rubber elasticity ^[74,76].

$$f = NKT(\alpha - 1/\alpha^2)$$

where f is the stress based on original cross section, N number of network chains per unit volume of rubber, α strain and relative elongation. At constant strain and temperature, the stress at any time should be proportional to the number of network chains maintaining stress per unit volume. Even if there were departure from this theory, it would be expected that a decay would still be related to a decrease in the number of network chains maintaining stress. Two types of stress-relaxation measurement may be made: continuous stress-relaxation, in which the sample is held extended throughout the experiment. The second type is intermittent stress relaxation, in which the sample is strained only at such time as the stress is to be measured. The decrease in stress in a continuously extended strip is a direct measure of the number of network chains removed, since any chains formed by cross-linking are part of a

new network in equilibrium in the extended state and do not contribute to the stress so long as the extension is unchanged. The new network will, however, give rise to "permanent set", i.e. to an increase in unstrained length when the strain is removed.

In intermittent measurements, the sample is extended only for periods at such times as the stress is to be measured ^[74,77]. So that any new network will be formed with the sample in the unstretched state will contribute to stress when the sample is extended. The measurements indicate the stress due to the residue of the original network, plus the stress due to the new network, and may differ considerably from the continuous measurements-the difference being the contribution to the network of any cross-links produced after ageing. Since a dynamic equilibrium between breaking bonds and reformation of new bonds is possible, 'intermittent' measurements are made in which the sample is stretched only for a period of time necessary to determine the stress, and then released to its initial position ^[74]. The intermittent measurement is believed to represent the difference between the rate of scission of bonds and the rate of formation of new bonds, whereas a continuous measurement of decay of stress is thought to measure only the decay of bonds, since any new bonds formed would be in equilibrium with the strained condition and contribute to the stress. The exponential decay of stress of a cross-linked rubber under anaerobic conditions and at constant extension has been shown to be dependent upon its temperature, cross-link density and the type of cross-links present ^[68,78-82]. This is thought to arise from the breakdown of covalent cross links such polysulphidic cross-links into mono, di and cyclic cross-link types that are not as effective in maintaining the stress.

Four types of relaxation mechanism have been distinguished, ^[77,80,82]. One is irrecoverable viscous flow due to translation of whole molecules. This is negligible in vulcanised rubber. Another is the physical process consisting in the attainment of equilibrium in the cross-linked network by rearrangement of whole chains or aggregates. A third arises from breakdown of the network due to a chemical reaction, for example with oxygen. Finally, a fourth contribution is observed in filled vulcanizates, due to the presence of reinforcing fillers. These mechanisms, though normally occurring simultaneously, show different time dependencies. The physical relaxation follows a characteristic law over long times, the stress decay being accurately proportional to the logarithm of the elapsed time in the deformed state. Thus, the relaxation becomes slower as time passes. On the other hand, the chemical attack of oxygen causes a stress decay which follows an exponential time dependence to a first approximation and thus accelerates with time. These two processes may be described as the first and second stages of relaxation since they predominate at short and long times, respectively.

At typical room temperature, the rate of chemical relaxation in general purpose rubbers such as natural, butyl rubbers, polychloroprene and styrene butadiene rubbers, is extremely small and the relaxation behaviour is dominated by the physical process except at very long times.

These physical processes involve the reorientation of the molecular network, the disentanglement and rearrangement of entanglements and breaking of bonds due to secondary forces.

1.4.6.2 Measurement of stress relaxation

Relaxation of stress in rubbers is sensitive to many experimental variables, including time, temperature, type and degree of cross-linking, the presence of low molar mass materials such as water and swelling agents, the presence of particulate fillers, and environmental factors [68,78-82]. Interpreting the stress relaxation behaviour of a rubber can, therefore, be difficult but it can be simplified by limiting the experimental conditions to a few of these variables. For all the general purpose rubbers [82], the behaviour at room temperature, i.e. well above the glass transition temperature, is dominated by a number of other factors. Among these are the nature of cross-links, the test strain and the filler content. Since physical relaxation is directly proportional to logarithmic time, the relaxation rates are quoted as percent per decade, i.e. percent relaxation per factor of ten increase in time. It has also been shown that the stress relaxation rate of a particular rubber test piece is not a unique quantity but depends strongly on its previous stress history [82].

The data from a stress relaxation experiment involve plotting of stress (load) against logarithmic time for reasons of convenience. The results are often quite reproducible [79].

A complete decay of stress is normally indicated in a time that becomes exponentially smaller with increase in temperature. For example, at 100°C the stress in natural rubber is practically decayed in 100 hours. At lower temperatures, especially when stress is plotted against linear time, the fact that stress would decay to zero in a sufficiently long time is not apparent. In most cases, however, the stress (load) is divided by the initial stress (load) and this is plotted against logarithmic time. The initial decay is due to relaxing of secondary network junctions. The relatively large decay of stress, which occurs later on, may be interpreted as due to either bond rupture by oxidation scission at some point along the molecular chains or at network junctions, or spontaneous bonds rupture at or adjacent to the cross-linking bonds put in by vulcanisation. The relaxation of secondary network bonds plays a role in the initial portion of the experiment at sufficiently low temperatures. These postulated bonds have a natural time of relaxation [79]. The bonds break and remake in new positions that allow the molecular chains to resume coiled conformation and thus release the stress. This phenomenon is distinguished from the breaking of primary bonds by being completely reversible.

1.4.6.3 Stress relaxation in vulcanised rubbers

Most stress relaxation measurements are carried out at elevated temperatures, and over long periods of time ^[74,76-79, 80-81, 83-86].

Berry and Watson ^[87] first examined the stress relaxation of vulcanisates prepared from deproteinised crepe cured with di-tert-butyl peroxide. The crepe had been fractionated to ensure an appropriately high molecular weight, with minimum oxygen and nitrogen contents. To prevent the oxygen diffusion from becoming rate controlling, very thin samples were used. When the ratio of final (F) to initial force (F_0) i.e. F/F_0 versus time was plotted, an apparent linear plot was obtained. This was considered as indicative of scission at the cross-link junctions ^[77,87]. In contrast, Ore using similar films of purified rubber cross-linked with di-tert-butyl peroxide and then acetone extracted, obtained curves for stress relaxation in oxygen at 90°C, which were autocatalytic in form after an initial slow period ^[77,88]. This initial slow period was considered to be due to the antioxidant effect of proteins remaining in the rubber even after purification, while the subsequent faster rate reflected main chain scission during autoxidation of the rubber hydrocarbon. The rate of degradation was greatly increased in the presence of copper stearate, which was consistent with autoxidation of the rubber chains leading to random scission of C-C bonds throughout the network.

Tobolsky et al. ^[79] observed complete relaxation at above 100°C for thin rubber bands of NR, neoprene and butyl rubbers. He also discovered that the manner in which the rate of relaxation depends on temperature, and the fact that the rate is independent of elongation, indicates that stress decay is caused by a definite chemical reaction which deteriorates the rubber structure and suggested that oxidative scission as the mechanism of breakdown of primary bonds. The stress relaxation data obtained over a wide temperature range by Tobolsky ^[79] verified the concept of network structure common in elastomers.

The exponential decay of stress of a cross-linked rubber under anaerobic conditions and at constant extension is known to be dependent upon its temperature, cross-link density and the type of cross-link present ^[78]. Farmer and Stuckey ^[78] determined the variation of the polysulphidic cross-link content of a natural rubber vulcanisate during cure from thermal stress relaxation data using a rheometer. They discovered ^[78] that the first order rate constant for the fast relaxation attributed to polysulphidic cross-link exchange reactions varied linearly with the total cross-link density of the vulcanisates. They concluded that the percentage of polysulphide cross-links calculated from rheometer torque measurements is a percentage of a physical manifest force which is the sum of the effects of chemical cross-links and physical entanglements. The relaxation of polysulphides in isolation was not possible despite removing

the viscous flow effect completely and compensating for network degradation reactions. Farmer and Stuckey ^[78] postulated that some maturation reaction involving the shortening of polysulphide cross-links and an increase in cross-link density, both of which proceeded during the relaxation process, are largely responsible for this discrepancy.

Chemical stress relaxation in air, of accelerated sulphur cures of unsaturated elastomers such as a natural rubber and SBR, occurs both through oxidative scission of the main chains and through cleavage of labile cross-links. The lability of the cross-links depends both on the type of the cure and the total length of cure. Under certain conditions, oxidative cleavage is more rapid than cleavage of labile cross-links. The complicating effect of oxidative cleavage in sulphur vulcanisates is largely removed in nearly saturated elastomers such as ethylene propylene terpolymer (EPT) ^[86]. In order to remove any effects arising from oxidative cleavage in sulphur vulcanised rubbers, Lyon et al. ^[86] carried out stress relaxation measurements on EPT to study the effect of type of cure, cure time and change of atmosphere on the stress relaxation characteristics of these saturated rubbers. Lyon et al. ^[86] conducted intermittent and continuous relaxation at 130°C over periods of up to twelve hours on peroxide cured, as well as accelerated sulphur cured EPT rubbers. They ^[86] found that the stress relaxation curve of peroxide-cured EPT at 130°C in air relaxes to zero stress within an hour, with negligible relaxation shown in nitrogen even over a period of 12 hours. For a sulphur-vulcanised EPT, the continuous stress decayed rapidly in both air and nitrogen. After two hours, the relaxation slows to a small rate. Since the curve for continuous relaxation for EPT in air and nitrogen appeared to be the same and that the EPT rubber is thermally stable, as demonstrated by the absence of stress relaxation of the peroxide-cured samples run in nitrogen, and that the accelerated sulphur sample absorbs oxygen at a low rate, Lyon et al. ^[86] concluded that the observed stress relaxation was due to non-oxidative degradation of the cross-links. Furthermore, they attributed the initial rapid decay to a thermal interchange reaction between labile linkages, which were probably polysulphide. As labile linkages interchange under strain, they re-form in an unstrained conformation. A point is reached where practically all the labile linkages are in an unstretched conformation, i.e. not contributing to the stress. At this stage, thermally stable mono- and disulphide cross-links present in the original network, are responsible for the residual stress. If, in the original network, the polysulphide linkages were replaced by thermally stable mono- and disulphide cross-links, the initial rapid relaxation would not be evident. To promote the formation of stable cross-links, an extended post-curing was conducted. Following extended post-curing Lyon et al. ^[86] noticed that longer post-cure eliminates the initial rapid decay and the samples relax very slowly, indicating that only a small percentage of labile cross-links were present. Post-curing for longer times e.g. 16 hours, produced a flat intermittent curve, indicating that an alternative modulus has been reached. Lyon et al. ^[86] postulated that once all polysulphide

links have broken down, the sulphur released is utilised in the formation of new cross-links contributing to a net increase of cross-link density. This behaviour was observed for both samples in air as well as in nitrogen, indicating again the absence of oxidative degradation.

Tarasova et al.^[81] established that stress relaxation of vulcanisates occurs at temperatures higher than 80°C, even if the effect of oxygen is rigorously eliminated. In vacuum, stress relaxation is purely due to thermal degradation of the weakest bonds in the three-dimensional networks. Thermal relaxation should fundamentally satisfy equations of first order kinetics, and the rate constant might characterize the energies of the ruptured bonds.

Tarasova and Dogadkin^[81] explained that relaxation of vulcanisates made from various rubbers with different vulcanisation agents in fact obeys the first order equation, (except in the initial region of physical relaxation). The constant calculated from this equation depends on the initial number of cross-links in the vulcanisates: the rate constant of relaxation falls within the number of cross-links and is non-linear^[81]. Tarasova and Dogadkin^[81] studied thermal relaxation measurement of vulcanisates containing various types of cross-links, among these were radiation vulcanisates, and rubbers containing metal oxides. Tarasova et al.^[81] observed that irradiation of rubbers in the absence of oxygen and other impurities produces solely carbon-to-carbon cross-links and the number of these cross-links is proportional to the radiation dose. In irradiated vulcanisates, the number of broken bonds is found to be almost independent of the initial number of cross-links. This suggests that thermal relaxation in radiative vulcanisates is preferentially due to rupture of the molecular chains themselves since the number of active network bridges is independent of the degree of cross-linking. In fact, Tarasova and Dogadkin^[81] found the cross-link density to increase notably by thermal relaxation in rubbers vulcanised by irradiation. This was thought to arise from the formation of free radicals, which become partly stabilised either by reactions with radicals of low molecular weight or by formation of intramolecular ring systems. Carboxylated metal oxide containing rubbers behave differently during thermal stress relaxation^[81]. Although, in the case of these vulcanisates, the relaxation constant also falls with the number of cross-links, the number of bonds broken rises linearly with the initial number of cross-links. This suggested that thermal relaxation in vulcanisates of carboxylated rubbers could be due, not to rupture of chains, but to rupture of salt cross-links. To prove this, Tarasova et al.^[81] measured the molecular weight of the rubber before and after thermal stress relaxation. Salt cross-links in vulcanized carboxylated rubbers are relatively easily broken by swelling in organic solvent containing acid, which results in the complete dissolution of a vulcanisate. When vulcanised carboxylate rubber was heated at 100°C and 40% elongation up to the point of complete relaxation of stress and then dissolved, the molecular weight of the dissolved rubber was found to be nearly equal to that of the original rubber before vulcanisation. This behaviour led Tarasova and Dogadkin^[81] to conclude that thermal stress relaxation in vulcanised

carboxylated rubbers containing salt cross-links is due to rearrangement of cross-links. When a carboxylated rubber containing metal oxides are irradiated in vacuum, then additional salt cross-links and hydrocarbon-hydrocarbon cross-links form. Although irradiation causes a drop in the relaxation constant, the number of broken bonds remains almost equal in all vulcanisates containing the same number of carboxyl groups. Tarasova and Dogadkin ^[81] concluded that thermal degradation involves the weakest, or the most mobile, cross-links if the network is built up of various types of cross-links.

Tarasova and Dogadkin ^[81] demonstrated through their results that the slope of the linear part of the relaxation curves decreased with the number of carbon to carbon cross-links (i.e. proportional to irradiation dose). At the same time, the initial, non-linear part of these curves (where the stress relaxation does not obey the exponential law) became smaller as the irradiation dose is increased. Furthermore, the rate constant for relaxation in air is also a function of the number of cross-links, but in contrast to experiments in vacuum, the number of bonds broken is independent of the number of cross-links. This behaviour was taken as an indication that relaxation in air preferentially proceeds by chain scission rather than by oxidative degradation.

Tarasova and Dogadkin ^[81] used the work conducted to examine the relation between the relaxation rate and the number of cross-links and made it possible to determine sites at which the heated vulcanised network were ruptured by mechanical means and by oxidation reaction. Thermal degradation by purely mechanical action in the absence of oxygen, takes place at the weakest points of the lattice, at polysulphide cross-links in rubber vulcanised with sulphur in rubbers vulcanised by irradiation cross-links are stable and degradation proceeds by chain scission.

Tarasova and Dogadkin ^[81] concluded that thermal relaxation of stress fundamentally obeys first order kinetics and the rate constants depend on the energy of the broken bonds. The activation energy calculated from the temperature dependence of the rate constant could be taken as a characteristic of the broken bonds. Furthermore, they found the relation between the rate constant and the initial number of cross-links, was evidently explained by the circumstances that the relation between stress and number of cross-links is non-linear and that the broken bonds differ in energy.

Heating stressed vulcanisates in the absence of oxygen results in purely thermal degradation of the three dimensional network, accompanied by the reduction of the stress. This process is called thermal relaxation. Thermal relaxation of various rubbers such as natural rubber, polybutadiene, isoprene, butadiene-styrene and carboxylated rubbers vulcanised with various vulcanising mixtures and methods, including vulcanisation by irradiation, is first order. The rate constants of thermal relaxation decrease with network density. The product of the rate constant and the initial number of cross-links that yield the number of bonds broken per unit time, is independent of the network density if degradation proceeds by rupture of the

molecular chains. This product increases with the network density if relaxation is due to rupture of cross-links ^[81].

Tarasova and Dogadkin further concluded that examination of the relationship between the relaxation rate and network density is a way to find the points where the network is ruptured. Thermal relaxation in rubbers vulcanised with metal oxides is due to rearrangement of the salt cross-links by exchange. In this case, the molecular chain remains intact, and the number of cross-links remains unaltered. Thermal relaxation in rubbers vulcanised by sulphur is due to preferential rupture and rearrangement of the weak polysulphide cross-links. The new cross-links contain a smaller number of sulphur atoms. In this case the number of cross-links may either rise or fall, depending on the secondary reactions of polymer radicals formed.

The rate of stress relaxation in NR vulcanisates is known to decrease markedly as the degree of cross-linking increases ^[68,77,80]. In fact, for very highly cross-linked materials the relaxation is often too small to measure accurately. This behaviour is observed for natural rubber materials vulcanised using various cross-linking agents, and therefore the nature of cross-links has been found not to influence the relaxation process. At extension of 250% or more, the stress decay becomes larger and less accurately proportional to the logarithm of elapsed time. The increase in the rate of relaxation at high extension is attributed to a different relaxation mechanism, i.e. the gradual ordering of parts of the molecular chains into a crystalline arrangement.

For filled NR vulcanisates, the rates of stress relaxation observed are seen to be large at all extensions, and of the same order of magnitude as those observed in the unfilled materials at high extensions. It has been suggested that the deformation of a filled system is virtually confined to unrestrained regions having similar properties to the corresponding unfilled vulcanisate. For example, in carbon black filled NR, the amount of unrestrained material is assumed to increase with the increasing deformation by breakdown of the rubber/carbon black associations that cause the relative rigidity of the original material. The extension in the unrestrained regions is, however, quite high even when the imposed overall extension is small. In actual fact, in order to cause the transformation from rigid to unrestrained material in reinforced vulcanisates, the extension in the unrestrained region appears to approach the breaking elongation of several hundred percent. Therefore, even at small imposed extensions, the regions taking part in deformation are very highly strained and the relaxation is expected to proceed as in highly stretched unfilled rubber, as found experimentally stress relaxation in filled systems takes place primarily in the unrestrained regions at rates appropriate to the high local strain there ^[80,82].

1.4.6.4 Measurements of stress relaxation at ambient temperatures.

At ambient temperatures, the rate of chemical relaxation in general purpose rubbers (e.g. natural rubber, butyl, polychloroprene, SBR), is extremely small and the relaxation is dominated by physical processes, except at very long times^[82]. In particular, the relatively slow rate of oxidation of many polymers means that aerobic reactions are essentially negated under these conditions. In fact, at ambient temperatures and over short period of times, only physical processes and chemical reactions that proceed very rapidly at ambient temperature can be responsible for stress relaxation. The physical processes involve reorientation of the molecular network, the disengagement and rearrangement of entanglements, and the breaking of bonds due to secondary valence forces. If the additional restriction of operating only at low extensions, (~100% or less), is applied, complications due to phase changes in the polymer, such as stress crystallisation, can also be excluded.

Mandell et al. ^[89] applied the method of reduced variables using short time data to predict very long time stress relaxation of natural (NR) and nitrile (NBR) rubbers. Their tests were conducted at room temperature, in air, over time periods ranging up to 16 years. The relatively short term stress relaxation measurements used in the reduced variables time-temperature superposition estimates were conducted in air at ambient temperatures. They found that the long term stress relaxation of NR and NBR could conveniently be shown by a plot with a double abscissa scale, one in units of $\log(\text{time})$ and other in units of time. When experimental data from their work for NR and NBR were plotted using the above method, they discovered the first scale yields a linear relation at short times, and the second, a linear relation at long times. The physical relaxation was essentially linear with logarithm of time. Under all normal conditions, physical and chemical stress relaxation would occur simultaneously. Mandell et al. ^[89] concluded that at typical ambient temperatures, the rate of chemical relaxation in rubbers like NR and NBR is very small, and that the relaxation behaviour is dominated by physical processes except at very long time ^[89].

Porter ^[68] measured the relaxation in a strip of rubber at a fixed (room) temperature after a linear extension of 100% had been applied to it. He found a time period of 10 – 15 minutes was convenient for such measurements. Porter suggested that in the absence of physical processes such as crystallisation and other phase changes, relaxation is due to internal changes in the conformation or topology of chains, including the release of slipping chain entanglements, that is, to viscoelastic processes. Where this is the case, relaxation of stress is generally characterised by being accurately proportional to the logarithm of elapsed time^[68]. Therefore, when load or stress, (as percentage of the peak load), is plotted on the y-axis against logarithm of time, a straight line should be obtained. In actual fact, when plotting load

decay versus log time, it can be noticed that the stress relaxation lines do not appear to meet the 100%-load (or 100%-stress) point after the same time. Close examination of many data plots showed that this was at least partly due to the fact that relaxation does not obey the log (time) rule at times less than 1 to 2 minutes, the data curving down from the 'origin' at very short times ^[68,81]. Part of this effect is probably due to delay in the response time of the measuring instrument and to inaccuracy in the timing of the peak load point. This deviation from linearity at very short times is generally more pronounced the faster the relaxation rate. Porter ^[68] proposed that the extent of this deviation be characterised by the apparent load drop at one minute after peak load is attained. This 'initial load drop' could be measured by the intercept of the relaxation line with the $\log(\text{time})=0$ axis. The rate of stress relaxation can then be conveniently measured as the percentage loss in stress (or load) per decade of time, which can be obtained by the slopes of the line ^[68, 77, 80, 82].

In cross-linked natural rubber films, the rate of relaxation falls progressively as the degree of cross-linking is increased in the vulcanised latex. In fact, Porter ^[68] observed that for any particular type of cross-links in NR, the rate of stress relaxation varies linearly with the inverse of the degree of cross-linking. That is, it varies directly with the average chain molecular mass, $M_{c, \text{phys}}$, between neighbouring cross-links^[68]. This applies equally to bulk rubber and latex vulcanisates. This behaviour is exemplified in **Figure 1.6**, which shows the relaxation behaviour of three pre-vulcanised natural rubber (NR) latex samples of different degrees of sulphur cross-linking referred to as low pre-vulcanised(LR)<medium-prevulcanised (ML) < highly pre-vulcnised(HR).

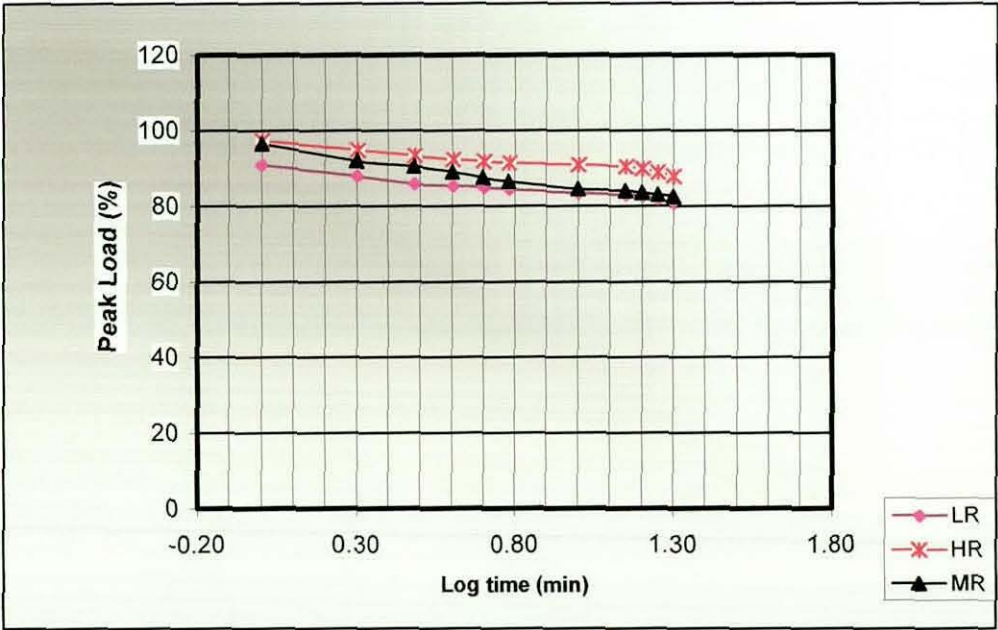


Figure 1.6 Stress relaxation of pre-vulcanised NR latex films at 100% extension ^[68].

1.4.6.5 Stress relaxation in block copolymers.

In block copolymers, the hard glassy domains act as network tie points for the elastomeric soft blocks which are the continuous matrix. The rubber network is held together by the physical intermolecular interactions in the domains and is only weakened when the domains are softened by heating above the glass transition of the hard blocks ^[25].

The improvement in properties that result from domain formation in block copolymers, is accompanied by an increase in the complexity of the relaxation mechanisms that are involved in mechanical deformation. Depending upon the two-phase structure, the separate and distinct domains may relax by different independent mechanisms ^[74, 90].

Tobolsky et al. ^[74] investigated the stress relaxation behaviour of two PU rubbers Vulcallon (polyester), and Adiprene (polyether) using a temperature range of 90 to 130°C and an extension of 20%. They carried out both intermittent as well as continuous measurements. Tobolsky ^[74] discovered that all samples appeared to approach zero stress asymptotically and that the greater portion of decay took place within two cycles of logarithmic time. This behaviour they concluded was similar to that shown by polysulphide rubber, natural rubber and silicon rubber.

Colodny and Tobolsky ^[85] also studied the stress relaxation of polyurethane rubbers and found that stress decay at constant extension in the temperature range 100-140 °C, could be expressed by the formulae $F(t) / F(0) = \exp (-t / \tau_{ch})$, where $F(t)$ is the stress measured at time (t) , $F(0)$ is the initial stress, and τ_{ch} is a constant of the system which depends on temperature. From their work, Colodny et al. ^[76] deduced that in a rubber network obtained by treating a hydroxyl-terminated ethylene-propylene adipate polyester with methyl triphenyl triisocyanate, the stress decay in the temperature range of 100-140°C was due to a cleavage of urethane linkages.

Singh and Weissbien ^[73] used a plot of $\log f(t) / f(0)$ versus time to study the thermal stress relaxation of polymeric materials. They discovered that with polyurethanes, such plots deviate markedly from linearity, suggested the inadequacy of a simple, viscoelastic Maxwell model in describing the thermal stress relaxation of these systems. They postulated from the nature of this deviation that the tendency of the plots of $\log f(t) / f(0)$ versus time to become linear at extended periods of time, suggests that these data might better fit a multi-component Maxwell model. Singh and Weissbien ^[73] prepared a series of polyurethane materials based diol or triol chain extenders. They then went on to measure the stress relaxation of their polyurethanes at constant 10% extension at 120°C. When they plotted $\log f(t) / f(0)$ versus time they discovered that although a pronounced non-linearity was apparent in the first part of all the plots, the

plots do appear to become linear after an extended period of time. They concluded that their data might better conform to a multi-component Maxwell model, expressed mathematically as:

$$E_r(t) = \sum E_{ri}(0) \exp\{-t/\tau_i\}$$

Singh and Weissbien ^[73] applied the above equation and assumed that the observed decay in modulus, $E_r(t)$, was due to m concurrent degradative processes, each functioning as a Maxwell element with its own modulus contribution E_{ri} and characteristic time constant τ_i . According to this model, the $\log f(t)/f(0)$ versus time function should approach linearity in the relaxation time regions where all but the slowest process have dissipated. They proposed this concept was feasible in view of ever-present possibility of inadvertently forming allophanates, urea, and biuret linkages when synthesising polyurethane materials. Simultaneous cleavage of these various types linkages would probably contribute to the observed stress relaxation behaviour. In addition to this possibility, other physical processes such as viscous flow, stress crystallisation etc, might also contribute to the observed decay. They used the above equation to resolve the different molecular processes that are responsible for stress-decay. In their work, Singh et al. ^[73] used a procedure previously employed by Tobolsky et al. ^[69] in which they fitted the data obtained for a polyurethane chemically cross-linked with trimethylol propane into the equation $E_r(t) = \sum E_{ri}(0) \exp\{-t/\tau_i\}$. They then extrapolated the linear portion of $\log E_r$ versus time to zero time. The linear portion of the plot they suggested was the contribution to the modulus decay arising from the slowest Maxwellian process, i.e. the one with the longest relaxation times τ_1 , and the intercept of the line gives the magnitude of the initial modulus component, $E_{r1}(0)$, established by the structural elements involved in this process. They calculated the slope of this line to obtain τ_1 . Similarly, a plot of $\log[E_r(t) - E_{r1}(0) \exp\{-t/\tau_1\}]$ versus time also approached a straight line which gave the values of τ_2 and $E_{r2}(0)$ of the next slowest process calculated from the slope and intercept, respectively. This procedure they repeated until the relaxation parameters of all resolvable processes are evaluated.

In a separate work Tobolsky and Colodny ^[76] carried out a series of experiments in which the relaxation behaviour of polyurethanes and poly(urethane-ureas) of various compositions were compared. From their experiments, they concluded ^[76] that materials consisting of urethane linkages only have relaxation times five times greater than those with 50% urethanes and 50% substituted urea and biuret groups. In contrast, samples containing only polyester urethane with no cross-linkers, and samples with polyester, urethanes and triol cross-linkers, would decay at a rate ten times that of urea and biuret containing groups. Since the relaxation time is inversely proportional to the rate constant for the chain scission reaction, it appears that the

rate constant for the dissociation of the urethane group is less than one tenth that for the combined effect of the substituted urea and biuret groups under these experimental conditions.

In a different study, Singh et al.^[91] synthesised well-defined polyurethane materials using polyesters, 2,4-toluene diisocyanate, and trimethylol propane in such a way that the level of urethane groups per network chain could be controlled. They then went on to examine the thermal cleavage of these networks by stress relaxation. The analysis of their data revealed two exponential decay processes differing in rates by about an order of magnitude. The rate of the slower process, which dominates the overall stress decay, was shown to be directly dependent on the content of urethane groups per network chain: the greater the number of urethane groups in the network, the steeper the slope of $\log E_r(t)$ versus time curve. The more transient stress-decay process, however, was not definable, and Singh et al.^[91] attributed this to the cleavage of one or more types of weak linkages found in small but variable proportions in the different polyurethane networks. Furthermore, in determining the rate constant and the thermodynamic constants associated with the urethane cleavage process, they discovered that the cleavage rates of the urethane groups differed depending on their position, and their adjacent groups.

Tobolsky et al.^[189] showed that stress relaxation in a particular sample of cross-linked polyurethane elastomer could be represented by a sum of two exponential decay terms. Polyurethane materials were found by Tobolsky and MacKnight^[189] to undergo non-oxidative stress relaxation at elevated temperatures even though cross linked. This phenomenon was referred to as chemical stress relaxation, or chemical flow and had previously been observed in polysulphide and silicon rubbers. Tobolsky et al.^[189] calculated the activation energy for the decay processes within cross-linked polyurethanes, using the sum of two exponential decay terms and presented a theoretical explanation. Tobolsky et al.^[189] concluded that although it is possible to identify two stress decay processes and to obtain activation energies for them, it was not possible to give certain chemical identification of the linkages responsible for the stress decay^[189].

Harget and Hepburn^[84] investigated the stress relaxation of several aliphatic polyether ureas that consisted of various bulky diamine chain extenders. They performed both continuous as well as intermittent stress relaxations at elevated temperatures (50-125°C), and in the presence of air as well as in a nitrogen atmosphere. They^[84] discovered that bulky symmetrical diamine groups show significantly low stress relaxation at elevated temperatures, and the more bulky the diamine the greater the stress retention at 125 °C.

1.5 Natural Rubber

As this research relates to the analysis and characterisation of water borne polyurethanes and poly(urethane-ureas) which are processed from water and are intended to have physical properties approaching natural rubber latex films, it is of interest to provide an account of natural rubber chemistry and its characteristics.

Natural rubber latex is a colloidal dispersion of cis-polyisoprene hydrocarbon in an aqueous serum^[92, 71]. Natural rubber latex consists of a dispersion which is composed of 86% rubber hydrocarbon, 10% water, 1% proteins and 3% lipids, by weight. The rubber hydrocarbon is 1,4-polyisoprene with a molecular weight of one million. Unlike most synthetic polymer latexes, NR latex has a wide range of particle sizes with diameter 0.01-5 μ m and an average between 0.25 and 0.8 μ m. Although the majority of particles have a diameter of less than 0.2 μ m, it is particles with diameters greater than this which contain the majority of rubber, over 90%. Particles are stabilised by an adsorbed layer of proteins and phospholipids. NR latex is normally compounded, and the compounding ingredient are usually ground in a mill with water and a dispersing agent to give a dispersion of between 30% and 70% by weight. The process of compounding does not affect the particle size and hence the viscosity remains the same^[92].

1.5.1 Processing of Natural Rubber Latex^[92]

In all latex processes a stable colloidal system is maintained until, at the desired time, it is made unstable and converted to a solid product. Preserving the balance between too much and too little stability constitutes a challenge to latex technology.

The compounds used in natural rubber latex product manufacture may contain four or more disperse phases and are highly polydisperse, with several surface active species, and have an aqueous phase of high ionic strength. These factors give natural latex compounds a relatively low colloidal stability, but equally facilitate conversion into solid products in a variety of ways.

The dominant area of manufacture using NR latex is the production of dipped goods. These include a wide range of gloves and catheters, which are produced by immersing a former into the latex compound. This produces a continuous film on the former and maintain film integrity during vulcanising stage. Natural rubber latex is outstanding in this respect as it forms strong films which can withstand rapid drying. Also, natural rubber products are

exceptional in terms of tensile strength and elongation coupled with quite low modulus, which are ideal characteristics for products such as gloves, condoms and catheters. The main constituents of the vulcanising systems are sulphur, zinc oxide and the accelerators. There are many variations and donors of these chemicals that are often used in the NR latex industry. However, their standard functions are that sulphur is the cross-linking agent and its level is responsible for the degree of cross-linking in the vulcanisate and hence the modulus and hardness. The accelerators such as zinc dialkyldithiocarbamates give fast vulcanisation rates with sulphur at 100C, and there are other types of accelerators which allow lower temperature curing. Zinc oxide is essential for latex vulcanisation as it provides further activation of vulcanisation and contributes to the gelation process.

1.6 Synthetic Latexes

Synthetic latexes, like the natural rubber latex from which natural rubber is produced, compromise a colloidal dispersion of small polymer particles stabilised in an aqueous continuous phase by amphiphilic molecules. Synthetics latexes are used in two forms: dry powders obtained after water elimination and latexes used directly to form films by coalescence.

These latexes have become of growing importance in comparison with polymer solutions because they present the major economic and ecological advantage of avoiding the use of organic solvents. Application of these kinds of latexes are found in the fields of paints, adhesives, paper and coating industries, and reinforcing fibre treatment. The latex is cast on a support, water evaporates, and particles lose their shape and coalesce. The result is a continuous polymer film. Thus, the essential properties of latexes are the ability to form films and adhesion of films onto various substrates. The types of synthetic latexes available produced are many and varied, and almost all synthetic latexes of industrial importance are produced by free-radical addition polymerisation of olefinically-unsaturated monomers in aqueous dispersion media ^[93]. The majority of synthetic latexes contain copolymers rather than homopolymers. This is because polymer properties intermediate between those of the respective homopolymers are usually required. An important reason is the inherent incompatibility of different types of homopolymers at the molecular level. The types of synthetic latexes that have gained commercial importance are: styrene-butadiene copolymers, acrylonitrile-butadiene, polychloroprene latexes, vinyl acetate, and copolymers, the family of latexes commonly known as acrylics, and vinyl chloride-vinylidene chloride latexes.

1.6.1 Methods of producing synthetic latexes ^[93]

There are many processes by which synthetic latexes are made. The first type of process is appropriately referred to as the phase inversion technique. Increasing amounts of an aqueous phase are dispersed into the polymer. Initially, the aqueous phase diffuses into the hydrophilic polymer and a dispersion of aqueous medium in polymer forms. As more aqueous phase is incorporated, so it becomes increasingly likely that an inversion of phases will occur, thereby creating the desired dispersion of the polymer in an aqueous medium. It is necessary to incorporate in one or both of the two phases surface active substances which are able to function as a dispersing agent and as a stabiliser for the dispersions which are formed, i.e. for both the water in polymer dispersion which forms initially, and the polymer-in-water dispersion which forms subsequently. The polymer is usually a rubber in character, and so both the mixing with a surface-active agent and the progressive incorporation of the aqueous phase can be effected using conventional rubber-mixing equipment.

The second process is called the mutual solvent technique. This is applicable only to more polar types of polymers. The polymer is dissolved in a water-miscible solvent. This solution is then mixed with water to give a three-component system comprising a dispersion of the polymer in an aqueous phase with the polymer solvent distributed between the two phases. The final stage of the process is the removal of the polymer solvent by evaporation. Unless the polymer is effectively self-dispersible in water, it is necessary to include a colloidal stabiliser in the components used to form the dispersion.

The third type is referred to as the solution-emulsification technique. In this process, the polymer is dissolved in, or is swollen by, a volatile solvent to form a solution. The polymer solution is then emulsified in water with the aid of one or more surface-active substances which function as a dispersing agent, as a colloid stabiliser for the emulsion which is formed, and also as a colloid stabiliser for the eventual latex. The final step is removal of the solvent from the emulsion, usually by vacuum or steam distillation. A dispersion of the polymer in an aqueous medium should be left.

The fourth type of process is known as the self-dispersion technique ^[93]. The polymer is functionalised with ionisable groups, which may be either acidic or basic. The polymer is then dispersed in an aqueous phase which contain an alkali or an acid, accordingly, as the polymer is functionalised with acidic or basic groups. The self-dispersing polymer systems are the ones most relevant to polyurethane dispersions and to this research. These are often referred to as ionomers. The following section provides an account of their chemistry and methods of manufacture in greater detail.

1.7 Ionomers

An ionomer can be defined as a copolymer consisting of a polymer main chain with a minority of the repeat unit carrying acid or a tertiary nitrogen groups that are completely, or partially, neutralised or quaternised, respectively. The chemical structure leading to an ionomer consists of a pendent salt group attached to the polymer chain ^[94-96]. Typical ionomer structures can be depicted as follows:

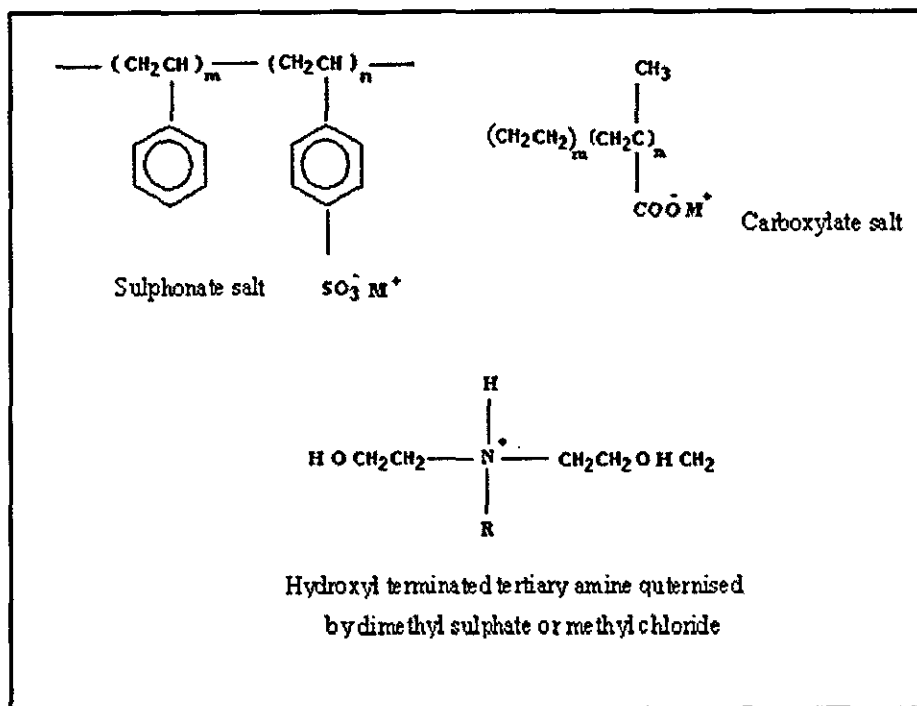


Figure 1.7 Chemical structures of typical ionomers

In cases where the level of the salt group is very high, i.e. where every monomer repeat unit has a pendent salt group such as in poly(acrylic acid), the polymers are generally water soluble. Such systems are referred to as polyelectrolytes. Ionomers, however, tend to have a lower level of ionic content and ionic bonding compared to polyelectrolytes. Nevertheless, the presence of ionic groups impart unusual characteristics onto the polymer that results in a class of materials of scientific importance. In these polymers, the pendent ionic groups interact to form ion-rich aggregates contained in the non-polar polymer matrix. The resulting ionic interactions strongly influence polymer properties and applications. Figure 1.8 shows a schematic representation of the ionomer structure.

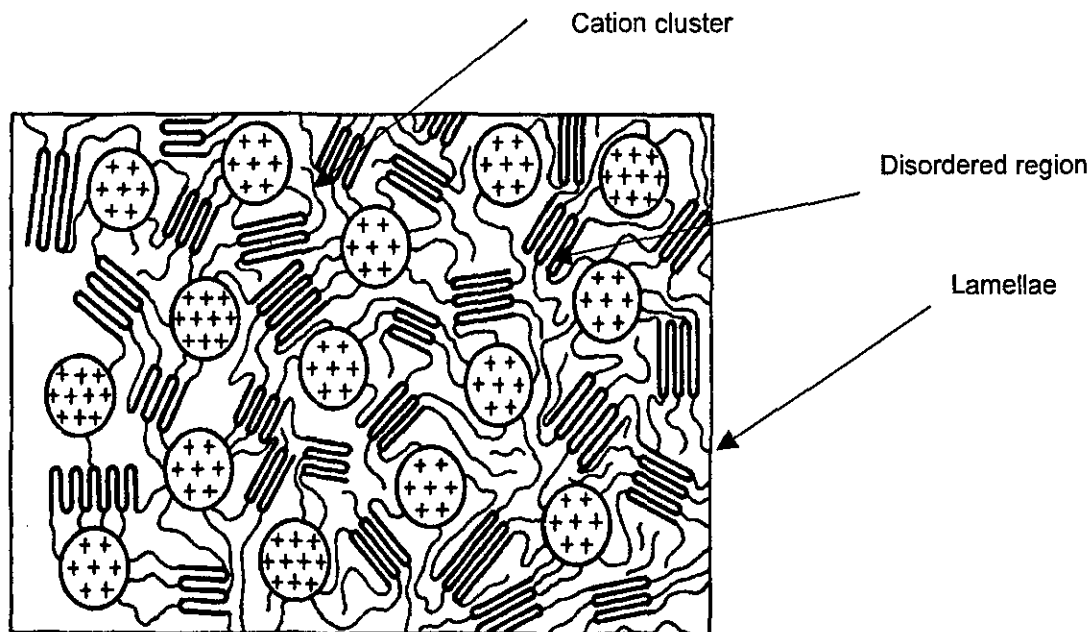


Figure 1.8 Schematic representation of the three-phase structure of a dry ionomer, consisting of cation clusters, lamellae and disordered regions ^[95,97].

The ionic interactions and the resultant polymer properties are dependent on the type of polymer backbone, (plastic/elastomer) the ionic functionality, weight percent of the ionic moiety 0 to 10 wt%, and the type of ionic moiety used. Examples of these are be carboxylate, sulphonate, phosphonate. Another factors influencing the properties are the degree of neutralisation which can vary from 0 to 100 wt%; and the type of cation (amine, metal, monovalent, multivalent) ^[95,98,99,100]. The ionic content, degree of neutralisation and type of cation dominate the properties of the resultant polymer system. With this range of variables, the spectrum of polymer properties within the ionomer family is extremely broad.

One of the most commercially successful ionomers are polyurethane ionomers. These are unique polymeric systems that are extensively used in industry and are collectively known as polyurethane dispersions (PUDs). Polyurethane ionomers are suitable for the preparation of aqueous two-phase systems, and have, therefore, gained particular importance in the coatings and adhesives industries ^[94,96,101]. These polymers which contain a hydrophilic ionic site between predominantly hydrophobic chain segments, are self-dispersing under favourable conditions, and spontaneously form stable dispersions in water without the influence of shear forces and in the absence of dispersant. Three types of PU ionomers have been reported according to the ionic charge on the main polymer chain, i.e. cationic, anionic and zwitterionomers. PU ionomers exhibit considerable differences in morphology ^[94,102-109] and physical properties in comparison to their respective conventional polyurethanes involving the same polyol (or polyamine), and diisocyanates. Polyurethane ionomers are the subject of the *current research study*, and hence their historic development, chemical structure-property relations as well as their colloidal characteristics will be discussed fully in the following sections.

1.8 Historical development of waterborne PU dispersions

Polyurethane dispersions are colloidal systems with unique characteristics that arise from their method of synthesis. There are two recognised methods of producing waterborne colloids ^[93].

1) Aqueous polymer dispersions prepared by emulsion polymerisation; and (2) dispersions of preformed polymers in water. The first method of preparation applies to chain reaction polymers synthesised by free radical reactions. Examples of this type of polymer are acrylic copolymers, vinyl-acrylics, styrene-acrylics, and styrene-butadiene^[93]. Emulsion polymers (latexes) are well established and the general method of synthesis involves a free radical polymerisation in water using a water soluble free radical initiator and surfactants to nucleate and stabilise the growing polymer particles. The product is a high molecular weight polymer in the form of a well-defined colloidal dispersion. The process and products have been well documented and extensively researched ^[93,110-111]. Examples of the latter class of colloids are aqueous polyurethane dispersions, aqueous polyesters and epoxides. This type of system is prepared by a different technology in which the mechanism of synthesis is step growth polymerisation and the dispersion in water takes place in a separate stage, using a fully reacted polymer.

The first isocyanate-based dispersion was developed as early as 1943 by Schlack ^[96,112]. In his work, a diisocyanate was emulsified in water with an equivalent amount of a diamine under vigorous stirring. The amine diffused into the diisocyanate dispersion to produce a finely dispersed polyurea suspension. To stabilize the dispersion, emulsifiers and protective colloids were used. Later on further research was carried out by Dupont in 1953, where instead of a simple isocyanate, NCO-terminated prepolymers made from polyethers and diisocyanates were prepared, and the viscosity was reduced using toluene to ease dispersion. The prepolymer in the presence of an emulsifier surfactant, was dispersed at low temperatures with high shear force while at the same time it was extended with a diamine. This method of dispersion resulted in a slightly branched poly(urethane-urea) having a high molecular weight suitable for coating textile or leather. The major disadvantage of this process is that the resultant dispersion was of coarse particle size of about 1 μm in diameter. The particle size affected film formation and inevitably the stability of the dispersion, and after a few months, an irreversible phase separation and coagulation occurred. The problem of stability and film forming properties were then overcome by use of specific hydrophilic polyethers (polyethylene glycol) or ionic groups which made the prepolymer self-dispersing with no high shear mixing or additional emulsifiers being required ^[96,112-115]. Typical examples of ionic monomers are given in Figure 1.9. In 1960, Dieterich ^[96] introduced the method of incorporating internal emulsifiers to produce PU dispersions. There were several approaches, some of which would require the use of chain extenders either diol containing tertiary amine or a diamines containing secondary amine groups. The tertiary amine could be quaternised by an alkyl, or aryl halide, or organic compounds containing an acid group. Chain extenders

containing secondary amines could be combined with sultones or lactones ^[116] to produce a polymer with reactive sulphonic or carboxylic acid side groups. These acid groups may be subsequently neutralised with various cations to produce anionomers. Ions can also be incorporated by using either a diol or a diamine chain extender that contain a pendent carboxylic or sulphonic acid ^[110, 117-119] group, which is subsequently neutralised with various cations to produce anionomers. The ionic groups exert a strong influence on the physical properties of the polymer by influencing the microstructure and domain morphology. These emulsifier-free ionomer PU dispersions are characterised by high mechanical and chemical stability, excellent film-forming properties, good adhesion and the potential for a wide variation in composition and property levels. The type and amount of ionic groups influence not only the properties of the dispersion, but also the performance of coatings and adhesives after the evaporation of water ^[120]. Furthermore, the process used to prepare waterborne PU ionomers can strongly influence their properties due to the effect the process has on the composition and molecular build up of the polymer. Except for the presence of the hydrophilic monomer and its method of introduction into the polymer backbone, the mechanism of synthesis for aqueous polyurethane dispersions is essentially step growth reaction like that of conventional polyurethane materials. In nearly all cases, the dispersions are made by synthesizing a polyether / polyester prepolymer with terminal NCO groups that can be mixed with water to yield reactive O/W emulsions, particularly when the molecular weight of the prepolymer does not exceed approximately 8,000. Figure 1.10 provides an example of the steps involved in the prepolymer methods of synthesis of PU ionomers.

Prepolymers containing ionic centres (ammonium, sulphonium, sulphonate or carboxylate groups) or hydrophilic polyether segments are self-emulsifiable. The isocyanate groups are the commonly available aliphatic isocyanates such as IPDI, H₁₂MDI, HDI, and the aromatic TMXDI (meta), which preferentially react with the hydroxyl group functionality of the polyol and diols. No reaction takes place between the NCO and the carboxylic acid groups of the ionic material. Normally the ionic group is sterically hindered as in the examples dimethylol propanoic and butanoic groups. The butyl and methyl groups in these species provide protection for the carboxylic acid groups by making the reaction sterically unfavourable ^[121]. Also esterification does not occur because this would require strong catalysts and temperatures in excess of 160°C. This means that upon mixing with water, they spontaneously form emulsions with particle sizes that decrease as hydrophilicity increases. Hydrophobic NCO-prepolymer necessitates the use of emulsifiers and high shear forces to disperse them in water ^[96].

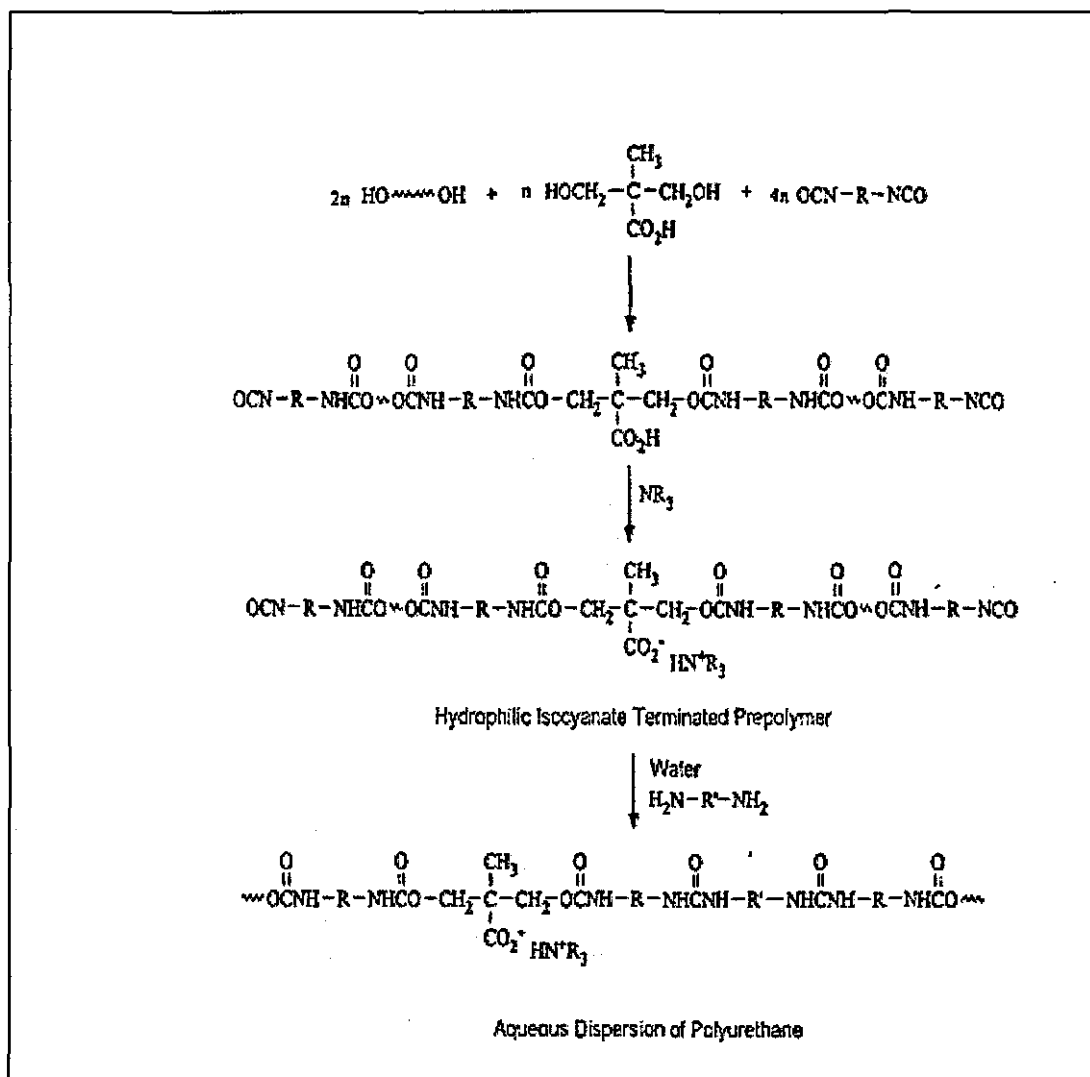


Figure 1.10 Prepolymer method of synthesising a polyurethane ionomer ^[108]

Highly viscous prepolymers must be diluted with organic solvents, which do not necessarily have to be miscible with water. The resulting aqueous emulsions can be further chain extended / crosslinked by the addition of di- or polyamines. Specifically suited are the highly reactive, only slightly water-soluble amines which have the ability to diffuse from the aqueous phase into the prepolymer droplets, thereby functioning as chain extenders/crosslinkers for the pendent NCO group. In the absence of amines, chain extension will occur upon reaction with water. The extent and speed of the reaction of the isocyanate with water depends on the type of diisocyanate and the reaction temperature^[96, 108].

When high molecular weight polyurethane containing hydrophilic centres or external emulsifiers are to be dispersed with water, preferably a solution of these polymers in a hydrophilic solvent is prepared, mixed with water, and the solvent is subsequently removed. Recent processes ^[108, 119] permit the preparation of aqueous polyurethane dispersions

containing high molecular weight polyurethanes without utilisation of a co-solvent. Very low hydrophilic modification of polyurethanes leads to sedimenting aqueous suspensions, which can be utilised to prepare thermoplastic or cross-linked PU powders. The section below outlines the most common processes used to manufacture of polyurethane dispersions.

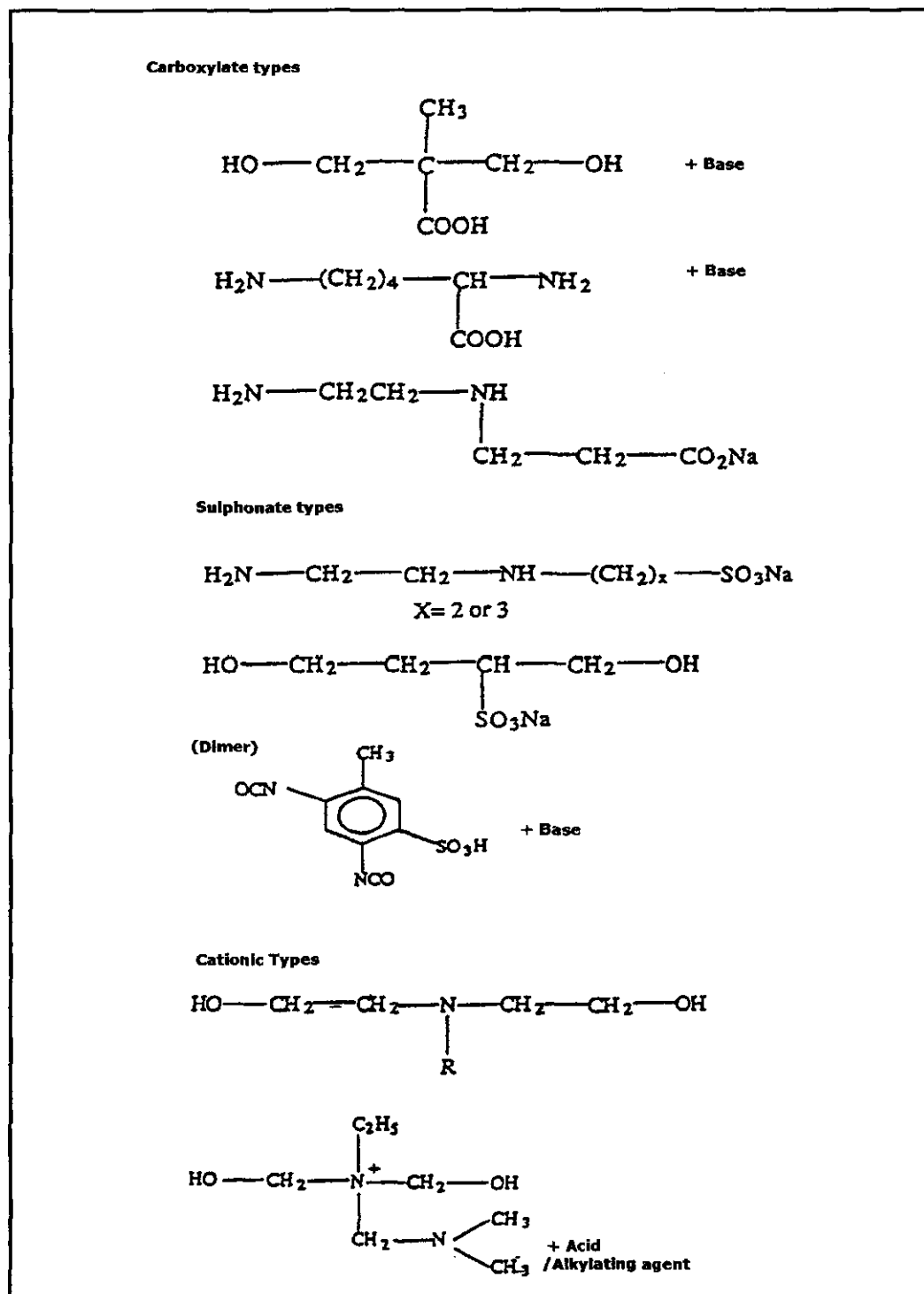


Figure 1.9 Typical ionic monomers used in manufacture of the polyurethane dispersions ^[122].

1.8.1 Industrial preparation methods of waterborne polyurethane dispersions

There are many routes to manufacture WPU's [94,96, 102-109, 123-124, 126-129]. The choice of synthesis procedure depends on the type of product being developed as it often determines the properties exhibited by the final PU dispersion. The most important dispersions are the emulsifier-free ionomer dispersions, which are characterised by high mechanical and chemical stability, excellent film-forming properties, good adhesion and the potential for a wide variation in composition and property levels. Emulsifier-free aqueous polyurethane dispersions can be prepared within a wide range of particle sizes. True high molecular weight polymer solutions or viscous gels on one side and coarse suspension of polymer particles in the millimetre range on the other side, can be synthesised. The preferred range of particle size for a stable dispersion is between 30nm and 800nm and for a suspension between 10^4 and 10^5 nm. Because of the fact that ionically modified particles are swollen by hydration,^[110] film-forming properties are good, even when the products yield very hard films and are applied at low temperatures.

Amongst the ionomers that are most commercially important are the anionics which contain in most cases the sulphonate group (very high electrolyte stability) or in some cases carboxylate groups (with very low hydrophilicity after baking). They can be blended with other common aqueous polymer dispersions, as well as with additives and pigments without any problems.

Cationic polyurethane dispersions are also easy to prepare and allow a wide variation of salt group-forming components. They are specifically suited for the preparation of good coatings with good adhesion onto anionic substrates (glass, leather). Aqueous solutions of bisulphite-blocked polyether prepolymers, as well as the corresponding prepolymers in organic solvents, are used for the shrink-proof treatment of wool. The following preparation processes have gained technical importance.

1.8.1.1 Acetone process

In the acetone process, a solution of high molecular weight polyester poly(urethane-urea) ionomer is prepared whereby a sulphonate salt is used as the ionic site in the presence a hydrophilic organic solvent, e.g. methyl ethyl ketone, tetrahydrofuran or acetone^[96,108]. In this process, the solvent is used to control the viscosity during the chain extension step. The solution is subsequently mixed with water and then the organic solvent is removed by distillation. An aqueous solution, or dispersion, of the ionomer is obtained. Depending on ionic group content and concentration, the dispersion will be formed either by precipitation of the hydrophobic polymer or by inversion of the phases of a primarily formed W/O emulsion. Advantages of this process are the wide variety of possibilities in the molecular weight build-

up of the polymer and the control of the average particle size, as well as the high quality of the final polyurethane product. There are, however, some disadvantages ^[108]. For example, the choice of emulsifiers are limited to the types that are either liquid or soluble in acetone. Also the process is restricted to predominantly linear polyurethanes, which are soluble in acetone prior to the dispersion step. The resulting coatings are not solvent-resistant. The use and distillation of large amounts of acetone is economically unfavourable. Figure 1.11 provides a schematic representation of the stages involved in the acetone process.

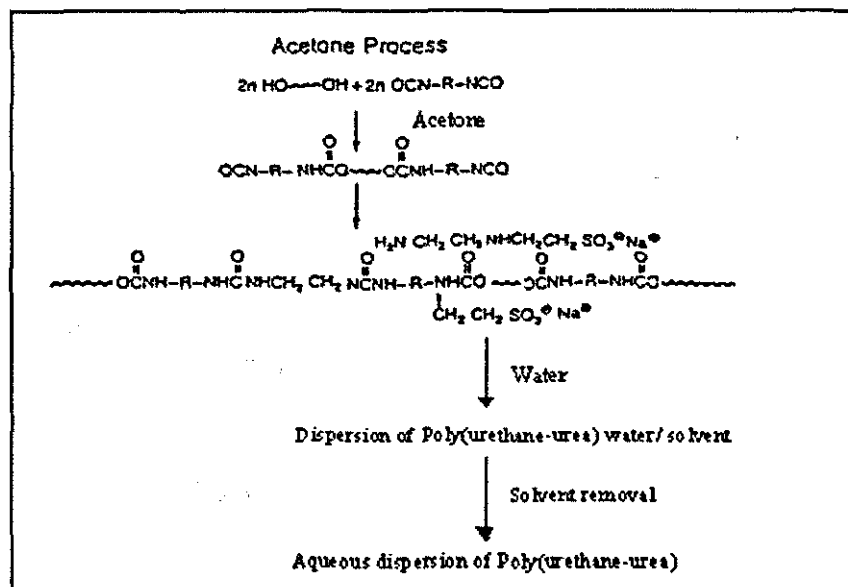


Figure 1.11 : Schematic representation of the acetone process ^[108]

1.8.1.2 The "melt dispersion" process with formaldehyde polycondensation

The reaction of a NCO - terminated ionic modified prepolymer with, e.g. ammonia or urea, results in a prepolymer with terminal urea or biuret groups, respectively. These are methylolated with formaldehyde. Before, during, or after the reaction with formaldehyde, the hot melt is mixed with water, forming a dispersion spontaneously. Afterwards chain extension or cross linking takes place via polycondensation (by lowering of the pH, increasing temperature) ^[113]. Figure 1.12 provides a schematic representation of the process.

1.8.1.3 Ketamine / ketazine process

Diamines and especially hydrazine, are reacted with ketones to yield ketazines. These can be mixed with NCO prepolymers containing ionic groups without premature chain extension.

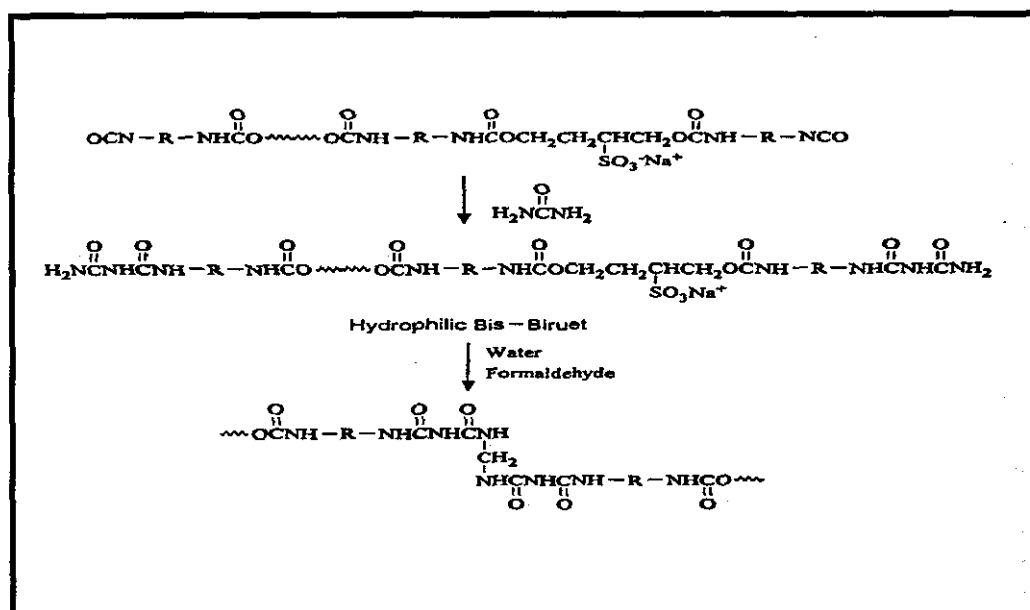


Figure 1.12 Schematic representation of the melt dispersion process ^[108,113]

These mixtures can be emulsified with water even in the absence of co-solvents. Reaction with water liberates the diamine or hydrazine which then reacts with the prepolymer. Figure 1.13 provides a schematic representation.

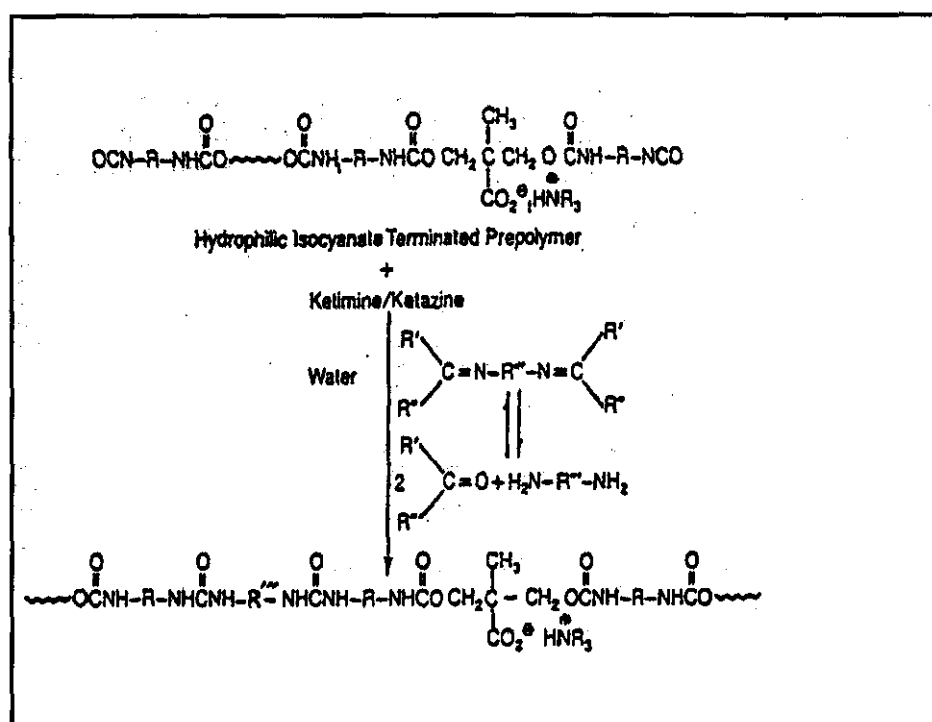


Figure 1.13 Schematic representation of ketamine/ ketazine process ^[108]

1.8.1.4 Non-ionic polyurethane dispersions

Non-ionic dispersions can be prepared similarly to ionomer dispersions if the ionic centre is replaced by lateral or terminal ^[96, 119] hydrophilic ether chains having a molecular weight of approximately 600-1500. The actual dispersion temperature must be kept to below 60°C. This is because polyethylene glycol ether units lose their hydrophilicity with increasing temperature, which will then result in unstable dispersions ^[108]. Advantages of polyurethane dispersions with built-in non-ionic stabilising residues, are their stability against frost, changes in pH, electrolytes, mechanical influences and solvents. Ionic and non-ionic hydrophilic groups exhibit a synergistic effect ^[108]. The total hydrophilicity of the polymer can be lowered while maintaining the good dispersibility.

1.8.2 Stabilization of aqueous latexes

Stability can be defined as the tendency for the system to remain unchanged as a colloidal dispersion as time elapses ^[93, 130-131]. There is usually a thermodynamic tendency for a lyophobic colloid to phase separate because aggregation and coalescence of the particles are accompanied by a loss of interface between the two phases, and the interfacial free energy between the two phases is positive ^[93]. Therefore, the aggregation and coalescence of the particles is accompanied by a reduction in the total Gibbs free energy of the system, thereby providing the thermodynamic motivation for these processes. The molecular origin of the thermodynamic tendency to particle aggregation and coalescence is the inter-molecular forces of attraction which cause molecules in the condensed states of matter to cohere. The particles in a lyophobic solution particles are continually undergoing Brownian motion. This continually brings them into close proximity with each other. The Brownian motion is a consequence of random imbalances in the bombardment of the particles by the molecules of the dispersion medium.

For a lyophobic solution such as a polymer latex, there is, therefore, both a thermodynamic tendency for the particles to aggregate and coalesce, and also a mechanistic pathway by which these processes occur. The latex is stable to the extent that other factors are present which prevent the occurrence of these processes over long periods of time. Therefore, the stability of a lyophobic solution is a consequence of the presence of barriers between the particles that discourage the close approach of the particles. Attractive and repulsive forces operate between two particles of a polymeric latex, and it is the balance between these forces that keep the system stable. Colloid stability is achieved if the balance between attractive and repulsive forces is such that, the two particles are confronted by a potential energy barrier as they approach each other closely. The higher is this barrier, the more stable is the colloid. The

measure of the driving force tending to ultimate particle aggregation and coalescence in a lyophobic solution is the reduction in Gibbs free energy which accompanies these processes. In order for latex particles to move from a stable to an aggregate state, a pair of particles have to overcome the free energy barrier.

To generate stable dispersions, it is necessary to provide repulsive interactions that out weigh the van der Waals attraction between the colloidal particles ^[130,132]. This can be achieved in several ways:

- i) Electrostatic stabilisation which exploits the coulombic repulsions operative between charged, colloidal particles and their respective double layers.
- ii) Polymeric stabilisation which for non-ionic polymers can be accomplished in at least two distinct ways. Steric stabilisation whereby stability is imparted by polymers adsorbed, or attached, to the colloidal particles. Depletion stabilisation, which is imparted by polymer chains in free solution, is another technique. In practice a combination of these methods are used to confer stability.

The best steric stabilisers are amphipathic in character. They take the form of block or graft copolymers composed of nominally insoluble anchor polymers attached to nominally soluble stabilising moieties. Examples of these are the poly(styrene-*b*-oxyethylene) or poly(vinyl alcohol-*g*-vinyl acetate). Whereas typical stabilisers for many non-aqueous dispersions are poly(acrylonitrile-*b*-styrene) and poly(vinyl chloride-*g*-isobutylene).

These anchor polymers prevent desorption of stabilisers under the stress induced by the close approach of a second particle in a Brownian collision. Since such stress could also induce lateral movement of the stabilising chains, complete surface coverage of the colloidal particles is also necessary to optimise stability. This process additionally minimises the possibility of the stabilising moieties attached to one particle absorbing on a second particle, and thus inducing bridging flocculation ^[132].

1.8. 3 Stabilisation of PU dispersions

In polyurethane dispersions stabilisation is achieved by employing a suitable ionic or hydrophilic moiety which is built into the polymer, as discussed in the previous sections. Polyurethane dispersions, characteristically, have a broad particle size distribution ^[110,133], a feature that is attributed to the statistical nature of the step growth polymerisation and chain extension process which results in a broad distribution of chain lengths. In fact, it has been

shown by Dieterich ^[96] that when synthesising PU ionomers a spectrum of molecules are formed. These include polymer molecules with no ionic groups, water soluble electrolytes, and polyelectrolytes in addition to the intended ionomer molecules. This wide spectrum of molecules contribute to the broad particle size and particle size distribution of PU ionomers. The type and the amount of the ionic group influences the properties of the dispersion but also the performance of coatings and adhesives after evaporation of the water ^[96,119,120]. In addition, the process used to prepare waterborne polyurethane ionomers can strongly influence their properties because of the effect the process has on composition and molecular build-up of the polymer.

Aqueous polyurethane dispersions are not monodisperse but show a wide particle size distribution ^[120]. The average particle size diameter can be varied considerable but normally is less than one micron, i.e. 1-1000nm or 0.001 – 1 μ m. The ionic group predominantly affects properties such as formulation stability, adhesion to substrates, water absorption and softening, as well as hydrolytic stability. The volatility of the counter ion is critical, so that counter ions can readily leave the polymer during the drying and the film formation process.

Studies by Dieterich ^[96, 119] prove that in PUR-ionomer dispersions, the ionic centres are located predominantly on the surface of the dispersed particles, while the hydrophobic chain segments form the interior of the particles. Particle stabilisation from this structure can be described by the well known model of the diffuse electrical double layer ^[120]. Figure 1.14 gives a pictorial illustration of a PUR- ionomer consisting of sulphonate anions. At the interface between ionomer particle and water, such a double layer is formed by dissociation of the salt groups.

The ionic constituents of the salt groups, that are chemically bound to the polyurethane remain fixed to the particle surface, whereas their counter ions migrate into the water phase as far as they are allowed by the attractive forces of the oppositely charged particle surface. This forms a layer of decreasing electrical charge ^[96,120]. The interference of the electrical double layers of different particles results in particle repulsion, which in turn is responsible for the overall stabilisation of the dispersion ^[108]. The evidence for this stabilisation mechanism is that PUR-ionomer dispersions coagulate upon addition of inert electrolytes. This behaviour can be explained by a compression of the diffuse electrical double layer caused by the presence of additional ions in the water phase. It results in a reduction of the range of double layer repulsion ^[120].

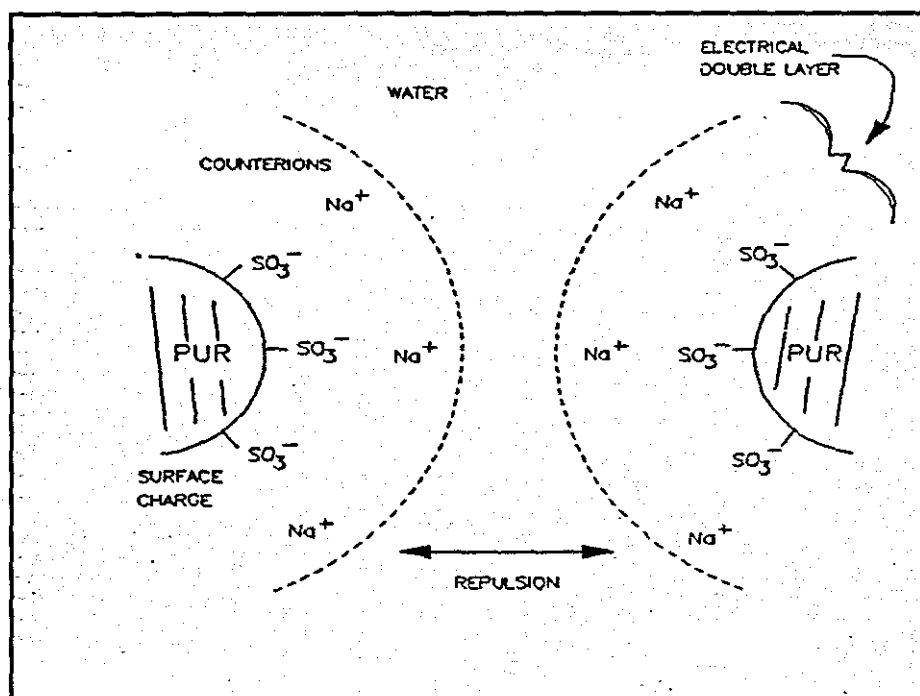


Figure 1.14 Stabilisation of polyurethane particles in water by a electric double layer ^[120]

PUR-dispersions of the non-ionic type have a particle structure similar to that of PUR ionomers. The hydrophilic polyoxyethylene segments should be positioned on the particle surface "stretching" into the water phase. The stabilisation mechanism for this type of particle structure is obviously different from the model of the diffuse electrical double layer. Alternative theories, such as entropic repulsion, can be used to explain stabilisation of the particles. Entropic repulsion results from the fact that upon close particle approach, the freedom of motion of the polyoxyethylene chains in the water phase is restricted, leading to a reduction of entropy. In addition, the hydration of the polyoxyethylene chains plays an important role ^[108,120]. A particle approaching close enough for coagulation would require the desorption of water molecules resulting in considerable short range repulsions. Because of their fundamentally different particle stabilisation mechanisms, non-ionic and ionic PUR-dispersions show considerable differences in their macroscopic behaviour. For example non-ionic PUR-dispersions have technical important advantages over the ionic ones in terms of stability against electrolytes, freezing and shear forces. They also have the disadvantage of being heat-sensitive due to the decrease of polyether solubility in water with increasing temperature. This characteristic is commonly used in industry to promote heat sensitive dipping.

It is important to note that although the two types of PUR dispersions are different in their performance and response to mechanical and chemical influences, mixing the two types of PUR does not lead to an improved synergistic effect of the blended dispersion ^[96, 110,119]. It is,

however, possible to enhance the performance of PUR ionomers by combining ionic and non-ionic hydrophilic groups in one and the same polyurethane. The PUR-dispersions possess good heat stability as well as the whole range of other desirable stability features. Especially important is their insensitivity to addition of electrolytes and other additives. These properties allow a wide latitude of formulation to the end user, including addition of thickeners, flow aids, and cross-linkers. Often mixtures of ionic and non-ionic prepolymers are synthesised. The combination of hydrophilic groups provide a synergistic effect on the dispersion stability and stable dispersions are obtained using a lesser total amount of emulsifiers. Resulting films have a minimum of overall hydrophilicity approaching properties comparable to those of polyurethanes from inorganic solvents.

1.9 Structure - property relationships in PU ionomers

Introducing ions into polymeric materials is a useful way to alter polymer morphology and physical properties due to the great differences in polarity between ionic groups and the polymer backbone^[178,200-201]. The ionic groups further augment the degree of phase separation by acting as reinforcing fillers, or thermally reversible cross links, and ion transport pathways. Factors such as ion content, chain architecture, compatibility between the ion and the matrix, type of cation and anion and thermal and mechanical history can all affect a PU ionomer's microstructure. So a clear understanding of ionomer structure-property relationships is invaluable^[94,96, 102-109, 114-115, 120, 133-142, 144-151]. The sections below aims to provide an outline of structure property relationships in PU ionomers with regards to various microstructures that could exist within the PU ionomer.

1.9.1 Effect of ionic moiety

Chen and Hsu^[102,134, 152] studied the phase inversion mechanism and the effect of emulsification on the properties of the films cast from solution and emulsion of polyether PU anionomers with the potassium ion as the counter ion. They followed the phase inversion phenomenon by conductivity and viscosity measurements during the addition of water. They observed that conductivity and viscosity go through three stages: in stage I, the solution conductivity increases linearly and the viscosity increases slowly. Therefore, as water is added slowly to the ionomer solution, it is absorbed by the carboxylate anions situated on the surface of the hard segment micro ionic latices, causing a separation from their neighbouring chains and aggregates.

Each micro ionic lattice that is formed during the ionization process in solution is an aggregation of unsolvated salt segments stabilised by coulombic forces. Chen and Hsu^[152] postulated that water may also enter into some of the disordered hard domains, since in the

ionisation process some water is normally added to the anionomer solution to reduce the viscosity of the solution, resulting from the aggregation effect of the hard segments. Thus, water may have time to penetrate into some of the disordered hard domains and the extension of chains in the interior of the disordered hard domains then leads to an increase in viscosity. Because of the existence of the two opposing effects, the resulting viscosity increases slightly in stage I.

In stage II, as more water is added, it continuously enters into the interior of the disordered hard segment micro ionic latexes. The hydrophobic segments (soft segments) lose their solvation sheath, and subsequently aggregate to form aligned hydrophobic aggregates which eventually become dispersed phases. The solution becomes turbid and turbidity increases with further addition of water. During this stage as water is added, conductivity increases slightly slower than in Stage I. The solution viscosity increases rapidly to a maximum, indicating incomplete dissociation of the hard segment disordered micro ionic lattice leading to an increased association of the hydrophobic segment.

In stage III, the viscosity drops sharply and the conductivity remains almost constant. This is when phase inversion is complete. There exists a continuous water-rich liquid phase and a dispersed polymer phase swollen with the organic solvent. Most of the ionic groups of the polymer chains subject to phase inversion are situated on the particle surface.

Chan and Chen ^[102] studied the effect of emulsification on the properties of toluene diisocyanate based polyether-urethane cationomers. They examined the conductivity and viscosity variation of their PU cationomers and also observed the three separate stages and viscosity changes on emulsification by following conductivity curves. Through their work, Chang et al. ^[127] also suggested the temperature at which the dispersion takes place influences the degree of phase separation in the cast film.

Hourston et al. ^[121] studied a series of polyether urethane dispersions that were synthesised by combining IPDI, hydrazine and polytetrahydrofuran ($M_n=1000$), and three types of ionic species. These were dimethylol propanoic acid, (DMPA), dimethylol butanoic acid (DMBA), and an experimental sulphonate diol (sodium salt). The acids were neutralised by ammonium hydroxide, or triethylamine. Neutralisation of the carboxylic acid was carried out in one of two ways. The first route was pre-neutralisation. In this case, the carboxylic acid groups in the prepolymer chain were neutralised by adding TEA to the molten prepolymer after which the neutralized prepolymer was added via a funnel to a three-necked round-bottomed flask containing the water and the chain extender. In the case of the inorganic neutralisers, they altered the process and added the neutralising agent to the aqueous phase with the chain extender. In both cases, however, they kept the process of dispersion the same i.e. the

prepolymer was added to the water. Furthermore, they also varied the degree of neutralisation from 40% to 100%, and examined the effects on the dispersion. Their work showed that the particle size decreased significantly with increase in neutralisation of the carboxylic acid groups of the ionic chain extender. This decrease is the consequence of the increasing number of carboxylate anions present, which results in the ability to stabilise a greater total particle surface area. They found the increase in % neutralisation changes the appearance of the dispersion from a white dispersion to an almost translucent solution at high degree of ionisation. The viscosity increased with decreasing particle size as is common for colloidal dispersions. Films tested from their PU dispersions were found to have improved tensile strength from 12 MPa to 23 MPa, as ionisation was increased from 40% to complete neutralisation of the ionic groups. The ionic sites augment the interchain interactions between ionic centres and the counter ions. However, because the ionic component contributes to the hard segments, interchain interactions mainly occur between hard domains. The tensile strength of films also improved when they were subjected to annealing.

In a separate study, Hourston et al.^[133] looked at the properties and characteristics of PU ionomer and solvent based PU materials of similar composition with regards to the level of chain extension. They found that, generally, a higher degree of chain extension results in lower molecular weight and inferior physical properties. This they attributed to the step growth nature of the polyurethane synthesis. They then went on to study the effect of DMPA on tensile strength, and concluded that small amounts of carboxylic acid group enhance tensile strength, but too high a concentration tends to disrupt the phase separation necessary for good mechanical properties in PUs. They also discovered waterborne and solvent borne PUs of similar composition and molecular weight exhibited similar properties. The domain structure was directly related to the level of chain extender and bonding within the sample.

When the level of chain extender was raised from 98 to 120%, the phase separation diminished due to greater variety of the chain length and composition encouraged by the increase in the chain extender concentration.

As more COOH groups were incorporated into the PU prepolymer backbone and the higher the degree of neutralisation, the greater the number of COO⁻ groups present in the prepolymer^[121]. This means more particles were formed, and also the particle size becomes smaller and the dispersion viscosity increases, which they attributed to the nature of the colloidal system. Figure 1.15 shows the effect of increasing the level of triethyl amine (TEA) or the degree of neutralization on COO⁻ formation.

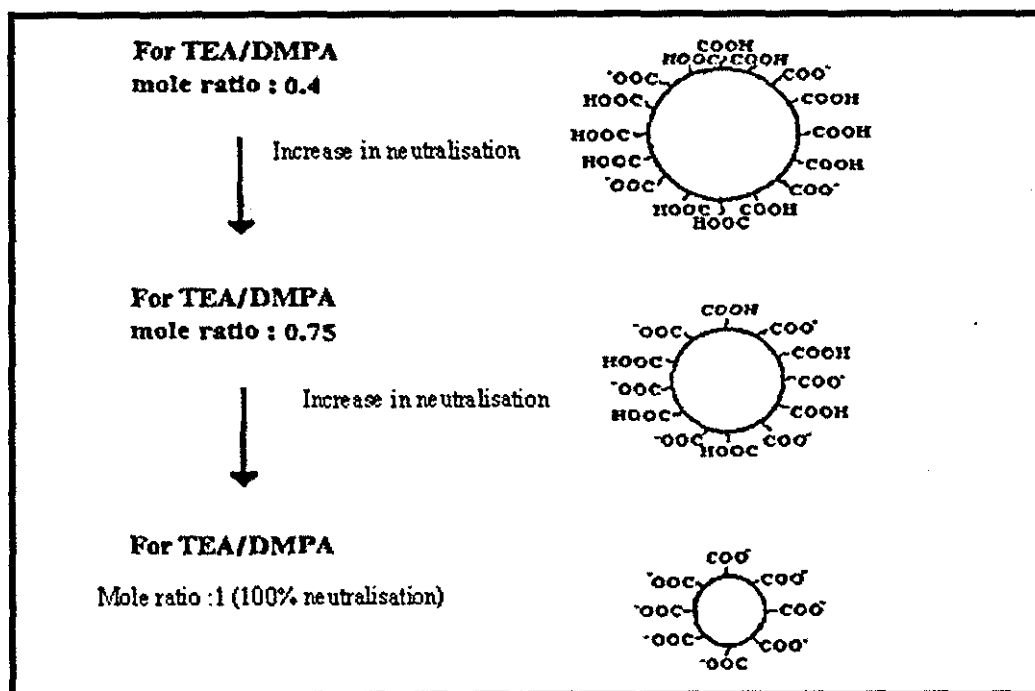


Figure 1.15 Effect of increase of the degree of neutralisation on particle formation ^[118].

Cooper et al.^[153] investigated the effect of different ionic pendent groups in a model polyurethane. In their work, they synthesized a series of PTMG, PEG and PPG and toluene diisocyanate based ionomers. Using derivatization with γ -propane sultones or β -propiolactone, a sulphonated or carboxylated ionomers were prepared. They discovered that the initial moduli were much greater than would be predicted by rubber elasticity theory. This modulus enhancement was attributed to trapped entanglements and the formation of additional interlocking loops during ionic aggregation.

The carboxylated ionomer exhibited lower overall tensile strength. This they attributed to the weaker acid strength of carboxylated groups. Carboxylated ionomers also showed high tensile moduli which arises from the high cross-linking efficiencies and the larger size of the ionic aggregates in the carboxylated compared to the sulphonated of ionomers. In addition, a noticeable difference in glass transition behaviour was seen between the carboxylated and sulphonated ionomers. Cooper et al. suggested ^[153] that there are two factors contributing to this behaviour: the length of the hydrocarbon chain attaching the ionic group to the polymer backbone and the type of pendent ionic group. Flexible pendent side chains on many aliphatic polymers have been shown to lower the glass transition temperature by acting as an internal diluent, lowering the frictional interaction between neighbouring chains in the bulk.

The PTMG-based ionomer gave the highest tensile strength and the highest flow temperature followed by the PPO-based ionomers and finally the PEG-based ionomers. The ability to stress crystallise contributes greatly to the higher tensile properties of the PTMG ionomers, whereas the high polarity of the PEG soft segments and their increased compatibility with the ionic groups gave the PEG-based ionomers the lowest tensile properties and the earliest onset flow. Overall, the use of carboxylate groups rather than sulphonate groups was seen to decrease the tensile strength, increase the degree of phase mixing, and increase the cross linking efficiency of the model polyurethane. Longer side chains, up to a certain length ^[153], lowered the glass transition further. Because the sulphonated ionomers contained side chains with three methylene groups, whereas the carboxylated ionomer side chain contains only two methylene groups, the dilution effect was used to explain 3 to 4 °C differences in the T_g s between the carboxylated and the sulphonated ionomers.

For the 1000 molecular weight soft-segment ionomers, whether based on PPO, PEO or PTMO, a difference of 9 to 10°C in the T_g s was seen for the fully ionized polymers, with the T_g s of the carboxylate always greater. The sulphonate groups form stronger physical cross-links in the material and result in more phase-separated structures. The T_g of PTMG 2000 based of both carboxylated and sulphonated ionomers are approximately the same as for a given soft segment types.

In a different study, Miller and Cooper ^[154] investigated the effect of ion incorporation and cation charge on ionomer properties. They prepared two series of zwitter-ionomers using polytetramethylene glycol(PTMG), diphenyl methane diisocyanate (MDI), *N*-methyldiethanolamine (*N*-MDEA). These were then converted to anionomers by reacting with three different metal acetates, sodium (I), zinc (II) and iron (III). The characterisation by DSC of films prepared from their anionomers showed a lower soft segment (T_{gs}) than their corresponding control polymers regardless of the type of cation used. This suggested that a greater degree of purity of the soft domain arises as a result of ionisation. All ionomers also showed small endotherms at about 70°C, possibly arising from short-range ordering of the hard domains. Once the samples were quenched from 200°C to -150°C and the scan repeated, this endotherm disappeared. The DSC traces of PTMG 2000 based anionomer were examined. Cooper et al. noticed no changes in the T_{gs} . Here, the PTMG 2000 showed a T_g less than that of PTMO 1000, as expected, but also T_g s of PTMG 2000 were not affected by the ionisation process. This behaviour they associated with the soft segment crystallisation. PTMG 2000 is capable of crystallisation which is a great driving force for phase separation. Kim and Kim ^[103,107] studied the effect of the ionic moiety dimethylol propanoic acid (DMPA) level, butanediol and non-ionic hydrophilic segment monofunctional ethylene-propylene oxide polyether polyol, on the particle size of the dispersion, and the mechanical and

viscoelastic properties of the emulsion cast films. They observed that in self-emulsified dispersions with no external emulsifier, particle size decreases with increasing hydrophilicity of dispersed phases, both anionic as well as non-ionic. However, they noted that particle size decreased rapidly at low DMPA content (≤ 3.0 wt %), and show an asymptotic decrease to about $0.1\ \mu\text{m}$.

Kim et al. ^[103] described the effects of PEG, non-ionic hydrophilic group, on particle size, mechanical and viscoelastic properties of their emulsion cast films as the DMPA level remained constant. Their study showed that the particle size and its distribution were independent of the amount of PEG. Similarly to Kim ^[148], who discovered PPG to be temperature-sensitive, it was concluded that the temperature sensitivity of PEG with respect to its hydrophilicity was the cause of this. They go on to say that PEG had rather a negative effect on rigidity and strength of the cast films, due to the weak inter-chain interactions of the ether-type polyol compared to those of ester-type polyols such as poly(tetramethylene adipate).

Several anionomers were studied by Al-Salah and co-workers ^[114] and their work showed that the mechanical properties are greatly affected by the various types of metal counter-ions: anionomers containing transitional metals exhibited good mechanical properties. The glass transition temperature of the soft segment increased by increasing the ionic potential. For monovalent and non-transition metals, the mechanical properties of the anionomers improved by increasing the ionic potential.

In a different study Al-Salah ^[155] studied the viscometric properties and conductivity of PU anionomer solutions and the results showed that the degree of dissociation of ion pairs depends on the polarity of the solvent and its solubility parameters. For a given polymer, the specific conductance increases as the size of the metal counter ion increases. In this work, Al-Salah ^[155] also described the different interaction of a PU anionomer with solvents of different polarity, and mixture of co-solvents. They discovered that PU ionomer solutions derived from polar solvents such as dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) exhibited the polyelectrolyte effect, while low polarity solvents such as 2-butanone, dioxane, and cyclohexanone swelled the anionomer. This behaviour was attributed to the strong ion-pair association.

The effect of the counter ion on the colloidal and mechanical properties of PU ionomers has also been extensively studied. For example, organic bases, such as triethylamine (TEA), are used to neutralise the carboxylic acid groups. However, some workers have discovered that other bases can also be used, especially those containing the group 1 and 2 metals ^[94, 156, 100]. Hence, this has generated a great deal of interest to determine the importance and the effect of

changing counter-ion and counter-ion concentrations. Rajan et al. ^[156] carried out a study of a new PU anionomer containing $\text{-SO}_3\text{H}$ groups. GPC and FT-IR spectroscopy were used for the characterisation of these samples and the effect of the counter-ion on the solution properties was investigated. They discovered that by changing the counter-ion, at fixed polymer concentrations, the reduced viscosities changed in the order of $\text{Li} < \text{Na} < \text{K} < \text{Ca}$, which is consistent with the increasing bonding of the counter-ion for the sulphonic acid group. Frisch ^[114] also investigated the effect of mono- and divalent non-transition and transition metal cations on the properties of a range of PUs based on MDI/PCL and DMPA. They discovered that the properties exhibited by the samples were dependent upon the metal counter-ion. For both the non-transition metals, the tensile strength improved with increasing ionic potential. The extent of water absorption also followed the same trends observed for the tensile strength. However, no relationship was established between the mechanical properties and the ionic potential for those samples with the transition metals. The T_g increased as a consequence of increasing electrostatic forces between the bound ions in the polymer chain and the counter-ions.

Chen et al. ^[94] studied a PU dispersions based on MDI, PPG and DMPA. They neutralised the acid using LiOH, NaOH, KOH, TEA, ammonia or trimethylamine. They concluded that the counter-ions with the metal cations resulted in PU dispersions of a significantly smaller particle size (60-75nm) than those neutralised with the ammonium cations (104-251nm). This phenomenon was explained as being due to differences in the hydration ability of the cations in the aqueous phase.

Chen et al. ^[152] examined the properties PU dispersion containing anionomer samples that had a K^+ counter-ion which were derived from MDI, PTMG and 2,2-bis(hydroxy methyl) propionic acid (HMPA). They studied the effect of the ionisation level of these samples with KOH in comparison with an un-neutralised sample and discovered a number of interesting phenomena. They discovered that only when the carboxylic acid groups were neutralised could soft segment crystallinity be identified and this increased the cohesion in the hard domains. Hence, increasing ionisation resulted in increasing tensile strength and elongation at break.

1.9.2 Effect of diisocyanate and polyols on PU ionomers

As described in detail in the previous sections, the properties of a polyurethane largely depend on the diisocyanate and polyol used and, therefore, an understanding of the influence of these is very important in formulating polyurethane ionomers.

Frisch and co-workers ^[141] investigated PUs prepared by incorporating a range of different diisocyanates. Using H₁₂MDI, 1,4-cyclohexane diisocyanate (CHDI), HDI, 1,12-dodecane diisocyanate (C₁₂DDI), 2,4,4-trimethylhexamethylene diisocyanate (TMHDI), TMXDI, IPDI and 2-methylpentamethylene diisocyanate (MPMDI), he discovered HMDI, IPDI and CHDI-based PUs to possess higher moduli, but lower elongations at break than the other samples. They explained that the asymmetrical structure and the methyl groups in TMXDI do not favour hard segment alignment and, hence, TMXDI-based PUs had the lowest moduli. Of all the samples studied, the C₁₂DDI-based PU possessed the highest tensile strength as a result of a high degree of crystallinity, (determined by DSC), due to its linear symmetrical structure. In fact, this crystallinity was also found to be responsible for its lower water absorption. However, TMXDI's hydrophobic structure had a similar effect on water absorption. Using DSC they discovered non-ring-containing diisocyanate-based PUs to have lower softening temperatures than the ring-containing PUs, but this increased with the degree of crystallinity. The ring-containing diisocyanates (H₁₂MDI) possessed high softening temperatures due to the double ring structure.

Lee ^[157] further investigated the reaction kinetics of a number of diisocyanates towards primary alcohols. He used both ether- and ester-type polyols in his studies and discovered that by monitoring the percentage of isocyanate groups remaining, % NCO values, during reactions over fixed time intervals that the reaction between aliphatic diisocyanates and primary alcohols was much slower than those with aromatic diisocyanates and alcohols under the same reaction conditions. This he found to be consistent with other similar studies. Finally, he proposed that the advantage of cycloaliphatic diisocyanates over aromatic diisocyanates lie in their stability towards water. Following this work, Lee et al. ^[158] proceeded to investigate the effect of DMPA content on the physical properties of PUs based on IPDI and reported on the structure-property relationships of systems containing different isocyanates. For their work, they used TDI, IPDI, and MDI, and polyadipate (2000) and polycaprolactone diol (2000). Their studies included an investigation of the stability of the three PUs based on TDI, IPDI and MDI and discovered that with the aid of photon correlation spectroscopy and viscosity measurements, the MDI-based system could not be dispersed in water because of its rapid reaction with water. The other systems were found to be readily dispersible in water. It was proposed that the reduced reactivity of IPDI towards water was due to reaction of NCO groups on the particle surface with water to form a high molecular weight polyurea layer. This layer then retards water diffusion into the interior of the particle, and, hence, protects the inner NCO groups. They report making an IPDI-capped MDI version that they successfully dispersed in water, and then compared it to the IPDI system. They found that the particle size and viscosity of the PU copolymer was much larger than that of the

IPDI-based dispersion. DSC studies of the two showed that the hard and soft segments of the copolymer were more miscible.

Although the TMXDI(m) diisocyanate contains an aromatic ring, the actual isocyanate is not conjugated and thus remains aromatic^[159, 160-161]. TMXDI shows particular characteristics as a monomer that when incorporated in the PU prepolymer imparts certain characteristics such as lower prepolymer viscosity, the tertiary isocyanate functionality results in lower reactivity and hence provides advantages in the production of PU dispersions and thermal stability.

The asymmetrical structure of TMXDI and the steric hindrance of the isocyanate group by the α - methyl group result in unique properties. Formation of allophanate, biuret and trimer forms are not feasible. Consequently, TMXDI tends to give PU dispersions of lower moduli and higher elongation at break than IPDI, and H₁₂MDI. A polyurethane dispersion based on TMXDI also gave UV resistance and weatherability.

Lee et al.^[158] investigated the effect of diisocyanate on the dispersion behaviour and the physical properties of the final film. They found that the different reactivities of diisocyanate results in different amounts of residual NCO groups during the dispersion process, which has a dramatic effect on the stability of an aqueous dispersion. They used FT-IR spectroscopy to measure the amount of residual NCO groups for prepolymers containing various diisocyanates. They used the NCO characteristic absorption band at around 2270cm^{-1} , its anti-symmetric stretching, and the -CH stretching vibration at about 2855cm^{-1} was taken as a reference for making a comparison of the amount of NCO groups at different stages, because the CH groups did not change during the entire reaction period. The absorbance attributed to the stretching of NCO group is divided by that of -CH group in the same spectrum to obtain the relative absorbance of NCO group to -CH group. The amount of residual NCO groups of IPDI- based, TDI-based and MDI- based polyurethanes at different times during the dispersion process were assessed by the relative absorbance of NCO groups to -CH groups. The amounts of residual NCO groups of the dispersion at any time were normalised such that they are 100% for each neutralised prepolymer. When neutralised, IPDI-based, TDI-based and MDI-based PU prepolymers were dispersed in water, the residual NCO groups dropped to 80.4%, 29.38, and 0%, respectively, of the amounts before dispersion. The more reactive the diisocyanate used was the less the amount of the residual NCO group present after the dispersion. When the IPDI-based PU prepolymer was dispersed in water, the amount of residual NCO group decreased to 57.5% within the first 20 minutes, then, remained nearly constant at 45.8% after 180 minutes. The NCO groups are not all consumed by reacting with water during the dispersion process, so that diamines can be added to the dispersion to react with the NCO groups and to increase the molecular weight of the PU.

When IPDI-based prepolymers were dispersed in water, Lee et al.^[158] that dispersions with significantly different physical properties by either adding diamines within 10 minutes or

after 20 minutes due to the existence of profoundly different amounts of residual NCO groups. In contrast, the TDI-based PU dispersions have to be chain extended as rapidly as possible since its amount of NCO dramatically decreases when dispersed in water. When the MDI prepolymer is dispersed in water, the NCO groups of MDI react rapidly with water to produce many needle-like foams and bubbles. In addition, the number of NCO groups suddenly decreases to zero. Therefore, they concluded that the MDI prepolymers can not be dispersed in water.

The NCO groups of the IPDI- based prepolymer when dispersed, are thought to react with water to form a high molecular weight polyurea layers on the particle surfaces^[158], which is regarded as an outer shell. The outer shell retards water diffusion into the interior of the particles, and consequently the unreacted NCO group of the particle is protected. In the case of MDI, however, the rate of reaction of the NCO group with the water is far too fast to allow the formation of an outer shell to protect the NCO, and hence the residual NCO rapidly drops to zero. This suggests the reaction kinetics of NCO groups with water determines whether a core-shell morphology is suppressed or successfully formed. Measurements of particle size, viscosity, and stability showed that IPDI, MDI and TDI-based PUDs can form stable aqueous dispersions while MDI-based can not. The MDI-based prepolymer also tends to give dispersion of much greater particle size and, hence, is in agreement with the trend in reactivities of the NCO groups of the corresponding diisocyanates. Additionally, a TDI- based PU dispersion is more viscous than the IPDI-based PU dispersion made under the same dispersion conditions.

Lee et al. ^[158] also synthesised MDI-based PU prepolymer which they end-capped with IPDI. The mixed (IPDI-MDI)-based PU prepolymer gives a stable dispersion of higher particle size and viscosity compared to that of IPDI-based PU prepolymer. These characteristics were attributed to the position of COOH group in the polymer backbone. In the case of mixed (IPDI- MDI) PU prepolymer, the hydrophilic COOH groups were incorporated into the hard segments in the first step, so that the COOH groups were distributed in the inner parts of the backbones. However, the COOH groups were randomly incorporated to the hard segments of the backbones of the IPDI-based PU.

Lee and Chao^[124] prepared PU anionomers using PPG 1500 (triol), PPG 1000 (diol), PPG 2000 (diol) and a polyester 2000 (diol). They used TDI as the diisocyanate and 4-amino benzoic acid as the chain extender. They characterised their dispersions by measuring viscosity and surface tension. In this work, Lee and Chao^[124] showed, that at a fixed ionic content, the viscosity of PPG-based PUDs increased as the NCO/OH increased. This rise in viscosity they attributed to an increase in the overall hard segment content, and therefore greater interaction of urethane hydrogen with water molecules. Also their work showed a

slightly higher dispersion viscosity for non-linear PPG 1500. They explained this effect as result of higher ionic content of trifunctional PPG 1500 having stronger electrostatic repulsion arising from intra-ionomer molecules, and with more ionic chains occupying a larger free volume. This repulsive interaction could force the PPG 1500-based ionomer molecule to form expanded conformations (i.e. large aggregates) resulting in an increase in viscosity. They also showed that for PU ionomers based on PPG 2000 and linear polyester 2000, at low ionic content ($\leq 7\%$ by weight), the viscosity rapidly decreased as the level of ionic group was increased. However, at high ionic content ($> 7\%$ by weight), the viscosities begin to rise in both cases and the rise in viscosity was larger in polyester 2000 ionomer. They thought that the ion association from inter- and intra-molecular electrostatic interactions between carboxyl anions (COO^-) and the associated ammonium counter ions may have lead to the formation of large ionic aggregates with increasing ionic content. These factors they thought were responsible for the rise in viscosity.

The effect of addition of water to a PPG 1000-based a PU ionomer in acetone was also investigated. They showed that the viscosity of an acetone solution of PU ionomer drastically increased and then decreased as the amount of water in the system was gradually increased. They explained that, at first, a small amount of water equal to or less than 10% (by weight) added to PPG 1000 ionomer can replace part of the acetone surrounding the PU ionomer, possibly causing such ionomers to form large aggregates and rapid hydrogen bonding formation with water molecules. These large aggregates then begin to move slowly into the aqueous-organic solution and the viscosity begins to rise. However, on further addition of water to the ionomer the viscosity begins to decrease since the amount of acetone in the system decreases and the PU ionomer due to intra-chain association may form more component aggregates.

1.9.3 Effect of Chain Extender on the Properties of Water- borne PU ionomers

The chemical nature of chain extender and its effect on polyurethane dispersion properties such as viscosity, pH value, and solvent resistance were studied by Li et al.^[162]. Their experimental work suggested that the stability and properties of PU dispersions improve with trifunctional or tetrafunctional amine chain extenders. Through their work, they discovered that chain extension can not only build up the molecular weight but also affect the stability, (both thermal and dispersion) and properties of polyurethane dispersions. In their work, Li et al.^[162] used a polyester ($M_n = 2000$), DMPA, N-methyl pyrrolidone (NMP) and IPDI to synthesise a PU ionomer. The prepolymer was then slowly poured into deionised water with vigorous stirring. The system was stirred for 20 minutes before the chain extender was charged into the PU prepolymer dispersion. The chain extension process was performed for about 30 minutes. They showed that the viscosity of the final dispersion was independent of

the triamine or tetramine chain extender added^[162]. However, the molecular weight of the prepolymer was the main factor in determining the particle size, viscosity, and changes in pH of the PU dispersion^[162]. Thermal stability of the dispersion at 70°C was examined using various chain extenders including ethylene diamine, triamine and tetramine. They found that PU dispersions which were chain extended using only 80% and 70 % of the required chain extender level, tend to separate into two phases when stored at 70°C for 72 hours. It was also found that the solvent resistance of the film cast from a dispersion synthesised using multifunctional chain extenders was improved, while the peel strength of the film increased when ethylene diamine is used as the extenders. However, the hydrolytic stability of the PU dispersion is reduced when the dispersion is extended with high percentages of ethylene triamine as it autocatalyzed the hydrolysis process of the polyester based PU dispersion.

In polyurethanes, imbalances in the molar ratios of the chain extender and the prepolymers leads to deterioration of the physical properties of the resulting film. In a polyurethane dispersion it is also important to determine the locus of chain extension, i.e. does the extension take place on particle surfaces or inside the particles^[163]. This enables control of the reaction mechanism and the particle morphology. Kim et al.^[163] studied the chain extension process by following the change of weight average molecular weight and time dependent variation of residual NCO group by GPC, and FT-IR spectroscopy.

Use of diamine monomers containing pendant aliphatic chain of the general types such as N-lauryl-1,3-diaminopropane, N-isodecyloxypropyl-1, 3-diaminopropane and, N-isotridecyloxypropyl-1,3-diaminopropane, were found to improve certain properties such as hardness, lower surface tension, adhesion to lower energy surface, moisture vapour transfer and tensile strength will change with levels of pendant aliphatic diamine monomer. The weight percent of these compounds within the PU dispersion formulation was used to enhance properties essential for the particular application^[163]. These amines yielded urea linkages upon reaction with isocyanates which in a poly(urethane-urea) increases resistance to heat, water and solvent while increasing hardness. This was thought to be due to both the urea bonds being stronger, more stable than urethanes bonds with enhanced hydrogen bonding between urea linkages and other polar linkages within the polymer. These improvements in polymer properties were in addition to improvements resulting from the long aliphatic moiety present in the polymer.

Long aliphatic diamine monomers will shorten polyurethane dispersion (PUD) preparation times due to the greater speed with which the amine-isocyanate reaction occurs (i.e. nearly instantaneous). The time to prepare a PUD can be decreased significantly. The way to speed up PUD preparation is by making an isocyanate-terminated prepolymer having a high NCO /

OH equivalent ratio, followed by reaction with the diamine monomer containing a pendent aliphatic chain to form the prepolymer. The NCO / OH equivalent ratio influences the rate at which the NCO-OH reaction occurs; higher ratios results in faster reaction times.

1.9.4 Cross linking of waterborne PU ionomers

One of the factors that determine the final properties of the polyurethane is the film formation characteristics of the dispersed particles. These particles must fuse or coalesce on the substrate surface at ambient or slightly elevated drying temperatures. Unlike their solvent-borne counterparts, the dispersion particles must first rejoin into a continuous organic phase before the individual polymer chains can entangle and develop the ultimate film properties. Poor coalescence can result in low gloss films, and usually in a reduction of overall physical properties.

The film forming properties of hydrated, swollen polyurethane particles are generally good. They can be somewhat improved by the addition of high boiling coalescent solvents such as N-methylpyrrolidinone^[108, 160], ketones or by the addition of plasticisers. This is often necessary with aqueous dispersions of cross-linked polyurethanes, whose film formation abilities decrease inversely with the cross-link density. Film formation properties also improve by increasing drying temperatures. The best solvent resistance is a result of highest possible cross-link density obtainable, either through hydrogen bonding or covalent linkages. Higher urethane and urea contents typically result in better hardness, abrasion resistance and solvent resistance. Better adhesion and elasticity is gained at somewhat higher contents of polyol, although hydrolytic stability may be poor with high polyester contents. Although there are many quality dispersion processes outlined in section 1.6, none can approach the performance level of two component solvent-borne polyurethane coatings. The reason for this is that all commercially available aqueous PURs are predominantly linear thermoplastic polyurethanes dispersed in water. They specifically lack the cross-link density and high molecular weight obtainable from two component solvent-borne polyurethane systems^[108]. As a result, the water and solvent resistance of the films derived from these dispersions are relatively poor. There are two main areas where aqueous PUR-dispersions are generally inferior to solvent-borne two-component polyurethanes^[123, 164]: solvent resistance and water resistance. Both of these obstacles are difficult to overcome because of the very nature of the dispersions themselves. Better solvent resistance could be obtained by higher crosslink densities, but two factors limit improvement in this area. Highly branched prepolymers have viscosities too high for them to be mixed with water at normal processing temperatures. Highly cross-linked polymers have high glass transition temperatures and therefore will not coalesce to form continuous films at normal drying temperatures. Better water resistance could be obtained by

eliminating the internal emulsifier. Unfortunately hydrophobic polymers would no longer form stable aqueous dispersions of particles. Improvement in the water and solvent resistance can be achieved by adding aqueous resins to the dispersion which provide cross-linking capability. Alkoxyated melamine/formaldehyde resins can be used in such a way. As the coating is cured at elevated temperatures, crosslinking occurs through the reaction of the methoxylated melamine resin with urea or urethane groups in the groups in the polymer. Figure 1.16 illustrates the steps involved.

Figure 1.16 illustrates the steps involved.

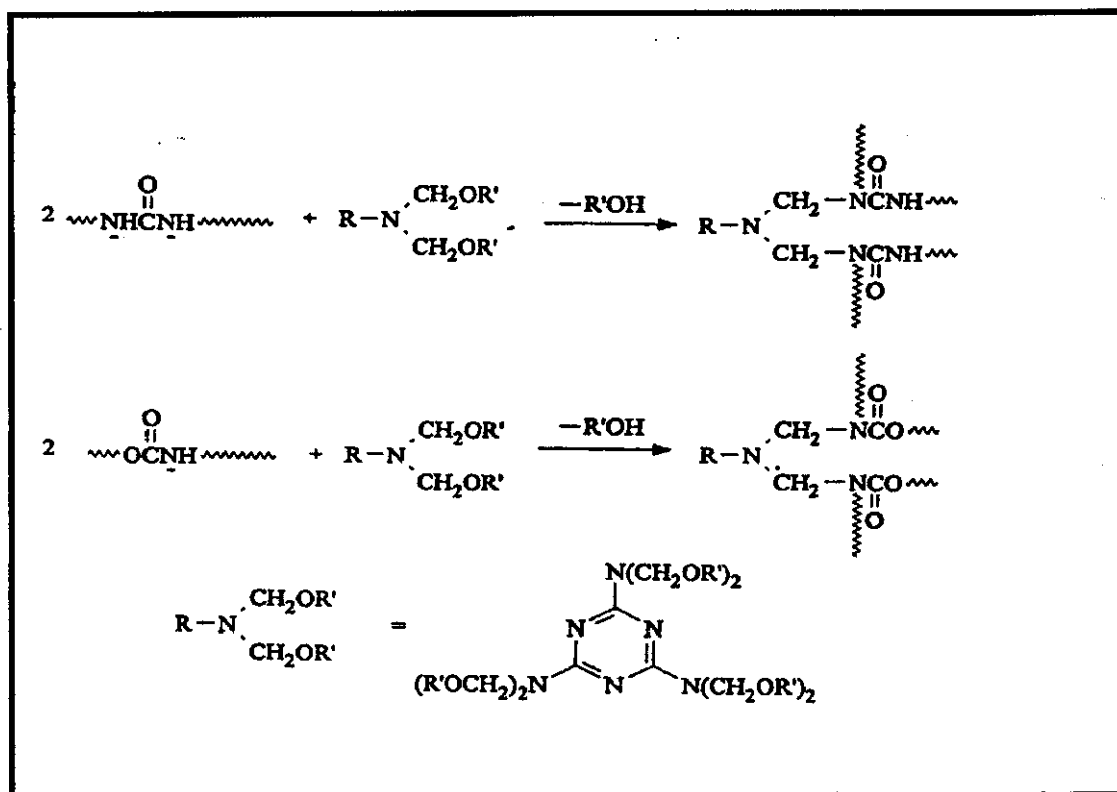


Figure 1.16 Cross linking of PU ionomer using melamine / formaldehyde ^[108]

Carboxylic acid functionality, which is present in many anionic polyurethanes, can be exploited for cross linking through reaction with polyaziridines. Figure 1.17 show the reaction scheme ^[108]. Relatively low temperatures are required to cure effectively a blend of polyaziridines with an aqueous dispersion.

A relatively new development in aqueous cross linkers are water-dispersible blocked polyisocyanates. Cross links are formed at elevated temperatures when the blocking agents are displaced by reactive groups present in the dispersed polyurethane.

An alternative approach to using an external cross-linker such as a melamine resin would be to synthesise directly cross-linked water dispersible polyurethane. However, incorporation of the crosslinking before dispersing the polymer results in gel formation. Attempts to cross-link

an already water-dispersed isocyanate-terminated ionomer using polyamine generally resulted in particles which precipitated and could be isolated in the form of powder. In a few cases where stable dispersions could be obtained, they lacked film-forming properties at ambient temperature ^[108].

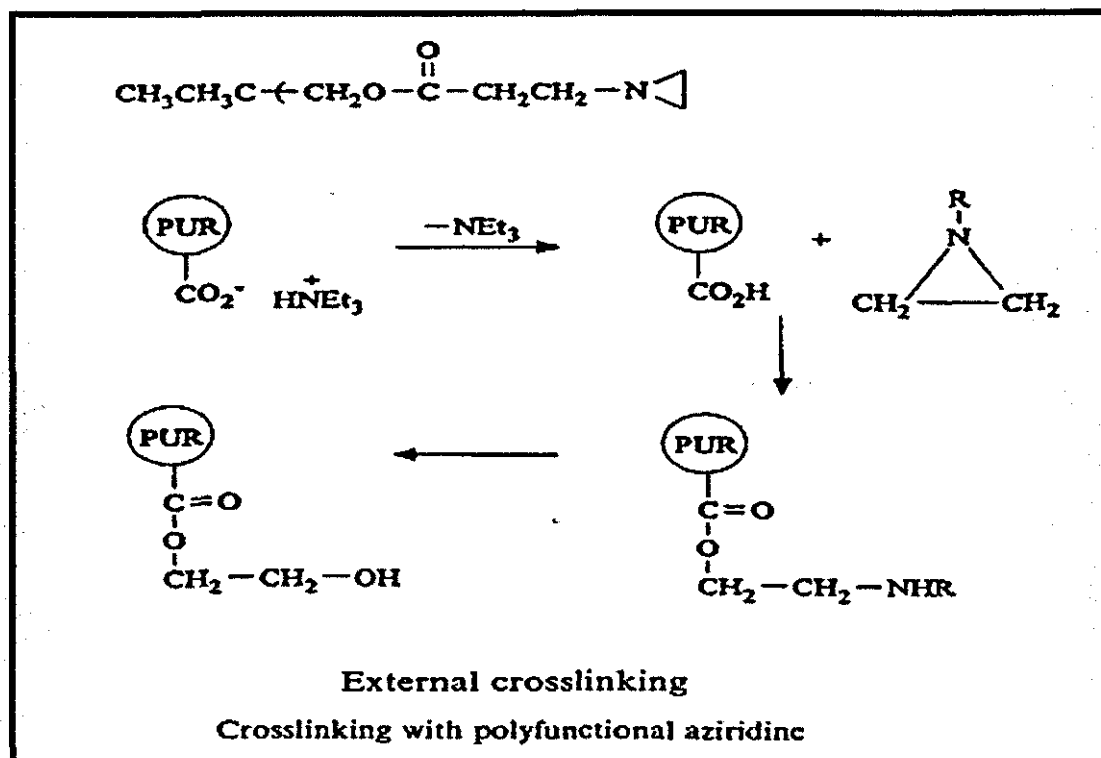


Figure 1. 17 Cross-linking of PU ionomers with a polyfunctional aziridine ^[108]

A hydrophilically-modified isocyanate-terminated prepolymer which contained ionic groups as well as polyoxyethylene units, dispersed in water and subsequently cross-linked the already dispersed particles with polyfunctional amines. The amount of hydrophilic ethylene oxide polyether segments was in the range of 0.4 to 10 weight percent based on solid polymer. The average functionality of the amines used ranged from 2.2 to 4. The ionic/non-ionic hydrophilic modification resulted in stable dispersions with fine particle size at an overall reduced hydrophilic group content. Surprisingly these water dispersed cross-linked polyurethanes showed excellent film-forming properties even at ambient temperatures.

1.9.5 Physical and thermal properties of PU ionomers

Chen and Hsu ^[102, 152] found stress-strain curves for PU anionomers based on MDI, PTMG and chain extender to show upwards trend. All samples showed stress whitening during elongation. PTMG, crystallisation during deformation was evident, which also suggested that

the hard domains had aggregated to act as tight cross-links. Ionisation of the ionic moiety resulted in an increase in tensile strength and in the elongation at break. This was attributed to a significant increase in the hard segment cohesion.

The emulsion cast films showed slightly higher tensile strength in MDEA/TDI ^[102] systems, since it was believed that the process of dispersion at 20°C caused alignment and greater degree of order in hard segments made from the 2,6-TDI symmetric isomer, which were separated from their asymmetric 2,6 TDI isomers which predominantly make up the disordered smaller size hard domains.

Hsu and Chen ^[152] compared the tensile properties of their MDI/HMPA/PTMO 2000-based PU anionomers with those based on polycaprolactone/MDI/HMPA. Both systems used potassium hydroxide as the ionizing agent. They found that the higher molecular weight PTMG resulted in higher tensile strength whereas the caprolactone-based anionomer showed higher elongation at break due to their greater flexibility. They also concluded that the high tensile strength obtained from the cast films of the emulsions was due to the presence of the potassium ion counter ion.

Dynamic mechanical analysis by Chung and Chen ^[102, 152] highlighted that soft segment (T_g) decreased as the hard segment (T_{gc}) decreased and the overall weight percent the hard segment was decreased. However, the soft segment T_g then increases with increasing ionic content, and both peaks becoming sharper, especially for the α peak after ionization. This suggested that ionization increased the degree of phase separation and the cohesion of hard domains. Their work also indicated that the temperature of dispersion resulted in increased mixing with the asymmetric 2,4-isomer of TDI, separated from the hard domains.

DMTA ^[154, 165] analyses of cast films of a series of zwitterions turned into sulphonate anionomers with metal acetates-sodium acetate trihydride, zinc (II) diacetate dihydride, and iron (III) diacetate hydroxide when tested at temperatures below their glass transition temperature indicate a high storage modulus and a much higher plateau modulus than the corresponding non-ionomers of equivalent chemical composition. Hwang ^[165] explained the higher rubbery plateau on the basis of improved hard domain cohesiveness due to the aggregation of ionic groups. The effect of the ionic groups was to provide inter-chain cross-linking within the hard domain thereby increasing the PU dispersion modulus. They further observed that when the soft segment consisted of PTMG 1000 a strong trend was seen in the plateau level as a function of cationic change in the neutralizing species. As the ionic change increased from Na^+ to Zn^{2+} to Fe^{3+} , the size of the modulus plateau in dynamic mechanical measurements increased. This was attributed to the clustering of the sulphonate groups around the cation. As the charge of the cation increased, the average number of sulphonate

groups around the cations increases. This leads to longer ionic aggregates and hence a higher plateau modulus. DMTA tests also indicated that ionization results in sharper transitions indicating greater purity of the domains.

1.9.6. Effect of interactions on PU ionomers

Polyurethanes are extensively hydrogen-bonded ^[12, 44, 49, 166] owing to the existence of a variety of polar groups and highly electronegative atoms such as nitrogen and oxygen. In polyether urethanes, the NH groups of the urethane linkages of the hard segment is the donor, ether oxygens in the soft segment and carbonyl groups in the hard segment are the hydrogen bonded acceptor. If NH groups are hydrogen-bonded with oxygen in the soft segment mixing is favoured. However, if they are hydrogen-bonded with carbonyl groups in the hard segment microphase separation is favoured. Microphase separation has a profound influence on the mechanical properties of polyurethane. Introduction of an ionic group into the polyurethane would be expected to alter intermolecular bonding and morphology.

Introducing ionic centres into the polyurethane chain is expected to have profound effects on the intermolecular bonding and morphology. In polyurethane ionomers, in addition to hydrogen bonding, ionic associations must also be considered ^[153, 165]. The microstructure in a block copolymer ionomer is quite complex and easily varied by factors such as changing the degree of ionisation, hydration, and casting solvent. The presence of the ionic groups that can be solvated by water presents unusual feature not observed in conventional urethane block copolymers. Non-aqueous organic media would be expected to solvate only the hydrophobic segments leaving ionic centres associated. Solvent systems of increasing water content will cause a progressive break up of ionic clusters, but increased association of the hydrophobic soft segments.

Ying et al. ^[136] synthesised a series of the poly(urethane-urea) emulsions and studied the effect of the ionic group on hydrogen-bonding and the properties of the poly(urethane-urea) emulsion by infra red spectroscopy, differential scanning calorimetry, transmission electron microscopy, and rotary viscometry. Using infra red spectroscopy, Ying's work showed that before the addition of the ionic group, urethane carbonyl groups are non-hydrogen bonded (peak at 1731 cm^{-1}), and more free-NH groups (peak at 3449 cm^{-1}), existed than hydrogen-bonded -NH groups (peak located at 3295 cm^{-1}) with -O- in the soft segment. When ionic groups were introduced, the urethane groups are completely hydrogen-bonded and the peak at 1731 cm^{-1} increased, and the peak area of free -NH groups at 3449 cm^{-1} decreased. From these IR spectroscopic analyses they concluded that -NH groups are hydrogen bonded not only with carbonyl groups in the hard segment, but also with the carbonyl groups from the

pendant carboxylic acid present in the polyurethane dispersion, as the ionic group causing the NH absorption to occur at 3295 cm^{-1} .

A considerable amount of research has been carried out on random ionomers due to the unique properties exhibited by these materials. A number of models for the morphology of random ionomers have been proposed but none of them are completely consistent with all of the experimental observations on these materials. It is now generally accepted that the ion pairs aggregate to form quadruplets, sextuplets and higher aggregates, collectively called multiplets. In addition ion-rich regions termed clusters may also exist at sufficiently high ion contents in some systems. The clusters behave as a separate phase in that they exhibit their own T_g . The exact structure of the clusters and multiplets, however, are not known.

The most important ionic parameter that affects multiplet formation is the strength of the electrostatic interaction between the ion pairs. This is determined by the size of the ions and the partial covalent character of the ionic bonds ^[167-171]. Although none of these parameters can be varied independently of the others, they are important factors in multiplet formation. If the electrostatic interaction between ion pairs is too weak to overcome the elastic forces of the chains to which they are attached, no multiplets will form. The firmness with which they are held together is also determined by the strength of these electrostatic interactions. Small highly polar ion pairs interact more strongly and thus tend to be more firmly held than larger groups. The firmness with which the ion pairs are held together in the multiplets is an important consideration in the current model.

The ion content is a crucial factor in influencing multiplet formation ^[204]. The proximity of the ion pairs to one another is determined by the ion content of the system. If the ion pairs are very dilute, they are too far apart to experience significant electrostatic attraction, and hence do not tend to aggregate. The characteristics of the host polymer is also important in determining the extent of multiplet formation in a random ionomer. Low dielectric constant and low T_g of the host polymer tend to favour ionic aggregation, while high dielectric constant and/or high T_g tend to inhibit multiplet formation. The presence of plasticisers, as well as specific interactions between plasticisers or backbone and the ionic groups, also influences the process. In ionomers in which ionic aggregation is energetically favourable, the size of the aggregates is limited by steric factors barring unusual aggregate geometries. In typical random polystyrene-based ionomers such as the (styrene-co-alkali methacrylates), steric factors prevent more than a small number of ion pairs from coming into direct contact with one another. The multiplets are thus postulated to be relatively small and rigid in these ionomers. In ionomers where the ions are situated at the ends of long flexible side chains, there is less steric hindrance to aggregation and larger multiplets. Each ion pair in a multiplet effectively anchors the polymer chain at the point to which it is attached. Hence, the mobility

of the polymer chains in the immediate vicinity of a multiplet is expected to be greatly reduced relative to that of a chain in the bulk polymer, with the mobility increasing gradually with increasing distance from the multiplet. The firmness with which the ion pair is anchored is important in determining how effectively the mobility of the polymer chain is restricted. For rigid multiplets to exist, strong electrostatic interactions must be operative between the ion pairs in the multiplet.

1.10 Objectives:

This study aims to determine structure-property relationships in elastomeric poly(urethane-ureas) and polyurethane ionomers (thermoplastic polyurethanes), and relate chemical compositions to their morphological features. The study also aims to investigate the feasibility of developing water-based polyurethane dispersions (WPUDs) of the desired elastomeric properties while at the same time identifying factors responsible for control of modulus and elasticity in these materials by formulating TPUs of equivalent chemical composition in an attempt to enhance further understanding of the morphological and chemical differences between these two groups of materials that lead to differences in properties. The study will be sub-divided into three sections.

Part . 1

In this part, the conventional method known as the prepolymer method of synthesising polyurethane dispersions will be investigated. The method will be fully evaluated with regards to the type of polyurethane dispersion that it yields, particularly with regard to the role of co-solvent and the ionic moiety, and the characteristics that they impart to the final dispersion. Various materials characterisation and testing will be performed to determine the effects arising from the synthesis process. Properties of the wet dispersions such as viscosity, particle size and their dependence on the polymer molecular weight, chemical composition as well as the method of synthesis, will be investigated.

Part. 2

In part 2, an alternative method for synthesising an elastomeric polyurethane dispersion, essentially TPUs, is proposed. These will be referred to as bulk polyurethane dispersions. The various stages of the synthesis technique and the process of generating a totally waterborne polyurethane elastomer will be explored and described. The characteristics of the final dispersions and the properties of the polyurethane materials generated via bulk reactions will be examined.

Part. 3

The polyurethane materials generated by the two synthesis methods will be compared for their wet dispersion characteristics as well as their physical properties and the differences in

behaviour will be related to the morphological features that occur as a result of the differences in chemical composition and on the method of synthesis.

Among the physical properties studied, stress relaxation and its origin will be extensively investigated and correlated to morphological and chemical structure effects.

Furthermore, as the research is focussed on elastomeric, and particularly soft elastomers, the physical properties i.e. stress-strain, and the stress relaxation behaviours of both types of polyurethane will be compared with the properties displayed by lightly cross linked natural rubber latex films.

CHAPTER 2 -

EXPERIMENTAL

- RAW MATERIALS
- SYNTHESIS
- ANALYTICAL METHODS OF CHARACTERISATION

2.1 Raw materials

The raw materials used in this project are listed in table 2.1.

Table 2.1 List of raw materials

Chemical	Supplier	Abbreviation	Hydroxyl Number mg KOH/ g	Molar Mass/ Formula Weight
Polyethylene butylene adipate, (PTMA)	Rohm &Haas (Bester 43H)	PTMA 2000	28.7	2000.9
Polytetramethylene glycol (PTMG)	DuPont	PTMG 2900	38.5	2919.4
Isophorone diisocyanate	Aldrich	IPDI		222.3
H12MDI 4,4'-Methylene bis (cyclohexyl diisocyanate)	Bayer	H12MDI		262
Dimethylol propanoic acid Tm (189 – 191°C)	Aldrich	DMPA		134.0
Triethylamine	Aldrich	TEA		101.2
N,N'-dimethylethylenediamine	Aldrich	NN'DMEDA		88.2
Methylethylketone (2-butanone)	Aldrich	MEK		
N-methylpyrrolidone				
Dibutyl tin dilurate	Aldrich	DBTDL		
1,4- Butanediol	Aldrich	BDO		90
Tetrahydrofuran	Aldrich	THF		
Hydrochloric acid (0.2M)	Fisher	Hcl		
Ethylenediamine	Aldrich	EDA		60
Dibutylamine	Aldrich	DBA		

2.2 Raw materials characterisation

2.2.1 Measurements of NCO content

The NCO groups have the tendency to react with themselves, or with atmospheric moisture, on storage. In addition, many of the commercially available diisocyanates e.g. MDI, and, in the case of this study, IPDI and H₁₂MDI, are often impure. All these factors can reduce the amount of free isocyanate available for the urethane reaction and lower the quality of the final material as well as influence reproducibility of the synthesis procedure. In order to determine the amount of free of NCO available for the urethane reaction, a titration method ^[7] using dibutylamine in chlorobenzene is used. Isocyanates generally react with primary and secondary amines to yield ureas, and in presence of excess amine the reaction is quantitative. After complete reaction, the excess amine is determined by back titration. The procedure outlined below was used for diisocyanates, polymeric isocyanates and the prepolymers used in all the reactions described in subsequent sections of this thesis.

A solution of 2.5% dibutylamine in chlorobenzene was prepared. 25 ml of dibutylamine was added to 2.0 - 2.5 gram of the diisocyanate, or to its intermediate. The mixture was stirred

well and allowed to stand for 3 to 5 minutes, after which 15 ml of isopropyl alcohol was added and the mixture was stirred. The mixture was then titrated against 0.2M hydrochloric acid using an alcoholic bromophenol blue indicator. For the example of IPDI, the expected percentage of free isocyanate should theoretically be:

$$\% \text{NCO} = \frac{\text{Molecular weight of NCO} \times \text{functionality (2)}}{\text{Molecular weight of IPDI}} = \frac{84 \times 100}{222.3} = 37.8 \%$$

$$\% \text{NCO} = \frac{(\text{Blank titre} - \text{sample titre}) \times 0.2 \times 42 \times 100}{\text{sample weight} \times 1000}$$

Table 2.2.1 Determination of weight percent isocyanate in IPDI and H12MDI

Blank titre (ml)	Titre (ml)	Sample weight (g)	isocyanate type	NCO (wt %)
26.4	0.1	0.59	IPDI	37.5
26.4	0.23	0.58	IPDI	37.9
26.4	0.54	0.58	IPDI	37.45
26.4	0.59	0.67	H12MDI	32.4
26.4	0.7	0.66	H12MDI	32.7
26.4	0.95	0.66	H12MDI	32.4

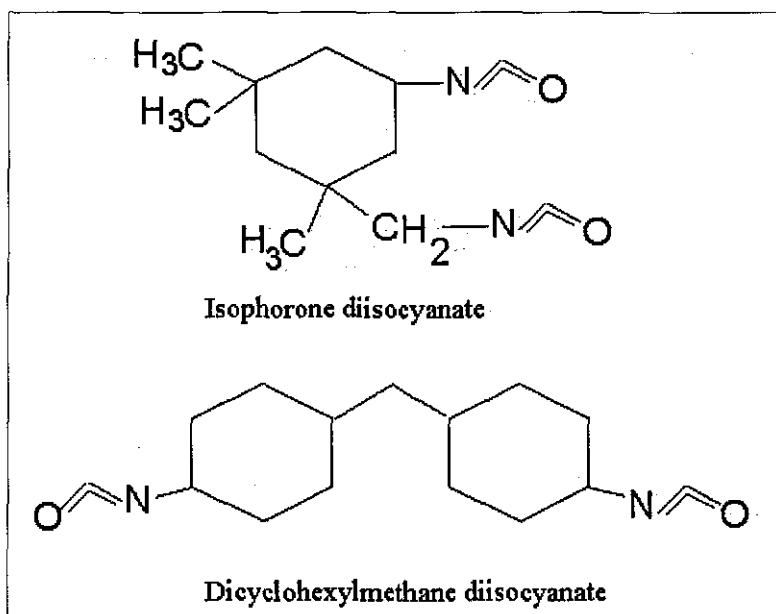


Figure 2.1 Chemical structures of IPDI and H₁₂MDI

2.2.2 Hydroxyl and acid number determinations of the polyols

For both the polyethers and polyesters that were used in polyurethane formulations, the acid and hydroxyl contents are of importance, since in polyurethane synthesis all active hydrogens take part in reactions with the isocyanate groups. Therefore unless all the active hydrogens were accounted for in the reaction, it is not possible to control accurately the NCO / OH ratio, and it will be difficult to synthesise polyurethanes of consistent quality.

Nearly all polyols and polyesters contained impurities e.g. residual acid from their method of manufacture, and being polymeric materials they differ in molecular weight and hence end groups. Therefore, the hydroxyl number and the water content determination by routine analysis were important.

2.2.2.1 Hydroxyl number analysis:

Hydroxyl number is defined as the number of milligrams of potassium hydroxide that is equivalent to the hydroxyl content of 1 gram of the polyol. The hydroxyl number is determined by reacting a known amount of the polyol (g) with a known excess amount of either acetic anhydride or phthalic anhydride in pyridine under reflux for several hours. The excess reagent is back titrated against a standard sodium hydroxide solution. A blank is run on the reagent to determine the amount of anhydride consumed. The sample size will depend on the expected OH value of the polyol.

$$\text{Hydroxyl number} = \frac{56.1 \times M \text{ sodium hydroxide} \times (\text{ml blank} - \text{ml sample})}{\text{Sample weight (g)}}$$

Table 2.2.2 summarises the hydroxyl number determinations for PTMG 2900 and PTMEA. Large variability was observed in sample titration particularly when the polyol sample size was > 8g.

$$\text{OH}_{(\text{PTMG})} = \frac{56.1 \times 1 \times (48.7 - 43.95)}{6.98} = 38.2$$

$$M_n (\text{PTMG}) = \frac{2 \times 56.1 \times 1000}{38.2} = 2937.2 \text{ g/mole}$$

Table 2.2.2 Hydroxyl number determinations for the polyesters and polyethers used in the syntheses

Blank titre (ml)	Titre (ml)	Sample(wt/g)	OH value mg/ KOH	M _n PTMG (g mole ⁻¹)
48.70	43.95	6.98	38.2	2937
47.13	42.56	6.7	38.3	2935
46.30	39.6	9.52	39.5	2840
Average:				2904

Blank titre (ml)	Titre (ml)	Sample(wt /g)	OH value mg/ KOH	M _n PTEMA (g mole ⁻¹)
48.1	40.19	7.81	56.8	2024.95
48.5	42.56	5.91	56.38	2001
47.7	41.6	6.11	56.00	1996.4
Average:				2007.5

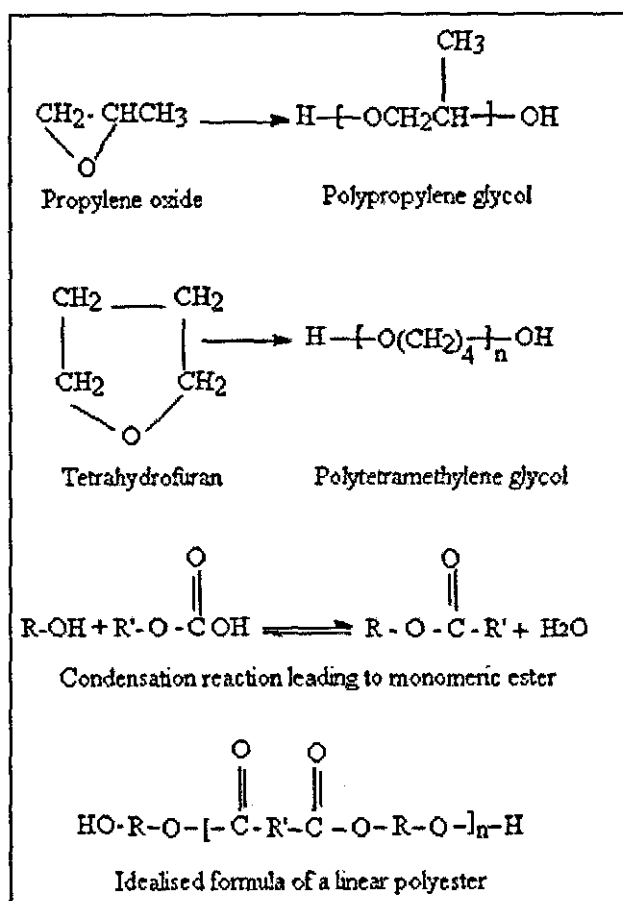


Figure 2.2 Chemical structure of typical polyester and polyether polyols

2.2.2.2 Water content:

Residual water was determined by the Karl Fischer method, which is based on the reduction of iodine by sulphur dioxide in the presence of water. The reaction is quantitative in the presence of pyridine and methanol only. The polyol was mixed with anhydrous methanol and the residual water was titrated with the Karl Fischer reagent, which consists of iodine, pyridine and sulphur dioxide in ethylene glycol monomethylether; the reagent is commercially available. To determine the end point accurately, potentiometric titrations were commonly used.

2.3 Equipment and test methods

2.3.1 Particle size analysis

Particle size and particle size distribution measurements were carried out using a Malvern Zeta Sizer. The Zeta Sizer measures latex particle sizes using the principle known as photon correlation spectroscopy^[152]. The principle is based on the phenomenon of Brownian motion. Particles suspended in a liquid or gas are constantly moving in a random way and when these collide with particles of the suspended medium, the diffusion rates of the suspended particles

are measured and related to particle size. The Malvern Zeta sizer uses laser light under optimised conditions to illuminate the sample. The principle of measurement is based on the fact that the incidence of scattered light fluctuates because of Brownian motion, giving an apparent speckle pattern. The changes in the speckle patterns are related to particle size. In this study each dispersion was diluted to very low solids content, typically 2.0 to 5.0 weight percent, and 3 samples in each case were analysed.

2.3.2 Viscosity measurement

The viscosity of each dispersion was measured using a Brookfield viscometer. The apparatus was Brookfield RDVII + viscometer and ancillaries such as appropriate spindle or T bar, a thermometer constant temperature water bath and appropriate viscosity standard fluids which were calibrated using the range of silicon fluid provided by the manufacturer. The spindle and the rotational speed used depended on the viscosity of the dispersions. For high viscosity the RV3 spindle was used and in cases where the viscosity was the low the LV1 spindle was used for the measurement.

The samples were subjected to a known shear rate, determined by the rotational speed of the instrument's measuring element. The resulting viscous resistance generated by the test dispersion on the measuring element is measured by driving it through a tension spring, the twist of which gives the torque, and, hence, the shear stress. The ratio of shear stress to shear rate gives the viscosity. The rotation speed can be discretely stepped to give viscosity as a function of shear rate.

In all cases, the spindle and speed was selected to give a reading of between 10-90% of the full scale deflection. If the reading was over 90%, a slower speed and smaller spindle were used. If the reading was under 10%, a higher speed and a larger spindle were used to determine viscosity. A minimum volume of 500 ml of the test dispersion was used in each case, and the viscosity was recorded in centipoise (cP) or the SI equivalent (mPas).

2.3.3 Gel Permeation Chromatography (GPC)

GPC is a non-interactive chromatographic technique where separation is based purely on the size of the molecules involved ^[173]. If a mixture of polymeric species is introduced at the top of a GPC column set, a general relationship can be written (see below) to describe mathematically this separation relating the size of a molecule that elutes at a given time to the volume of eluent that has passed through the chromatographic column set.

$$\text{Log}(\text{size}) = F(v)$$

If the flow rate through the column is constant, then the size of the molecule can be related to the time it takes to elute from the column.

$$\text{Log}(\text{size}) = F(t)$$

The size in solution, or hydrodynamic volume, of a molecule is directly proportional to the product of its intrinsic viscosity and its molecular weight ^[173]:

$$\text{Log} ([\eta] \times [M]) = F(t)$$

where $[\eta]$ is the intrinsic viscosity.

The intrinsic viscosity of a molecule is related to its molecular weight via the Mark-Houwink-Sakurada equation^[173] for a given polymer/solvent system at a given temperature.

$$[\eta] = K.M^\alpha$$

where K and α are specific constants to the given polymer/solvent system. Hence, substituting and rearranging for η in the above equation:

$$\text{Log} (K.M^{(1+\alpha)}) = F(t)$$

$$(1+\alpha) \log (M) + \log (K) = F(t)$$

$$\text{Log} (M) = \frac{F(t) - \log(k)}{(1 + \alpha)}$$

$$\text{Log} (M) = F'(t)$$

In order to determine the molecular weight distribution and the weight averages for an unknown sample, the column set used for the analysis must be calibrated using either narrow, well defined polymer standards, or a single broad standard. There are two possible approaches to calibrating a GPC column set ^[173]. The first plots the hydrodynamic volume, given by the product of the intrinsic viscosity and the molecular weight, against the retention time and requires measurement of the intrinsic viscosity on line or a knowledge of the K and α values of the polymer / solvent system in question. This is known as the "universal" calibration plot^[173] and unknown polymers may be analysed against this calibration plot provided a) either the intrinsic viscosity is measured on line or K and α values are known or b) the unknown is a well behaved polymer obeying the universal calibration and does not adsorb on the column packing material.

The second more common approach is to plot the molecular weight of the polymer calibrant against retention time. This gives a calibration file relating molecular weight to retention time for the specific polymer calibrant type and conformation.

The GPC system used in this study consisted of a Hewlett Packard 1047A refractive index detector, a Waters column oven, 510 Waters pump and a Wisp 712 autosampler linked to a Viscotec data station. The columns used were Polymer Laboratories P1-gel connected in series and the column packing material was porous styrene-divinylbenzene polymer with pore sizes ranging from 10^4 , 500 and 100 angstroms. Narrow polystyrene standards of the correct molecular weight range were used as calibrants, with stabilised N-methyl pyrrolidone (NMP) used as the mobile phase. In all cases, a 0.2 % w/v sample solution in NMP was prepared and filtered through a 0.45 micron membrane prior to injection onto the column.

2.3.4 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) ^[174] measures the temperatures and the heat flow associated with transitions in materials as a function of time and temperature. Such measurements provide quantitative and qualitative information about physical or chemical changes that involve endothermic or exothermic processes, or changes in heat capacity. DSC measurement of heat flow into or out of a sample provides valuable data on vulcanization rate, degree of cure, glass transition temperature, percent crystallinity, melting point, specific heat and also degradation ^[174].

The polyurethane materials synthesised in this work were analysed using a TA DSC 910 instrument to determine differences in the degree of phase separation within and between the two groups of polyurethane ionomers arising from differences in chemical composition and their methods of preparation. Each sample was cooled to -120°C and then heated to 250°C in the DSC at a heating rate of $20^{\circ}\text{C}/\text{min}$ in nitrogen gas atmosphere at a rate of $40\text{ ml}/\text{min}$. TA Instruments Graphware software was used to measure the heat flow, T_g , and any other endothermic or exothermic activities in the materials.

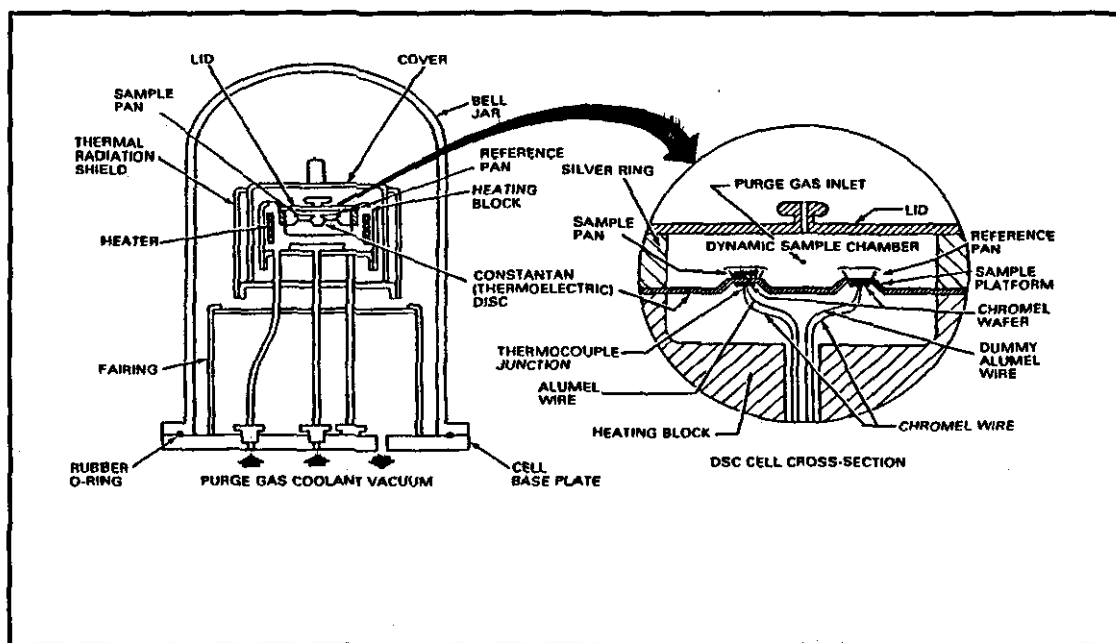


Figure 2.3 Schematic diagram of DSC 910 cell assembly ^[174]

2.3.5 Dynamic Mechanical Thermal Analysis

Dynamic mechanical analysis is a technique which investigates the viscoelasticity of polymers by subjecting the specimen to an alternating strain and simultaneously measuring the stress ^[97]. For a linear viscoelastic material, when equilibrium is reached the stress and strain both vary sinusoidally but the strain lags behind the stress by a certain angle, i.e. the

strain does not occur at the same instant as the maximum stress. The strain, ϵ , and the resulting stress, σ , in the polymer can be written as:

$$\begin{aligned}\epsilon &= \epsilon_0 \sin \omega t \\ \sigma &= \sigma_0 \sin (\omega t + \delta) \\ \sigma &= \sigma_0 \sin \omega t \cos \delta + \delta \cos \omega t \sin \delta\end{aligned}$$

where ϵ_0 and σ_0 are the stress and strain amplitudes, t is time, ω is the angular frequency of deformation in radians, (equal to $2\pi \times$ frequency (Hz)), and δ is the phase lag between stress and strain.

It can be seen that the resulting stress consists of two component. One is in-phase with strain having an amplitude of $\sigma_0 \cos \delta$, and the other is out-of-phase with strain having an amplitude of $\sigma_0 \sin \delta$. Similarly the modulus consists of two parts, the so-called storage modulus, E' , which is in-phase with strain and is a measurement of the elastic energy stored and recovered during each cycle and the loss modulus, E'' , which is completely out-of-phase with the strain. E' and E'' are given as:

$$\frac{E''}{E'} = \frac{\frac{\sigma_0 \sin \delta}{\epsilon_0}}{\frac{\sigma_0 \cos \delta}{\epsilon_0}} = \tan \delta$$

The ratio of loss modulus to storage modulus is defined as the mechanical loss or damping factor. E' and $\tan \delta$ are two important parameters. E' provides a measurement of a material's effective stiffness, which is proportional to the energy stored per cycle, and $\tan \delta$ is proportional to the ratio of net energy dissipated as heat to the stored energy per cycle. The relation between stress and strain can be written as ^[61,97]:

$$\sigma = E^* \epsilon$$

where E^* is the complex elastic modulus, which can be defined as:

$$E^* = E' + iE''$$

E' and E'' are the real and imaginary parts, respectively, as shown schematically in Figure 2.4.

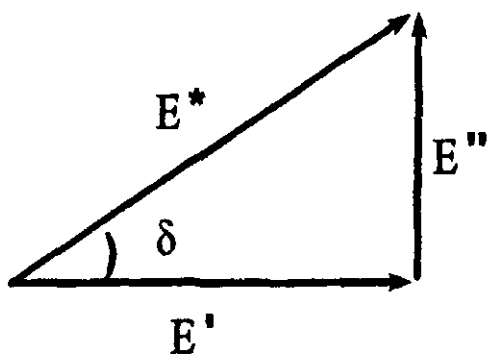


Figure 2.4 Diagram showing the $E^* = E' + iE''$ relation.

When dynamic data are recorded as a function of increasing temperature at a given frequency, the storage modulus E' will decrease and a maximum value will occur in E'' and $\tan\delta$ at the glass transition or at secondary transitions ^[61].

The loss modulus, E'' , is a quantitative measure of energy dissipation in the elastomer ^[23]. Low values of E'' are indicative of low energy dissipation, low hysteresis and, consequently, low heat build up. The loss modulus values are high at low temperature, but decrease as the temperature is increased. Dynamic mechanical investigations can be used to demonstrate the existence of a two-phase structure. The $\tan\delta$ plot as a function of temperature for a well phase separated block copolymer may show several peaks. These may be structural changes that correspond to a soft segment T_g , (δ_s), soft segment crystalline melting (α_c) hard segment T_g , δ_h and hard segment melting α_h ^[48].

The measure of $\tan\delta$ is a qualitative tool to determine the hysteresis or heat build up in an elastomer during dynamic flex conditions. Both WPUDs and bulk polyurethanes were analysed by dynamic mechanical (DMA) thermal analysis. The object of this analysis was to identify any transitions that it may not be possible to determine using the DSC, but also to determine the elastic and loss moduli of the materials and relate their physical properties to their structure and chemical composition. For example, the effect of ionic moiety concentration and the method of synthesis was expected to impart certain characteristics to the material.

Dynamic mechanical analysis was used to highlight fine differences in the structural features of the polyurethanes and illustrate how these differences manifest themselves in the physical properties or the performance of WPUDs and bulk polyurethanes. The work was carried out using a TA Instruments DMA Analyzer. The instrument was calibrated for temperature, length and force measurement on a monthly basis, in accordance with the manufacturer's instructions. The experimental parameters were selected as follows.

Clamp type: tension, film

Heating rate: 3 °C/minute

Clamp preload: 0.05 or 0.02 N (the force was reduced to try and delay 'yielding')

Atmosphere: air

Frequency 1 Hz

Amplitude: 10 micrometres

Autostrain 150%

Sample length: ca. 6mm

2.3.6 Tensile Testing

Tensile stress-strain measurements^[97] are one of the most useful and convenient methods to assess the mechanical properties of solid polymeric materials. The load-extension curves are measured in tension and conversion of load-extension data to the corresponding stress-strain curves enables the Young's modulus, yield stress, yield strain, ultimate stress and ultimate strain to be evaluated. The total energy required to break the specimen is measured as the area under the stress-strain curve and is defined as the tensile toughness. The Young's modulus is a measure of the stiffness of the material and is obtained from the slope at the origin, where according to Hooke's law^[97], stress is approximately proportional to strain and the constant of proportionality is known as the Young's modulus.

$$\sigma = E\epsilon$$

where σ is the tensile stress, ϵ the tensile strain and E the Young's modulus. Polymeric materials show a wide range of mechanical behaviour from brittle and rigid as glasses to soft tough elastomers, which yield very different tensile curves.

The stress-strain curve for a rubber is simple in that it does not show a yield point, although orientation and crystallisation of the molecules (strain-induced crystallisation) may enable the rubber to reach very high elongations before fracture. The tensile stress-strain measurements in this study were carried out on polyurethane films cast from dispersions using an Instron tensometer model (4301 HO92A). The method used was based on BS903 Part A2 with type II dumb-bell test pieces, at a crosshead speed of 200mm/minute, at 50% relative humidity and at of 23-25°C in a controlled environment room. Five test pieces in each case were taken and the average value reported.

2.3.7 Stress relaxation

In a simple stress relaxation test, the deformation is held constant and the resulting stress is measured as a function of time. Deformation produces an initial stress that decays with time in the case of viscoelastic materials. A diagram of a simple stress-relaxation apparatus is shown in Figure 2.5. The sample is held by a set of clamps. The upper clamp is attached to a

strain gauge, and the lower clamp is attached to a device for rapidly elongating the sample by a controlled amount. During the experiment, the sample is rapidly deformed and the resulting force is measured as a function of time.

In this study, Bongo test pieces were prepared, according to the BS 903 part A41 standard (crosshead speed: 1200mm/min) from dispersion cast films. The test pieces were strained to 100% extension and load (N) decay was recorded over a period of 10 minutes. All measurements were conducted at room temperature. The data were analysed by plotting changes in load, (%of peak load or initial) against log time. The plot obtained was used to determine various viscoelastic processes that occur within the polyurethane materials. The gradient of the linear region of the plot was used to calculate the rate of stress relaxation (RSR), and determine the overall extent of relaxation of the material. The initial non-linear region of the curve was characterised by the apparent load drop at one minute after peak load was attained. This 'initial load drop' was measured by the intercept of the relaxation line with the $\log(\text{time}) = 0$. The values of 'initial load drop' and the RSR were taken as indicators of various relaxation processes that occur on application of stress within the polyurethane polymeric chain of different chemical composition.

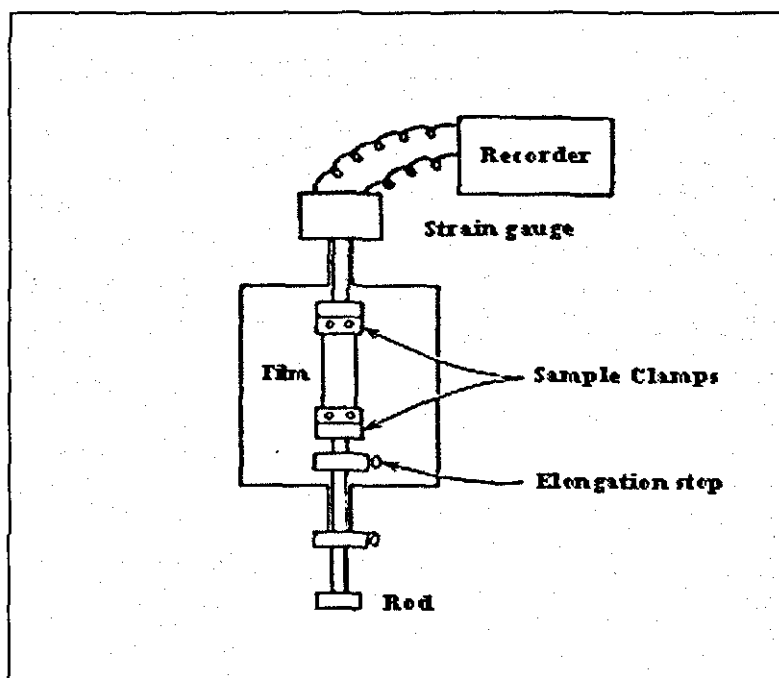


Figure 2.5 A schematic diagram of a simple stress-relaxation apparatus^[68]

2.4. Polymerisation

To determine the most suitable method of synthesizing the desired polyurethanes, two groups of polyurethane materials were synthesised: waterborne dispersions as well as thermoplastic types that contain hydrophilic groups using conventional bulk polymerisation. To establish feasibility, preliminary reactions were conducted to identify the most suitable raw materials and procedures. Moreover, the effects of change in the chemical composition of hard and soft

blocks on the physical and thermal properties, as well as the colloidal stability of water dispersed urethanes, were examined.

2.4.1 Synthesis of the Waterborne Polyurethane Dispersion (WPUD)

Waterborne polyurethane dispersions (WPUDs) were made using the prepolymer mixing method which yields conventional WPUDs, and the bulk method of synthesis which leads to the formation of poly(urethane-ureas) containing hydrophilic groups, thereby enabling the polyurethane to be dispersed in water. The sections below detail the experimental procedures and chemical compositions used for each method.

a) Coding system.

All polyurethane dispersions were labelled as PUD. In order to identify polyurethane dispersions of various compositions, each dispersion was given a material code. The soft segments were given the codes ET if they were based on a polyether, or ES in cases where a polyester was used to synthesize the polyurethane. The materials were then sub-divided as shown below.

b) Co-solvent.

In this case, the initial PUD code identifies the material as a dispersion which is followed by the letters, N, or M that refer to the type of cosolvent present i.e. N-methylpyrrolidone (NMP), and methylethylketone (MEK), respectively. The number following the letters relates to the weight percent co-solvent present. For example, PUDN0 means, a polyurethane dispersion synthesised via the prepolymer reaction with no NMP present. Similarly PUDM5.5 means a polyurethane dispersion prepared via the prepolymer method which contains 5.5 (wt%) MEK.

c) Effect of change in the level of emulsifier and hard segment

In cases where the level of emulsifier was altered in the dispersion, the PUD code will be followed by either ET or ES determining the polyol type, a figure that shows the level of ionic moiety concentration in the dispersion as well as the letter P or H that indicates the dispersion is IPDI/ NN'DMEDA or H₁₂MDI/EDA based. For example, the dispersion PUDET1.5P has been synthesised using the polyether PTMG, 1.5(wt %) DMPA as the emulsifier, IPDI as the diisocyanate, the secondary amine NN'DMEDA chain extender, and, the co-solvent of choice was MEK. To determine the type of chain extender, the abbreviation EDA for ethylene diamine and N,N'DMEDA were used for dimethylethylene diamine.

2.4.2 Prepolymer mixing method for the WPUD synthesis

The prepolymer reaction apparatus consisted of double walled 2-litre flask and lid fitted with a thermometer and a stirrer paddle. The reaction temperature was controlled using a constant temperature oil bath. The reaction set up is given in figure 2.6. The reactions were standard prepolymer reactions in which a hydrophilic isocyanate-capped prepolymer was prepared by reacting the polyol (PTMG 2900), the ionic moiety (DMPA) and the diisocyanate (IPDI) to an end point. The end point was determined by doing the standard dibutyl amine back titration^[138] to estimate the % NCO. A schematic representation of the reaction steps involved in this prepolymer mixing method is given in chapter 1, section 1.3.

The conventional method of prepolymer mixing often requires the use of a small quantity of co-solvent that has several functions. Co-solvents are used to reduce the prepolymer viscosity prior to dispersion, to facilitate particle coalescence by reducing the T_g of the polymeric particles, and frequently co-solvents are used to solublise the ionic moiety, DMPA^[121,160].

In this study, WPUDs were synthesised in the presence of two co-solvents: MEK or NMP. The effect of co-solvent level and the type of co-solvent on the dispersion were evaluated.

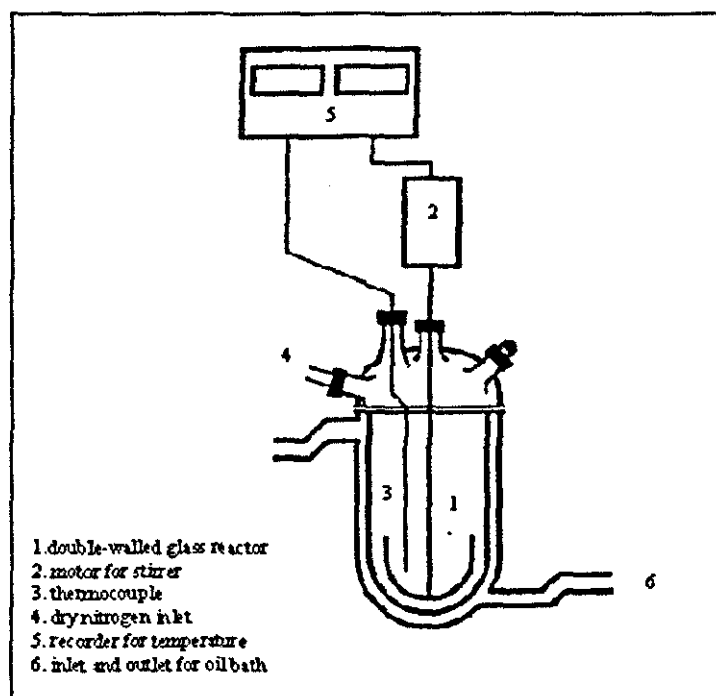


Figure 2.6 Reaction vessel used to synthesise WPUDs and bulk polyurethanes

2.4.2.1 WPUD synthesised using NMP as co-solvent

DMPA is a high melting, crystalline compound (T_m 189 - 191°C) and in order for it to react fully with the isocyanate, either a polar solvent such as NMP has to be used or the reaction temperature needs to be raised to in excess of 140°C. If the reaction temperature is raised above 100°C, isocyanate side reactions and branching will take place, and it would be possible that the isocyanate will react with the carboxylic acid pendant groups, which are only protected sterically by the presence of the methyl group^[121]. This would cause a depletion of the carboxylic acid or the ionic moiety, eventually giving rise to poor stability of the dispersion, as well as to a stoichiometric imbalance. Therefore, initially, NMP was used to solubilise DMPA and facilitate its reaction with the isocyanate. In addition, the effect of an increase in the level of NMP on PUD characteristics was studied in a series of reactions in which the overall chemical composition with respect to NCO content, weight percent DMPA and hard segment were kept constant. Table 2.4.1 summarizes the formulations for the reactions performed in the presence of NMP.

To achieve complete reaction, the polyol, DMPA, NMP and the catalyst (DBTDL) were mixed at 50°C for 30 minutes before adding the IPDI. The reaction temperature was maintained at 95°C – 100°C for 2 hours, after which the temperature was lowered to determine the isocyanate content by back titration^[121] by the method described in section 2.2.1. Following the end capping, the prepolymers were pre-neutralized by adding TEA, in molar quantities equivalent to DMPA to the prepolymer at 60°C with rapid mixing for 30-45 minutes. This process converts the carboxylic acid groups into the ionic salt; the formation of the ionic salt then enables the prepolymers to be dispersed in water^[108].

After neutralisation, dispersions were prepared by adding a sufficient amount of water to the prepolymer to achieve dispersions of solids content of 20 to 22 wt%. Dispersion was carried out using a IKA RW28 high speed mixer at 1400rpm and the dispersion temperature was maintained at 38- 40 °C so as to avoid microgel formation. Chain extension was carried out by diluting the ethylene diamine (EDA) or N,N'-dimethylethylene diamine (NN'DMEDA) in 100ml of deionised water and adding it within a few seconds of making to the dispersion. This process was chosen to minimize the reaction of IPDI with water and encourage the reaction between the IPDI end groups and the diamine, and hence generating high molecular weight final polyurethanes.

The WPUDs were stored at 40°C at 50% relative humidity for a period of at least one week before characterisation and testing for physical properties were carried out. Cast films were prepared by pouring the dispersions into flat petri dishes and allowing them to dry initially at room temperature until the films were transparent. Final drying was carried out at 110°C for 20 minutes in a vacuum oven.

Table 2.4.1 Chemical composition of WPUDs containing various levels of NMP (co- solvent)

Code	NMP (wt%)	Molar ratios	DMPA (wt%)	% NCO prepolymer	HS (wt %)
		<u>PTMG: DMPA: IPDI: NN'DMEDA</u>			
PUD-N0	0	1: 0.71 : 2.97 : 1.15	2.55	2.7	22.6
PUD-N 5.4	5.4	1: 0.70 : 2.97 : 1.2	2.53	2.7	23.0
PUD-N8.8	8.8	1 0.71: 2. 90: 1.13	2.56	2.7	22.6
PUD-N12.2	12.2	1: 0.704 : 2.98 : 1.28	2.52	2.8	22.0
PUD-N18	18.0	1: 0.7 : 2.93 : 1.12	2.54	2.6	22.7
PUD-N 22.2	22.20	1: 0.7 : 2.90 : 1.13	2.55	2.7	22.6
PUD-N 26.7	26.7	1 : 0.702 : 2.9 : 1.16	2.57	2.6	22.7

2.4. 2.2 WPUDs synthesised using methyl ethylketone (MEK) as co-solvent

As DMPA is not soluble in MEK, and the reaction temperature could not be raised to above 100°C to melt the DMPA and facilitate its reaction with the isocyanate, a different approach for the syntheses containing MEK had to be identified.

Preparation of co-solvent-free WPUDs are frequently undertaken in industry ^[160]. This was achieved by mixing the DMPA and polyols at high temperature 135-140°C for a period of 30 minutes. Once the DMPA is thoroughly dissolved, the temperature of the mixture is reduced to 80-90°C and the diisocyanate and the catalyst were added and the reaction was allowed to proceed at 90°C until the desired NCO content was reached.

By following this process, all the DMPA remained soluble in the polyol and could react fully with the diisocyanate. To determine the effect of MEK as co-solvent and compare the dispersion characteristics with those prepared in the presence of NMP, WPUDs of comparable chemical composition were prepared. Table 2.4.2 gives a summary of these reactions.

Table 2.4.2 PUDs of comparable chemical composition differing only in co-solvent type.

Code	Co- solvent	Co- solvent (wt %)	DMPA (wt%)	NCO /OH	HS (wt%)
PUD-N5.4	NMP	5.4	2.53	1.74	23.0
PUD-N8.8	NMP	8.8	2.56	1.70	22.6
PUD-M5.5	MEK	5.5	2.50	1.72	22.6
PUD-M8.4	MEK	8.4	2.53	1.70	22.6

2.4.2.3 Effect of change of ionic moiety concentration on the properties of WPUDs

Having established the effect of co-solvent on the synthesis procedure, the dispersion properties such as particle size, dispersion viscosity and the tensile properties of films from dispersions containing NMP and MEK, it was decided that MEK should be selected as the co-solvent of choice, and therefore the work using NMP was stopped at this stage of the research programme.

A series of WPUDs were synthesised in the presence of MEK containing various levels of DMPA. The effect of DMPA on the dispersion characteristics and the physical properties were then studied. Table 2.4.3 gives the WPUDs formulations containing varying levels of DMPA emulsifier.

2.4.2.4 Effect of change of hard and soft block chemistry on the physical properties.

Furthermore, to investigate the effects of hard segment and soft segment chemical structure on the properties of WPUDs, two further sets of WPUD materials were synthesised. The first group were polyether-based WPUDs which differed in the hard segment chemistry, while the second group were polyester-based WPUDs whose soft segment consisted of a mixed copolyester of poly(ethylene butylene adipate) at approximately 2000 number average molecular weight. Tables 2.4.4, 2.4.5 and 2.4.6 provide a composition details.

Table 2.4.3 WPUDs synthesised in MEK using different level of DMPA

Code	Molar ratios PTMG :DMPA :IPDI: N'DMEDA	DMPA (wt%)	Total HS (wt%)	%NCO prepolymer
PUDET1.5P	1: 0.4 : 2.5: 1.1	1.49	19.5	2.5
PUDET2.0P	1: 0.6: 2.8: 1.21	2.1	21.5	2.8
PUDET2.5P	1: 0.7: 2.9: 1.2	2.5	22.6	2.8
PUDET 2.9P	1: 0.82: 3.2: 1.32	2.9	24.3	3.1
PUD ET3.2P	1: 0.92: 3.4: 1.4	3.2	25.5	3.2
PUDET3.8P	1: 1.2: 3.8: 1.6	3.8	27.9	3.5
PUDET4.3P	1: 1.3: 4.0: 1.7	4.3	29.0	3.6

Table 2.4.4 Polyether WPUDs based on H₁₂MDI and EDA hard segment

Code	Molar ratios <u>PTMG :DMPA : H₁₂MDI: EDA</u>	DMPA (wt %)	Total HS (wt %)	%NCO prepolymer
PUDET2.8 H	1.0 : 0.82 : 3.2: 1.32	2.8	26.0	3.5
PUDET3.2 H	1.0 : 1.0 : 3.9:1.8	3.2	30.6	3.3
PUD ET 4.1 H	1.0: 1.3 : 4.0 : 1.7	4.1	31.6	3.45

Table 2.4.5 Polyester WPUDs with IPDI and NN'DMEDA hard segments.

Code	Molar ratios <u>PTMA :DMPA : IPDI: NN'DMEDA</u>	DMPA (wt %)	Total HS (wt %)	%NCO prepolymer
PUDES2.8P	1.0 : 0.5 :2.2 : 0.7	2.6	23.6	2.3
PUDES3.2P	1.0 : 0.7: 2.8: 1.1	3.4	29.0	3.4

Table 2.4.6 Polyester WPUDs with H₁₂MDI and EDA hard segments

Code	Molar ratios <u>PTMA :DMPA : H₁₂MDI: EDA</u>	DMPA (wt %)	Total HS (wt %)	%NCO prepolymer
PUDES2.8H	1.0: 0.6: 2.8: 1.2	2.8	30.7	3.6
PUDES 3.2 H	1.0 : 0.7 : 2.7 : 1.0	3.3	30.1	3.0

2.4.3 Polymerisation of thermoplastic polyurethane elastomers.

This series of syntheses were undertaken to determine the feasibility of producing polyurethane dispersions via a one-step bulk reaction of the polyurethanes. A further aim of this part of the study was to identify physical properties and dispersion characteristics that may be obtained from a polyurethane dispersion consisting solely of polyurethane linkages, and to compare this with WPUDs that contain both urethane as well as urea hard blocks that were produced by the conventional route described in the previous section. To enable direct comparison of dispersion characteristics and physical properties, a series of thermoplastic

PU's of the same chemical composition as the WPUDs outlined in section 2.4.2.3, and 2.4.2.4 were synthesised. Similarly, to determine the effect of different hard and soft segment chemistry on the physical properties, and particularly on stress relaxation bulk dispersions of various chemical composition, were synthesised.

The synthesis was performed in a reaction vessel similar to the one described in section 2.4.2. The procedure involved homogenisation of DMPA in the polyol until a clear solution was obtained as described in section 2.4.2. The reaction temperature was then reduced to 90°C, the chain extender diol (1,4-butanediol), and the catalyst were added to the mixture. After thorough mixing of all of the OH-containing chemicals, a sufficient amount of the diisocyanate (H_{12} MDI or IPDI) was weighed to produce polyurethanes of 25-33% weight percent hard segment, and gradually added to the mixture. The reaction system was rapidly mixed and once the temperature stabilised the mixture was poured into trays and cured in a vacuum oven at 110°C for three hours. The cured polymer was then granulated and dissolved in THF to produce a PU in THF solution at 12-15 % total solids. The polymer solution was neutralised by adding triethylamine in equal molar ratio to the DMPA and mixing rapidly at RT for 30-45 minutes. Following the neutralisation process, a sufficient amount of deionised water was added to the neutralised PU solution to obtain a very low solids content (5-7 wt%) dispersion. To remove the solvent and obtain a high solid polyurethane, a rotary evaporator was used. All evaporations were performed at 55-60°C under vacuum. Table 2.4.7 summarises the chemical composition of these thermoplastic polyurethanes synthesised in the bulk using a range of polyester and polyether polyols. Like their WPUD counter parts, two groups of materials were synthesised, one group examined the effects of a change in DMPA concentration, while the second group was synthesised and characterised to determine effects of hard and soft segment structure on the physical properties.

2.4.3.1 Material codings

To assist identification, each of the polyurethanes was given a code name. The word 'Bulk' indicates the material was synthesised in the bulk with no solvent or water, followed by ES or ET determining the soft segment chemistry, followed by a figure indicating the level of DMPA and finally by the letters P or H referring to the type of hard segment used in the polymer backbone i.e. IPDI or H_{12} MDI/BDO, respectively. For example, Bulk ES3.2P is a polyurethane synthesised via bulk polymerisation. It is based on polyester polyol and IPDI/BDO, and contains 3.2 weight percent DMPA. The chain extender was in all cases 1,4-butane diol.

Tables 2.4.7, 2.4.8, 2.4.9 and 2.4.10 summarise the chemical compositions of the bulk PUs of differing ionic moiety content, soft and hard block chemistry, respectively.

Table 2.4.7 Chemical composition of bulk thermoplastic polyether-urethanes

Code	Molar ratios PTMG2900:DMPA: IPDI: BDO	DMPA (wt %)	Total HS (wt %)	%NCO index
Bulk ET0.0P	1: 4.54 : 3.52	----	31.3	100.4
Bulk ET2.6P	1: 0.76 :3.3 : 1.6	2.63	25.1	99.7
Bulk ET2.9P	1 : 0.83 : 3.14: 1.30	2.9	24.1	100.3
Bulk ET3.2P	1: 1 : 3.4 : 1.4	3.2	25.6	100
Bulk ET3.8P	1 : 1.2 : 4.4 : 2.2	3.8	31.5	99.5
Bulk ET4.2P	1: 1.3 : 4.0 : 1.7	4.2	29.5	100

Table 2.4.8 Bulk polyether-urethanes based on H₁₂MDI

Code	Molar ratios PTMG2900:DMPA: H ₁₂ MDI:BDO	DMPA (wt %)	Total HS (wt%)	% NCO index
Bulk ET 3.2P	1.0 : 1 : 3.4 : 1.4	3.2	25.6	100
Bulk ET3.8P	1.0: 1.2: 4.4 : 2.2	3.83	31.5	99.5
Bulk ET4.2P	1.0: 1.3: 4.0: 1.7	4.2	29.5	100
Bulk ET3.2 H	1.0:1.0:4.0:2.0	3.2	31.8	99.5
Bulk ET 3.8H	1.0: 1.23: 4.1: 2.0	3.8	32.7	99.3

Table 2.4.9 Chemical composition of bulk polyester urethanes with IPDI /BDO hard segment.

Code	Molar ratios PTMG2900:DMPA: or IPDI H ₁₂ MDI:BDO	DMPA (wt%)	Total HS (wt%)	% NCO index
Bulk ES2.8P	1.0: 0.52: 2.8:1.2	2.8	28.6	99.5
Bulk ES 3.2P	1.0:0.7:2.9:1.15	3.2	29.6	101.8
Bulk ES 3.8P	1.0: 0.8: 3.0: 1.2	3.7	30.6	100

Table 2.4. 10 Chemical composition of bulk polyester-urethane of H₁₂MDI/BDO hard segments.

Code	Molar ratios PTMG 2900:DMPA: H ₁₂ MDI:BDO	DMPA (wt%)	Total HS (wt%)	% NCO index
Bulk ES 2.8H	1.0: 0.6:2.6:1.0	2.8	29.9	100
Bulk ES3.8 H	1.0: 0.9:3.1: 1.2	3.9	34.2	100

CHAPTER 3 -

RESULTS AND DISCUSSION

- POLYURETHANE DISPERSION
- BULK POLYURETHANES

3. 1 Polymerisation and Dispersion Characteristics

Water-based polyurethane materials were prepared by two methods of synthesis to investigate the effect of synthesis procedure, the level of ionic moiety and the hard block chemical composition on the dispersion characteristics and on cast film morphology and physical properties. The ultimate aim was to determine which one of the two methods of synthesis was more likely to yield a soft elastomer whose physical properties approach those of lightly cross-linked natural rubber film. The ideal physical properties for soft elastomeric polyurethanes are taken to be: tensile strength ≥ 25 MPa, S100 modulus ≤ 1.5 MPa, and EAB $\geq 800\%$ ^[175]. Since the final material was intended for use as an elastomer, the stress relaxation and elastic recovery inevitably were also of significant interest.

3.1.1 Conventional method- Prepolymer mixing of WPUD synthesis

The most prevalent methods of producing a waterborne polyurethane dispersion is the prepolymer mixing method ^[96,102, 108, 112-115] which as has been described fully in Chapter1. It relies upon the formation of a hydrophilic prepolymer for the emulsification and dispersion process, and also on diamine chain extension for the development of a high molecular weight polyurethane. Generally the nature and characteristics of the hydrophilic prepolymer are determined by its chemical composition and the final application ^[110,112,153].

Since the objective of this research was to determine the possibility of producing soft elastomeric polyurethane dispersions of physical properties comparable to lightly cross-linked natural rubber film ^[175], the selection of starting materials was quite critical. The choice of raw materials for the hard and soft blocks as well as the ionic moiety for this study were, therefore, dictated by the physical properties specified. To achieve the tensile strength in the final elastomers, the polyurethane materials were synthesised using the polyol PTMG 2900 or a mixed monomer polyester PTMEA of 2000gmole^{-1} molecular weight. The use of PTMG and PTMEA as the soft segments is known to promote higher tensile strength in polyurethane materials by the ability to stress crystallize rapidly ^[23,176]. Moreover, the high molecular weight polyols were chosen to promote a greater degree of phase separation ^[13-14, 177].

Although, in principle, IPDI was the diisocyanate of choice in the study to control hardness, and to promote greater elongation at break (EAB) ^[178], dicyclohexymethyl diisocyanate was also evaluated to determine its effect on phase separation and physical properties. The secondary diamine, N,N'-dimethylethylene diamine (NN'DMEDA), and ethylenediamine were also compared in terms of the characteristics they impart to the final materials. The ionic moiety used was the readily available dimethylol propanoic acid (DMPA).

3.1.1.1 WPUDs synthesised using NMP as co-solvents

As the physical property specification limits the investigation to polyurethanes that are flexible and of low hardness, the overall hard segment content of the polyurethane had to be rigidly controlled. To achieve low hardness in the final material, a prepolymer of low % NCO content, and, therefore, of high viscosity had to be synthesised. The choice of high molar mass and, hence, high viscosity PTMG 2900 and PTMEA 2000 as soft segment also contributed to the highly viscous nature of the prepolymers synthesised as described in both sections 2.4.2.2, and 2.4.2.3. This required the use of some diluent to reduce viscosity in order to facilitate the water dispersion process became necessary. The effect of performing the dispersion in the absence of a co-solvent diluent is well illustrated in the case of PUD-N0. As can be seen from table 3.1, although this material contained comparable amount of DMPA to the rest of the WPUDs in that series, the absence of the NMP diluent has resulted in a highly flocculated, large particle size, unstable PUD.

It is well known that during the water addition stage the polyurethane ionomer goes through a phase inversion process during which a viscosity transition i.e. an initial maximum, followed by a rapid drop in the viscosity, is observed ^[102, 108, 153, 179]. If, however, efficient mixing and homogenisation of the system is hindered because of the high initial viscosity of the prepolymer and by the gradual increase in viscosity during the inversion process, gelation occurs and particle formation is interrupted causing the system to become unstable. Effective mixing and homogenisation during the water addition stage is one of the factors that govern the formation of fine particle and yield a stable PUDs ^[108]. Having established that in order to convert a high viscosity prepolymer into a dispersion some co-solvent was necessary, a suitable solvent material and the optimum level of solvent had to be determined. Initially NMP, which is a viscous, high boiling solvent, was experimented with. A series of polyether prepolymers at 2.6 to 2.8 % NCO were synthesised containing 5 to 27 wt %NMP. The PUDs synthesised in the presence of NMP were characterised for dispersion properties as well as the physical properties of the cast films. Figures 3.1 to 3.6, illustrate the effect of increasing NMP concentration on particle size, viscosity and physical properties. The effect of increasing NMP level on dispersion particle size and viscosity are tabulated in tables 3.1 and 3.2, respectively. The results indicate that in order to obtain a stable dispersion of fine particle size, a small amount of NMP co-solvent,(5 to 8 wt %) is required.

However, as the level of NMP was gradually increased from 5 to 27 wt %, the viscosity and particle size of the dispersion also increases. These effects are ascribed to the swelling of polyurethane particles and complete solvation of polymer, brought about by increasing the NMP content. The greater the polarity of co-solvent, the greater its ability to breakdown the hydrogen bonding association within the polyurethane hard segment regions.

Table 3.1 Effect of increasing NMP content on the particle size of the dispersions
at 2.5 %wt DMPA content

Code	NMP (wt%)	Particle Size (nm)
PUDN0	0	≥ 980 -1000
PUDN 5.4	5.4	202 -215
PUDN8.8	8.8	223
PUDN12.2	12.2	334 – 506
PUDN17.7	17.7	≥ 486
PUDN 22.2	22.0	≥ 1700
PUDN 26.7	26.7	≥ 1160

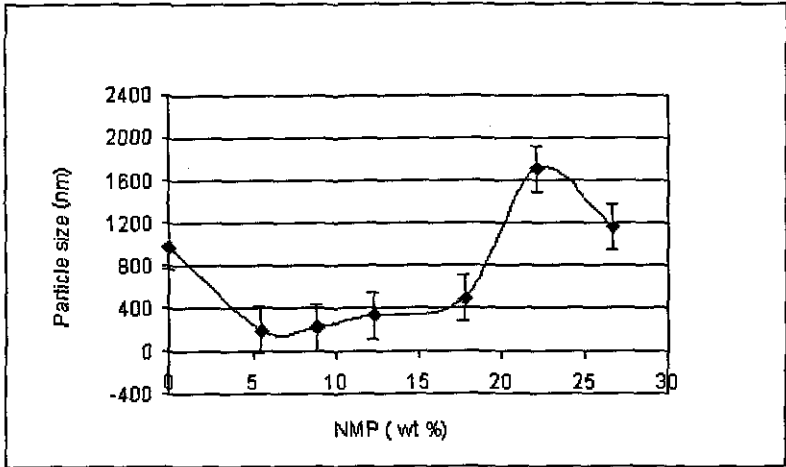


Figure 3.1 Effect of NMP content on the particle size of PUDs

Table 3.2 Effect of increasing NMP content on the viscosity of the dispersions
at 2.5 %wt DMPA content

Code	NMP (wt%)	Viscosity (mPas)
PUD-N0	0	1700 flocculated
PUDN 5.4	5.4	60-100
PUDN8.8	8.8	≥4900
PUDN12.2	12.2	≥ 6000
PUDN17.7	17.7	≥ 4730
PUDN 22.2	22.0	≥ 5100
PUDN 26.7	26.7	≥11100

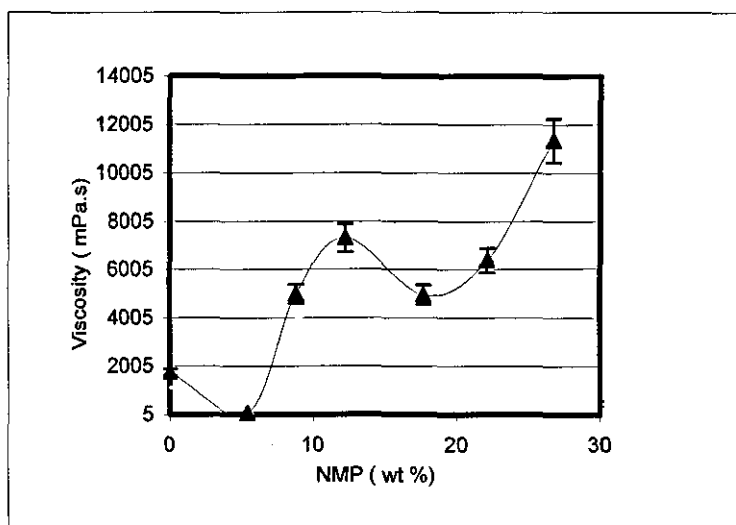


Figure 3.2 Effect of NMP content on PUD viscosity

The minimum amount of NMP required was determined to be 5 wt %. As the level of NMP was gradually increased, the viscosity and the particle size of the dispersion were influenced. Tables 3.1 and 3.2 give a summary of changes in both particle size and viscosity. These effects were attributed to the swelling of the polyurethane particles by NMP. NMP is a highly polar solvent with a strong solvating power for PU materials and when in contact with PU it will cause expansion of the polymer coils from their unperturbed dimensions, disrupting the interchain forces. NMP has the ability to solvate both components of the PU particles i.e. the highly polar hard blocks as well as the lower polarity soft blocks. As the level of NMP in the PUD is increased, both PUD viscosity and particle size tended to increase and the dispersion characteristics changed from a colloid to a highly viscous, gel-like solution^[180].

3.1.1.2 Physical properties of WPUDs synthesised using NMP as co-solvent

The physical properties of films cast from PUDs were greatly influenced by residual NMP. The drying regime used, i.e. 20 minutes at 110°C, to make the films results in some residual NMP in the films and the greater the level of NMP the higher the residual co-solvent which inevitably greatly influences the physical properties of PUD films, as indicated in table 3.3. This is due to NMP having a boiling point of 202°C, and hence a drying temperature of 110°C is obviously inadequate to ensure complete removal of NMP. When higher drying temperatures and times were used in an attempt to remove residual amounts of NMP, degradation of the films occurred and they became tacky and adhesive-like with insufficient strength to obtain stand alone (unsupported) films, to allow physical property measurement. Figures 3.3-3.5 clearly indicate progressive reduction in S100 modulus, tensile strength and EAB with increasing NMP levels, which is possibly the result of plasticization of the film by the residual NMP. A comparison of the tensile properties shown by PUD-N0, which was synthesised in the absence of any co-solvent, with the rest of the PUDs synthesised with NMP, showed the highest tensile strength and S100. This

PUD, however, was of large particle size, unstable and flocculated within two days of preparation. Despite the flocculation, rapid high-shear mixing allowed some films to be cast and tested from this dispersion. An important characteristic of a water-based latex to be used as a coating material is its film forming behaviour.

When dried, some latexes produce continuous, strong films, while others form powdery layers. The mechanism of film formation during drying is of theoretical and practical importance since film properties affect the performance of the resultant coatings. Also the minimum film temperature of a film forming copolymer has been found to be a function of a latex particle size, as was the degree of fusion of films dried at temperatures above the minimum film temperature^[181-184]. Measurement of minimum film temperature, viscoelastic properties and scanning electron microscopy have been used to evaluate the various theoretical models that have been proposed to account for why it is possible to obtain films from some latexes and not others. One of the most important characteristics of film forming latexes is the minimum film temperature (MFT). MFT is defined to be the minimum temperature at which a latex cast film becomes continuous and clear. Below this critical temperature, the dry latex is opaque and powdery. It has been shown that for film fusion^[169], there is a maximum latex particle size for coalescence at a given temperature. In order for fusion to occur in latexes having a particle size greater than the critical value, the modulus of the polymer must be reduced^[181]. This can be achieved by raising the temperature, or introducing a plasticizing agent. In this case the NMP is acting as the plasticizer.

Table 3.3 Tensile properties of PUD synthesised in NMP

Code	NMP (wt %)	Tensile strength (MPa)	S100 modulus (MPa)	Elongation at break (%)
PUDN0.0	0	42.8 (sd=5.8)	2.78 (sd=0.3)	600 (sd=25.0)
PUDN5.4	5.4	33.2 (sd=2.3)	2.4 (sd=0.084)	573 (sd=26.9)
PUDN8.8	8.8	29.1 (sd=4.7)	2.1 (sd=2.9)	606 (sd=40.3)
PUDN12.2	12.2	29.1 (sd=2.7)	2.1 (sd=0.18)	606 (sd=22.8)
PUDN17.7	17.7	27.2 (sd=1.62)	1.7 (sd=0.36)	718 (sd=31.6)
PUDN22.2	22.2	26.0 (sd=7.64)	1.7 (sd=0.082)	736 (sd=132)
PUDN26.7	26.7	14.0 (sd=2.53)	0.9 (sd=0.048)	1099 (sd=24.8)

Note: Average of 5 test pieces were taken in each case.

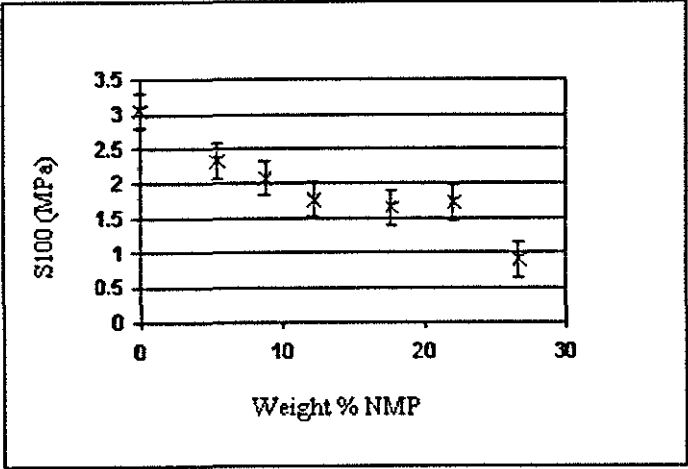


Figure 3.3 Effect of NMP content on S100 modulus.

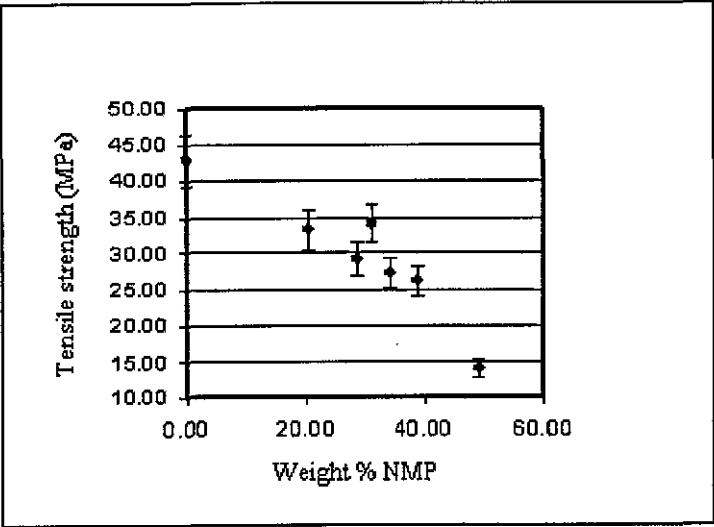


Figure 3.4 Effect of NMP content on tensile strength

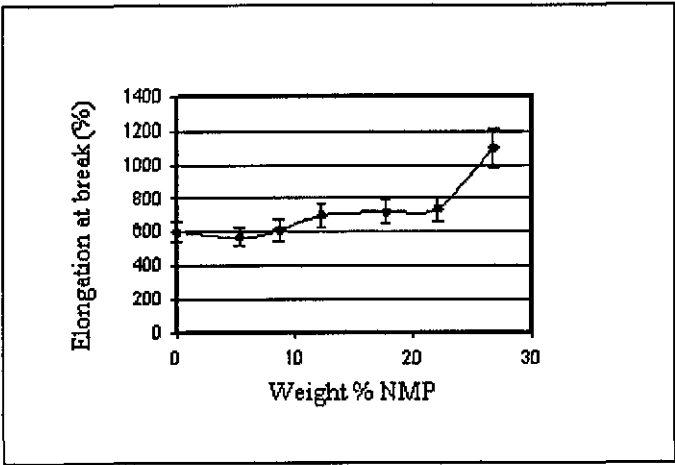


Figure 3.5 Effect of NMP content on elongation at break (EAB)

3.1.1.3 Stress relaxation behaviour of PUDs synthesised in NMP

As expected, residual NMP also influenced the stress relaxation behaviour of PUDs, as shown in figure 3.6. The highest stress retention is shown by PUDN5.4 followed by PUDN-8.8 and PUD-N0. The behaviour of PUD-N0 is surprising since this PUD gives the highest physical properties but has indicated a lower stress retention than PUD-N5.5. One possible explanation for the poor stress retention could be ineffective particle coalescence and film integration of this PUD as there is no co-solvent in this PUD to assist the process of film formation and the process is further hindered by its relatively large particle size.

Table 3.4 Effect of NMP content on load of the WPUDs

Code	Initial load (% of Peak)	Final load (N) (% of Peak)	Initial load drop (100 – initial load) (%)	Rate of stress relaxation (per decade)
PUD-N0	68.9 (sd=13)	53.1	31.3	15.8
PUDN 5.4	78.5 (sd=16.5)	68.2	21.5	10.3
PUDN 8.8	70.9 (sd=7.2)	54.3	29.4	16.6
PUDN12.2	63.5 (sd=5.72)	44.7	36.5	18.8
PUDN17.7	64.1 (sd=12.2)	45.8	35.9	18.2
PUDN 22.2	65.0 (sd=18.17)	45.5	35.0	19.5
PUDN 26.7	62.8 (sd=12.1)	44.6	37.3	18.2

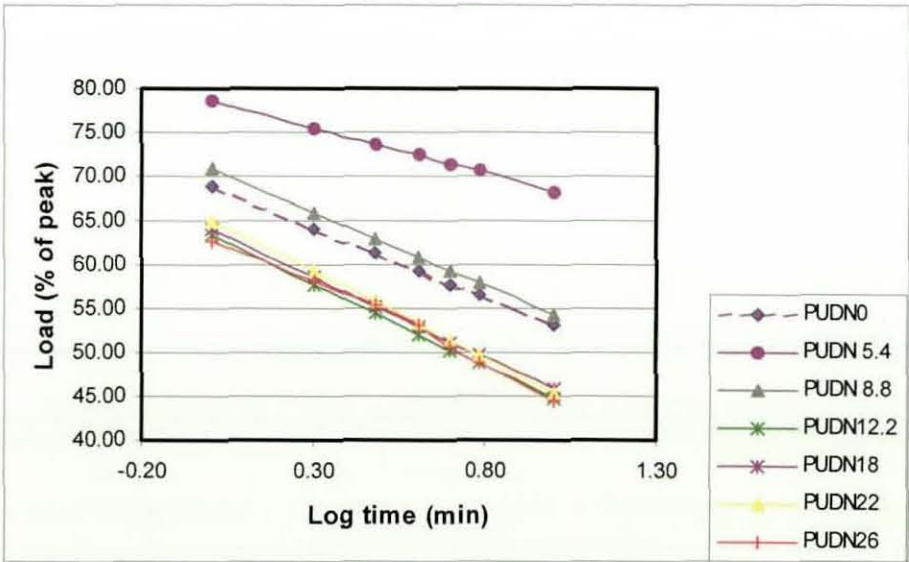


Figure 3.6 Effect of NMP on stress relaxation of PUDs

3.1.1.4 Comparison of NMP PUDs and MEK PUD

To demonstrate the effect of co-solvent type on the dispersion characteristics and film properties, a series of PUDs of equivalent chemical composition to the NMP-containing PUDs, but synthesised in the presence of 5 to 8 wt% MEK, were prepared and analysed for particle size, viscosity measurement and tensile properties. Table 3.5 compares the dispersion particle size and viscosity of PUDs prepared in NMP and MEK. As indicated in table 3.5, in general, the use of MEK as co-solvent for the PUDs produced finer particle size dispersions of lower viscosity at equivalent chemical composition and emulsifier (DMPA) concentration. MEK is not as polar a co-solvent as NMP and, hence the particle swelling effect that gave rise to large particle size and the increase in viscosity was not seen with the MEK-based PUDs. Figures 3.7-3.10 compare the particle size distribution curves for PUD containing 5.4, and 8.4 wt %NMP with those of PUDs containing 5.5 and 8.8 wt% MEK as co-solvents.

Table 3.5 Effect of co-solvent type on particle size and viscosity

Code	Co-solvent	Co-solvent (wt %)	Particle Size (nm)	Viscosity (mPa.s) $\pm 5\%$
PUD-N 5.4	NMP	5.4	203-218	60
PUD-N 8.8	NMP	8.8	221-243	4900
PUD-M 5.5	MEK	5.5	153-160	80
PUD-M 8.4	MEK	8.4	155-189	60

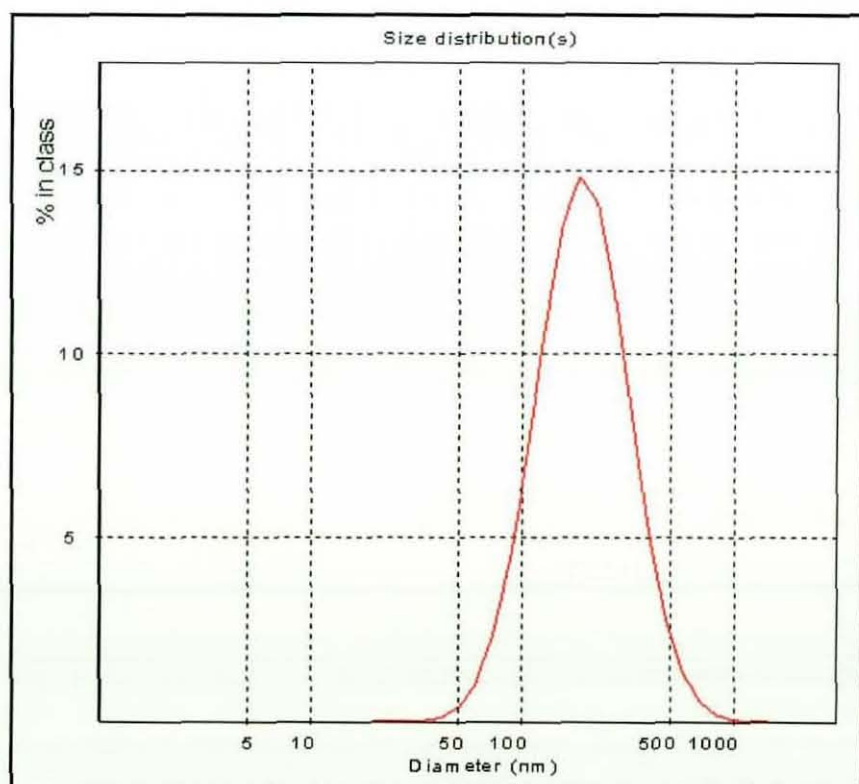


Figure 3.7 Particle size distribution curve for PUDN5.4

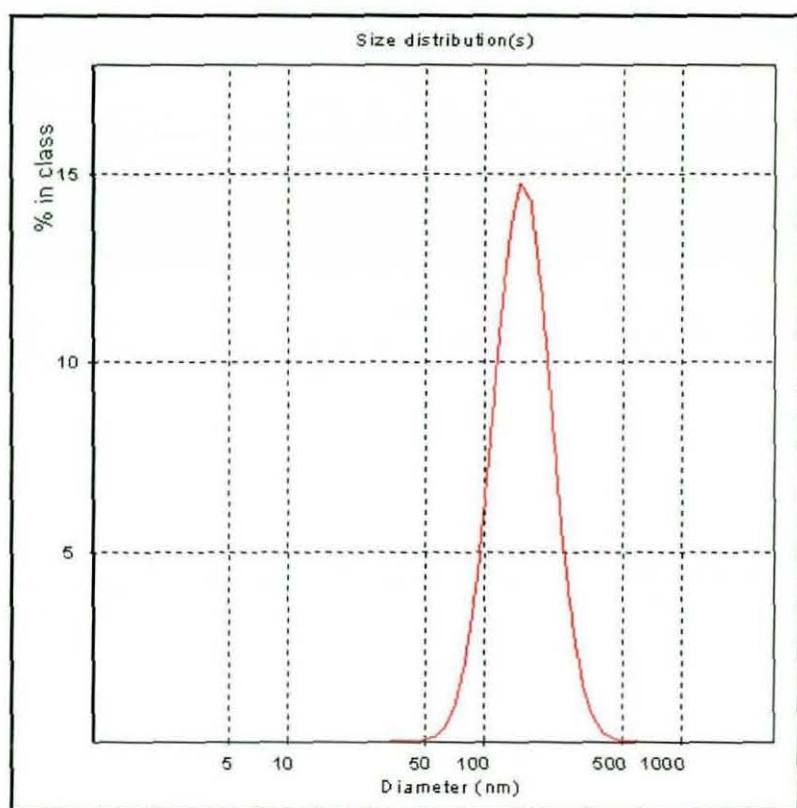


Figure 3.8 : Particle size distribution curve for PUDN8.8

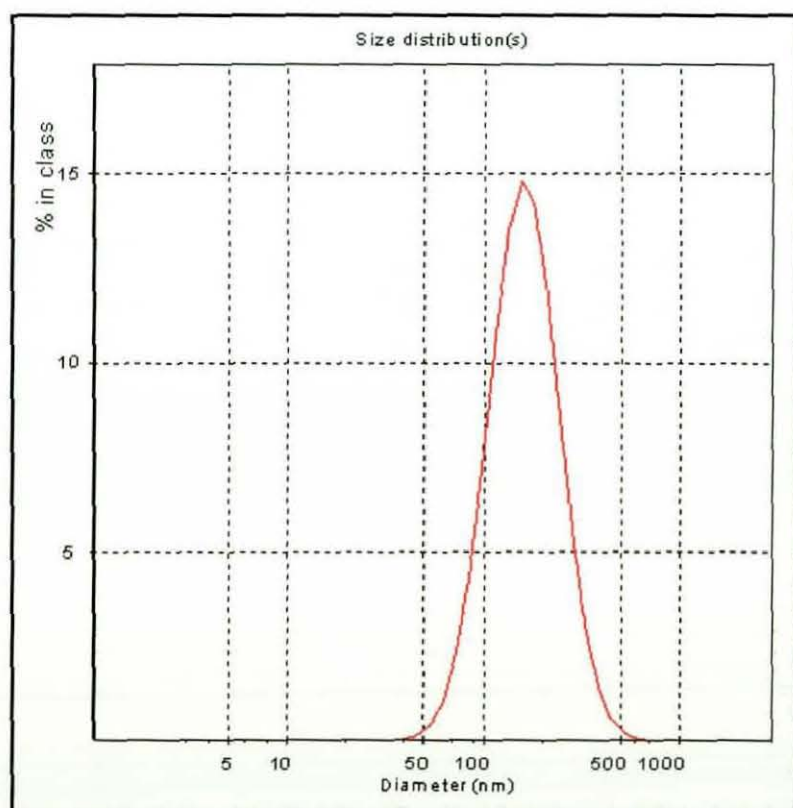


Figure 3.9 : Particle size distribution curve for PUDM5.5

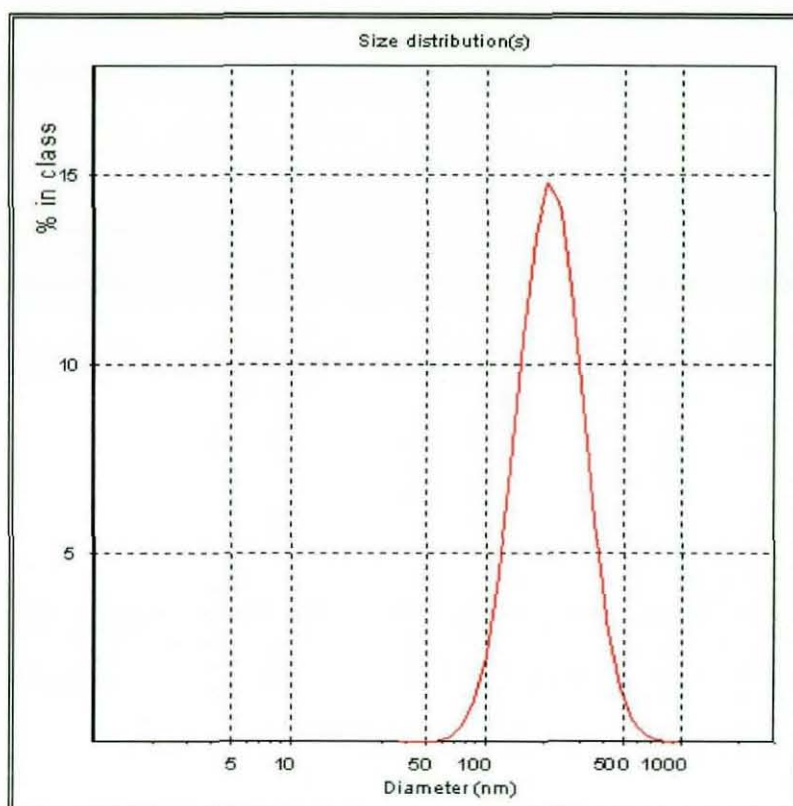


Figure 3.10 Particle size distribution curve for PUDM8.8

Table 3.6 Effect of co-solvent type on tensile properties of the WPUDs

Code	Co-solvent	Co-solvent (wt %)	S100 (MPa)	Tensile strength (MPa)	EAB (%)
PUD-N 5.4	NMP	5.4	2.4	33.2	575
PUD-N 8.8	NMP	8.8	2.1	29.1	610
PUD-M 5.5	MEK	5.5	2.6	49.6	620
PUD-M 8.4	MEK	8.42	2.64	43.7	610

*Note: average of 5 test pieces are reported.

Table 3.6 compares the tensile properties of NMP-and MEK-based PUDs. The MEK-based PUDs showed superior tensile properties compared to their NMP equivalents. This may be because unlike NMP, MEK(boiling point 80°C) tends to evaporate completely at the 110°C drying temperature resulting in much stronger films.

MEK is a less polar solvent and may be regarded as a poorer solvent for these PU materials. When prepolymers of similar chemical compositions were prepared in MEK, generally lower particle size and viscosity were observed. Table 3.5 compares the particle size and viscosity of the NMP-and MEK-containing PUDs. The MEK based PUDs (5 to 10 % wt) showed lower viscosity and smaller particle sizes which favour dispersion stability.

The greatest drawback with the use of NMP in a stand alone polyurethane film, was found to be its high boiling point. Although 5 - 8wt % level of NMP was found to give rise to PUDs of acceptable viscosity and particle size, it was not possible to eliminate NMP from the PUD cast films completely by the conventional method of casting and oven drying, without causing degradation in the PU film. Therefore, the true measurement of the physical properties was not possible. Table 3.6 clearly illustrates the plasticization and the corresponding reduction in the physical properties that NMP causes in the final film. However, since the boiling point of MEK is 80°C, it completely evaporates from the cast film during the drying process. The higher tensile strength and S100 modulus for MEK-based PUD is a clear indication of this effect. It was, therefore, decided that subsequent PUD syntheses should be carried out in 5-10 wt % MEK.

3.2 PUDs synthesised using methylethyl ketone (MEK) as co-solvent

3.2.1 Dispersion characteristics

Having determined the more suitable co-solvent for PUD synthesis to be MEK, the effect of DMPA concentration on the particle size, dispersion viscosity and tensile properties of PUD was studied. The polyether PUDs of IPDI and NN'DMEAD were used for this purpose. The intention was two fold. First, to determine the optimum concentration of DMPA, and secondly to study its influence on the dispersion characteristics as well as the tensile properties and particularly the elastic properties, of the cast films.

Table 2.4.3 summarises the chemical compositions in this series of PUDs with regards to molar ratios of reactants, DMPA concentration and overall hard segment content. The overall hard segment (HS) is made up of the diamine chain extender, DMPA, and the diisocyanate. From the results, it appears that when the DMPA concentration was at 1.5 (wt%), i.e. PUDET1.5P a powder of coarse particles was produced which although capable of coating a glass plate would not form a sufficiently coherent film that could be removed from the glass plate and tested for physical properties. Similarly, the particle size measurements of PUDET 1.5 P, indicated particle size in the region of 1µm and higher. PUDET1.5P was a low viscosity suspension of large polymer particles in water with no stability. Generally, the particle size of polyurethane dispersions can vary from approximately 200 to 5000nm^[96,110] and this has a direct impact on PU dispersion stability. Dispersions with large average particle sizes > 1000nm are generally unstable with respect to sedimentation, while those of smaller average particle sizes < 200nm are the most storage stable^[121,129,185], and possess a high surface energy, resulting in a strong driving force for film formation. The effect of DMPA on average particle size is shown in table 3.7 and in figure 3.11, where the particle size decreased from 1700nm to 91 nm as the DMPA concentration was increased from

1.5 to 4.3wt%. The particle size decreased rapidly at low and slowly at high DMPA contents. PUDET1.5P and PUDET2.1P at 1.5 and 2.1 wt % DMPA produced dispersions of very large particle sizes, and, although they were initially dispersible, on storage, they flocculated and became unstable after 2 days. No films could be prepared from PUDET1.5D as the product was powdery with no film forming ability. PUDET 2.1P, however, could with the aid of rapid mixing, be re-dispersed and cast into films for testing. Viscosity measurements on PUDET1.5D and PUDET2.1D were hindered by the dispersion large particles and the texture, as the rotation of the viscometer spindle caused the dispersions to destabilise and flocculate.

In PUDs it is well established that an increase in the hydrophilicity, in this case, an increase in the concentration of the ionic moiety, leads to a reduction in particle size ^[103,107,121,136,157,185]. The degree of neutralisation used for this study was 100%, ensuring all COOH groups of the DMPA incorporated in the polymer back bone are converted into COO⁻ anions which are principally located at the particle surfaces thereby bringing about stability of the PU dispersions by the formation of a double electrical layer. Tables 3.7 and 3.8 summarise the changes in viscosity and particle size of PUDs with increasing DMPA concentration. Figures 3.11 and 3.16 illustrate the changes in the particle size and PUD viscosity with increasing DMPA concentration. As expected, an increase in DMPA content brings about a reduction in particle size but an increase in dispersion viscosity. Examples of particle size distribution curves are given in figures 3.12 to 3.15. The results of particle size and viscosity measurements showed that in order to obtain a stable WPUD of acceptable particle size, an optimum DMPA concentration of 2.5 to 3.2 wt% was required.

Table 3.7 Effect of DMPA content on PUD particle size

PUD	DMPA (wt%)	Particle size (nm)
PUDET1.5P	1.49	1700 flocculated
PUDET2.1P	2.1	950 ± 5%
PUDET2.5P	2.5	360 ± 5%
PUD ET2.9P	2.9	217 ± 5%
PUD ET3.2P	3.2	223 ± 5%
PUD ET3.8P	3.8	176 ± 5%
PUD ET4.3P	4.3	91± 5%

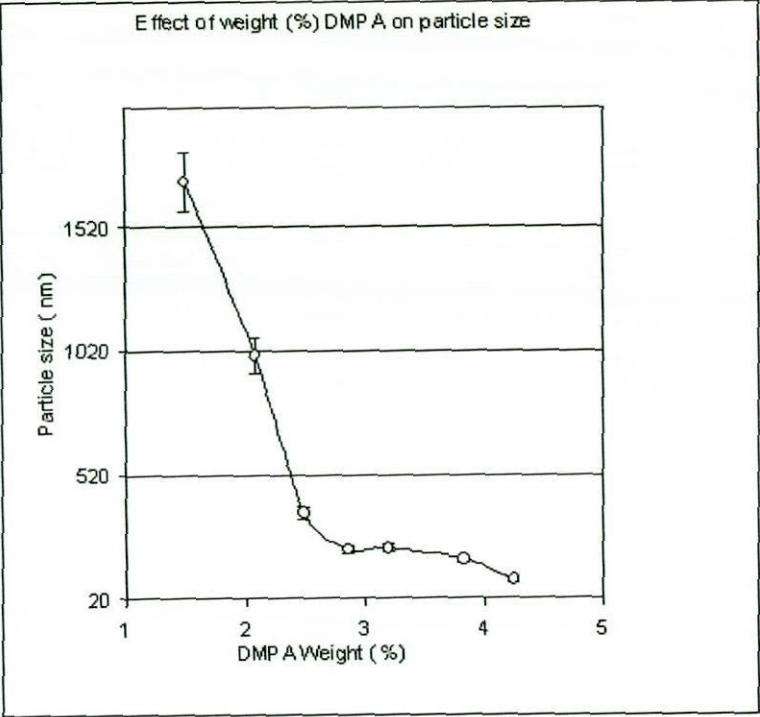


Figure 3.11 Effect of DMPA on PUD particle size.

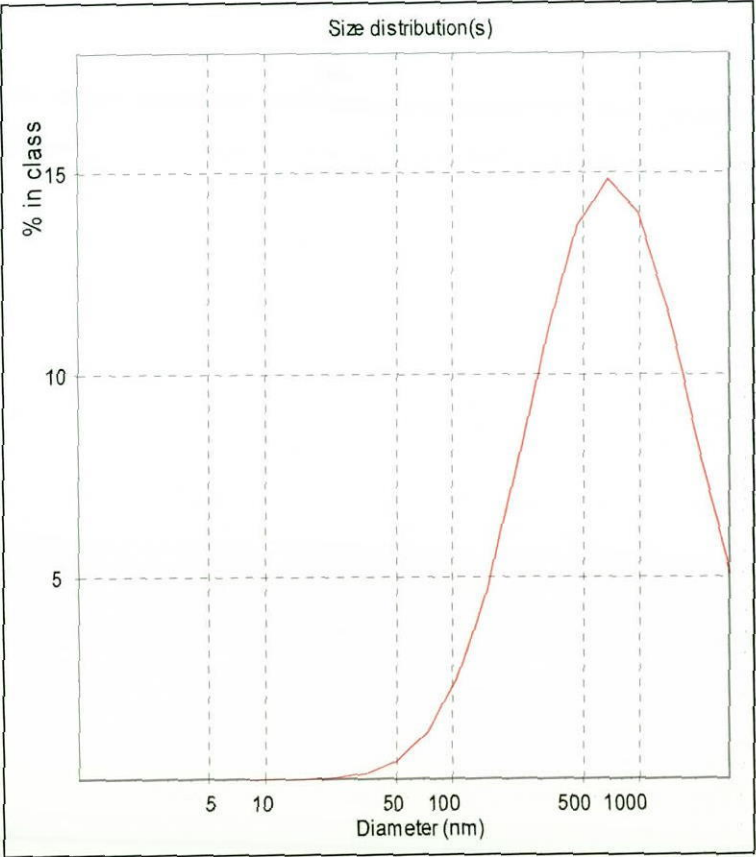


Figure 3.12 : Particle size distribution curve for PUDs containing 1.5 % DMPA

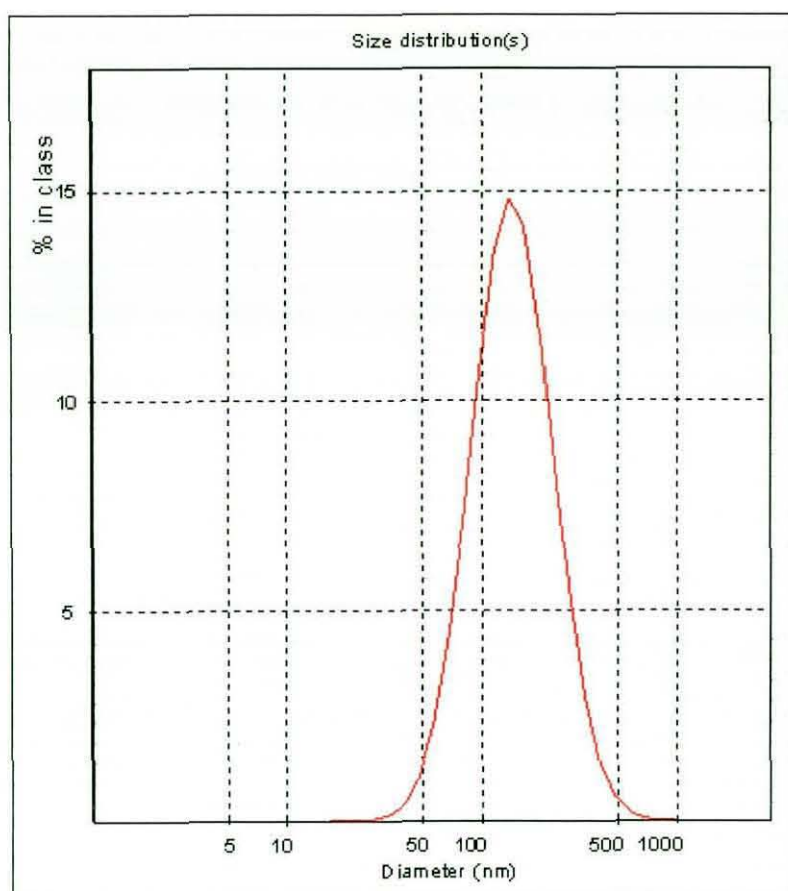


Figure 3.13 : Particle size distribution curve for PUD containing 3.2 wt % DMPA

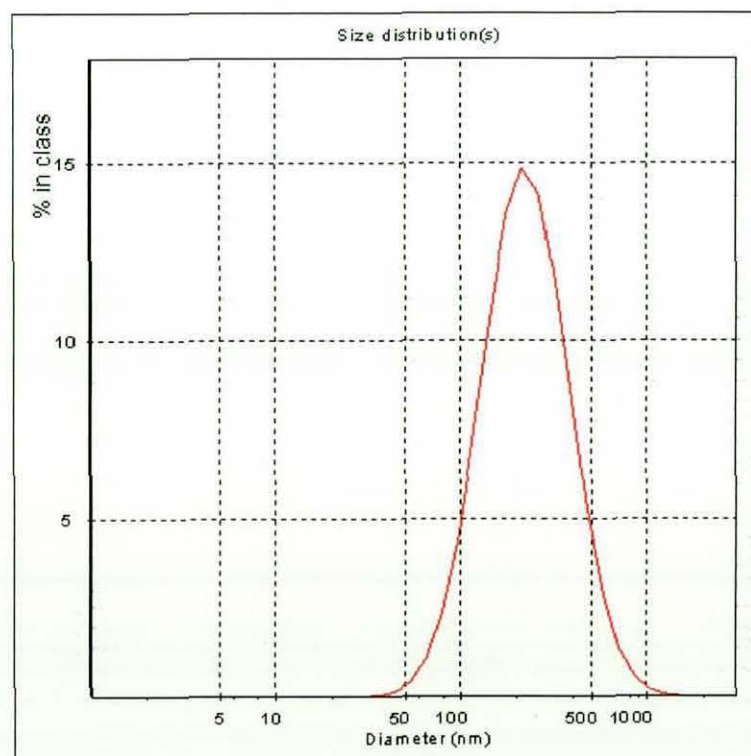


Figure 3. 14 : Particle size distribution of PUD containing 3.8 wt % DMPA

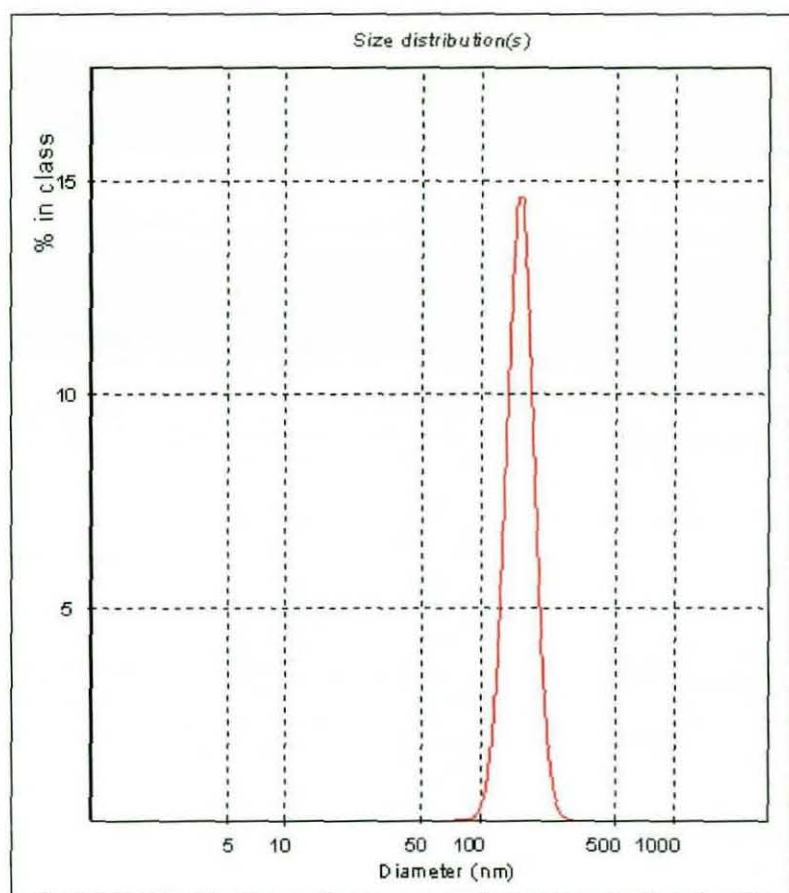


Figure 3.15 : Particle size distribution of PUD containing 4.25 wt % DMPA

3.2.2 Effect of ionic moiety concentration on the PUD viscosity.

As expected, there is a relationship between the particle size and the dispersion viscosity. A decrease in particle size or an increase in a ionic moiety concentration leads to an increase in the dispersion viscosity. A PU ionomer solution in the relatively polar solvent such as MEK spontaneously formed a dispersion when water was stirred in. The transformation of an organic solution into an aqueous dispersion took place in several stages ^[96,102,108] Initially, the viscosity of the MEK solution of PU ionomer drastically increased on addition of a small quantity of water due to the loss of the solvating hydrophobic sheath surrounding the soft segments. At this stage the viscosity increased via hydrophobic interactions induced by the alignment of the hydrophobic soft segment chains. Further addition of water brought about turbidity, indicating the beginning of a dispersed phase formation, which was accompanied by a drop in the viscosity due to a rearrangement of the agglomerates to microspheres where the ionic groups were situated at the particle surfaces. Once the viscosity of the PU ionomer solution reaches a plateau, further addition of water to the system appeared not to affect viscosity significantly. The water was first adsorbed on the surface of the hard microionic latex domains, and then entered successively, into the ordered and disordered domains. As the number of ionic groups on the particle surfaces increased due to an increase in the concentration of the ionic moiety, the thickness of the electrical double layer was augmented due to the effective structuring of the micelles, leading to an increase in the effective volume of the dispersed phase of the emulsion ^[136,185]. This meant the rate of water swelling also increases as the particle size decreased, due to the increased total surface area of the particles of greater hydrophilicity.

Therefore, at a fixed total volume, the effective hydrodynamic volume increases with decreasing particle size. All these contribute to an increase in the effective hydrodynamic volume of the dispersed phase leading to a drastic increase in the dispersion viscosity. This effect was clearly observed in this study with a gradual increase in DMPA, and, hence, ionic concentration increased in the MEK-based PUD series described in chapter2, table 2.4.3. Figure 3.16 and table 3.8 show this effect where significant increases in viscosity are shown beyond a DMPA content of 3.0 wt %.

Table 3.8 Effect of DMPA content on PUD viscosity

PUD	DMPA (wt%)	Viscosity (mPas)
PUDET1.5P	1.49	200
PUDET2.1P	2.1	625
PUDET2.5P	2.5	80
PUD ET2.9P	2.9	1112
PUD ET3.2P	3.2	2887
PUD ET3.8P	3.8	6900
PUD ET4.3P	4.3	25750

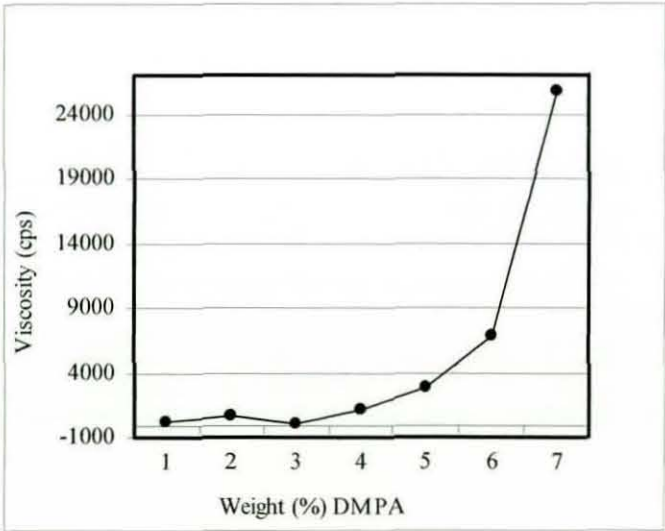


Figure 3.16 Effect weight percent DMPA on the viscosity of PUDs

3.2.3 Effect of ionic moiety concentration on the physical properties of IPDI-based polyether PUD

Table 3.9 summarises the tensile properties for the IPDI-based PUDs of differing ionic moiety concentration. From the results, it appears that a change in DMPA concentration influences the tensile properties of films cast from the dispersions. The variation in tensile strength (TS) and S100 modulus are shown in figures 3.17 – 3.18. The relationship between the ultimate properties of a block copolymer and polymer morphology has been extensively studied ^[14,177] and has shown that, in general, the behaviour of a strained block copolymer depends on the size and concentration of the hard segment domains, the strength of the hard segment aggregation and the ability of the hard segment to orient in the direction of stretch and the ability of the soft segment to crystallise under strain. Polyurethane elastomers have been widely accepted as having mechanical properties that are particularly dependent on the nature and the extent of domain formation. In these elastomers, when the segments containing urethane links are relatively long or have high cohesive energy they aggregate into plastic (hard) domains which markedly affect the mechanical properties ^[17]. However, when the segments are relatively short and their cohesive energy is not particularly high, phase separation does not occur, and the elastomeric properties may then be quite similar to those of cross-linked homopolymers ^[26,67,186]. Even when phase separation does not occur, the size and nature of the hard and soft segments may affect the strength and the viscoelastic properties too. The factors which determine the final morphology include segment compatibility, intra-segment and inter-segment interactions such as hydrogen bonding, chemical composition, molecular weight and thermal history ^[11-13, 17].

Similarly, the physical properties of polyurethane dispersions essentially follow the same principle that is shown by block polyurethanes, although the properties of these materials are also influenced by the presence of the ionic / hydrophilic groups present in their backbone ^[116,154]. For example, the properties of a quaternised ionomeric polyurethane depend both upon its quaternary nitrogen content as well as the type of the urethane hard segment.

The WPUDs synthesised in this study contained two types of hard segment(HS): urea domains that create strong hydrogen bonding interactions, which arise from the reaction of the diisocyanate and diamine chain extender, and the second type results from the reaction of diisocyanate with the ionic moiety, DMPA. The latter create the ionic interactions arising from the COO⁻ group produced during the neutralisation process of the pendent carboxylic acid of DMPA. The PU ionomers of the current study were made by synthesising prepolymers at NCO/OH values of 1.7-1.8, giving rise to overall hard segment contents of 22 to 29 wt %. Table 2.4.3, in chapter 2, details the composition breakdown of each ionomer. It can be seen that as the level of DMPA was gradually increased, the level of diisocyanate also had to be increased causing an increase in the overall hard segment content. The higher DMPA levels not only provide greater stability for the dispersions, but it also bring about greater coulombic forces i.e. greater inter-chain interactions within the PU ionomers and a greater inter-segment incompatibility and a greater degree of phase separation, and a

morphological structure in which ionic domain act as discrete reinforcement entities. The net effect appears to be an increase in stiffness as indicated by the gradual increase in the S100 modulus. The variation in S100 with DMPA concentration is outlined below in figure 3.17. The results show that the S100 modulus of the WPUDs is sensitive to small changes in DMPA concentration. The variations in tensile strength (TS) with DMPA are shown in figure 3.18.

Table 3.9 Tensile properties of PUDs with varying DMPA concentration

PUD	HS (wt %)	DMPA (wt%)	Tensile strength* (MPa)	S100* (MPa)	Elongation at break* (%)
PUDET2.1P	21.5	2.1	19.0	1.9	540
PUDET2.5P	22.6	2.5	51.0	2.6	630
PUDET2.9P	24.3	2.86	41.0	3.0	560
PUDET3.2P	25.5	3.2	39.2	3.2	550
PUDET3.8P	27.9	3.8	51.4	4.1	540
PUDET4.2P	29.0	4.25	36.5	5.2	640

* 5 test pieces used. Average physical properties quoted in each case.

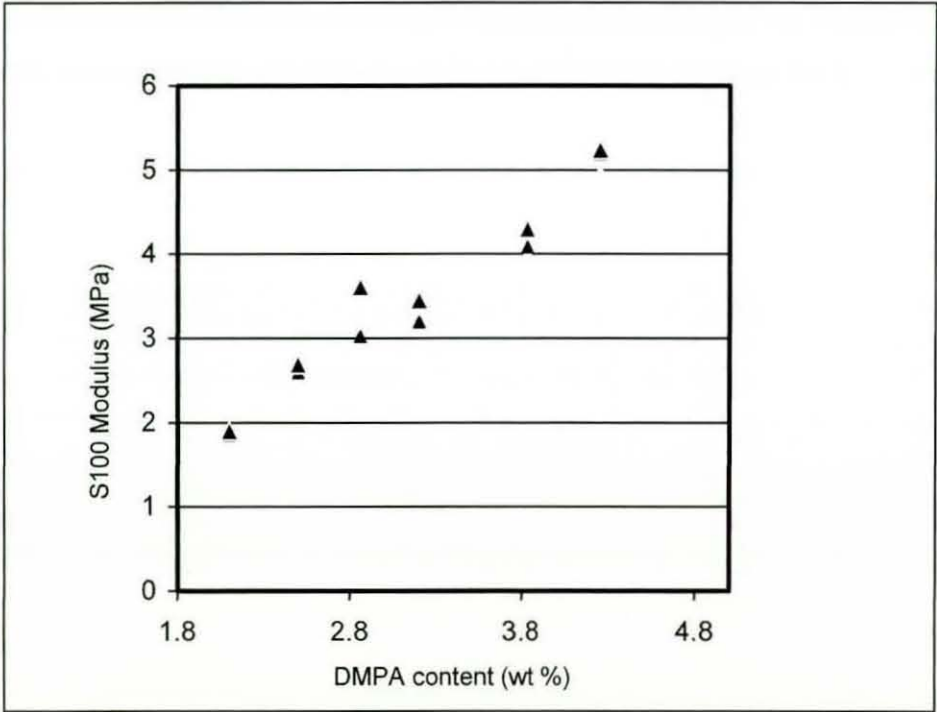


Figure 3.17: Effect of DMPA content on the PUD S100 modulus

In the case of tensile strength, although in general an increase with higher HS (wt%) is shown, the tensile strength appears to fluctuate significantly. Tensile strength of polyurethanes is thought to be highly dependent on the overall molecular weight of the polymer ^[121, 185]. In order to explain these fluctuations, GPC measurements were made. Although absolute measurements of molecular weight were not obtained from GPC, it was however possible to gain some insight into the variation of

the molecular weight on increasing the DMPA content and relate these variation to the tensile strength shown by these WPUDs. Figure 3.19 clearly indicates a variation in the molecular weight that corresponds to changes in tensile strength. The bimodal nature of the GPC chromatogram suggest the presence of at least two types of species of different molecular weight. Given the step growth nature of polyurethane dispersions and their reaction mechanism, polymeric chains of various molecular compositions could result which would explain the differences in the hydrodynamic volumes exhibited by the GPC analysis. This may also explain the variations observed in the tensile strength of the WPUDs of the current study. Examples of molecular weight chromatograms are given in figures 3.20 and 3.21.

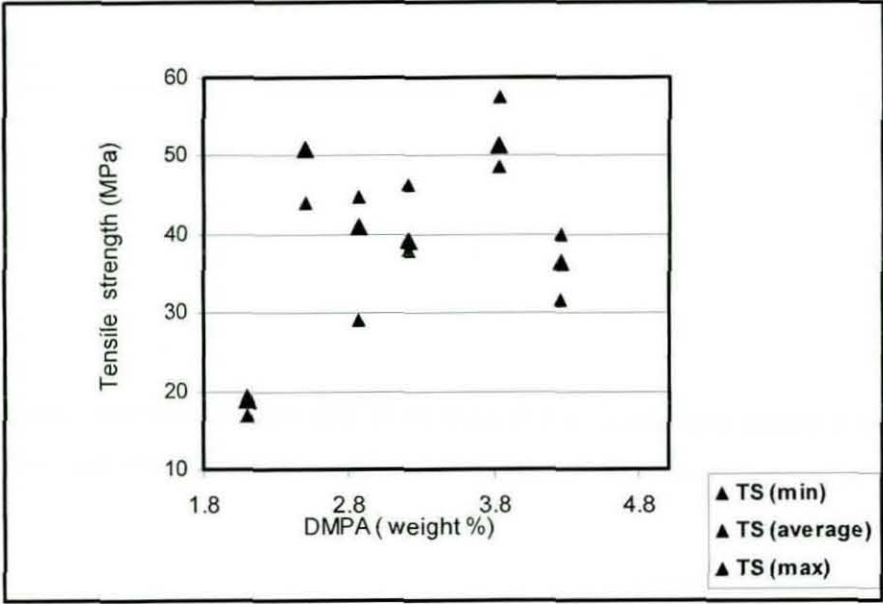


Figure 3.18 Effect of DMPA content on the tensile strength of WPUDs

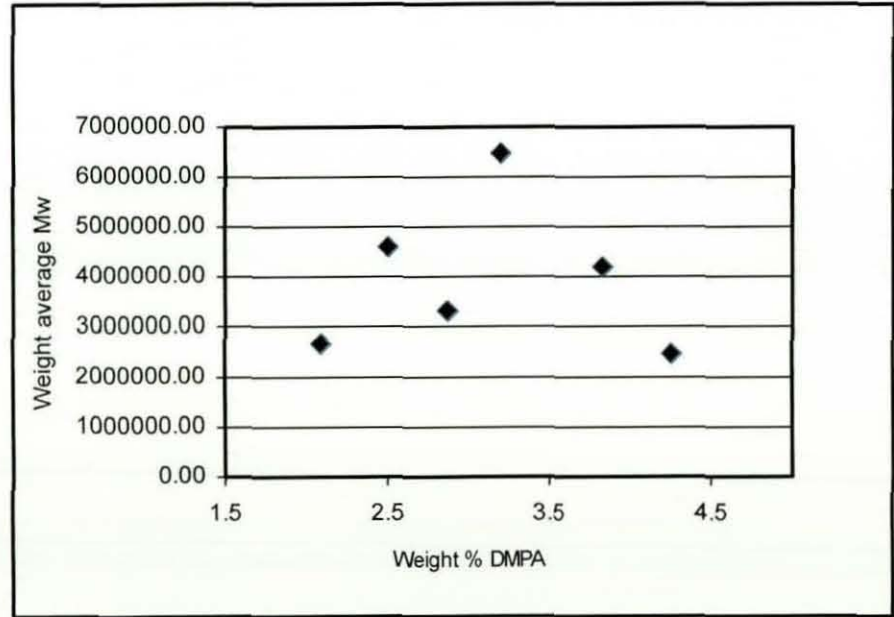


Figure 3.19 The variation in the molecular weight with DMPA content

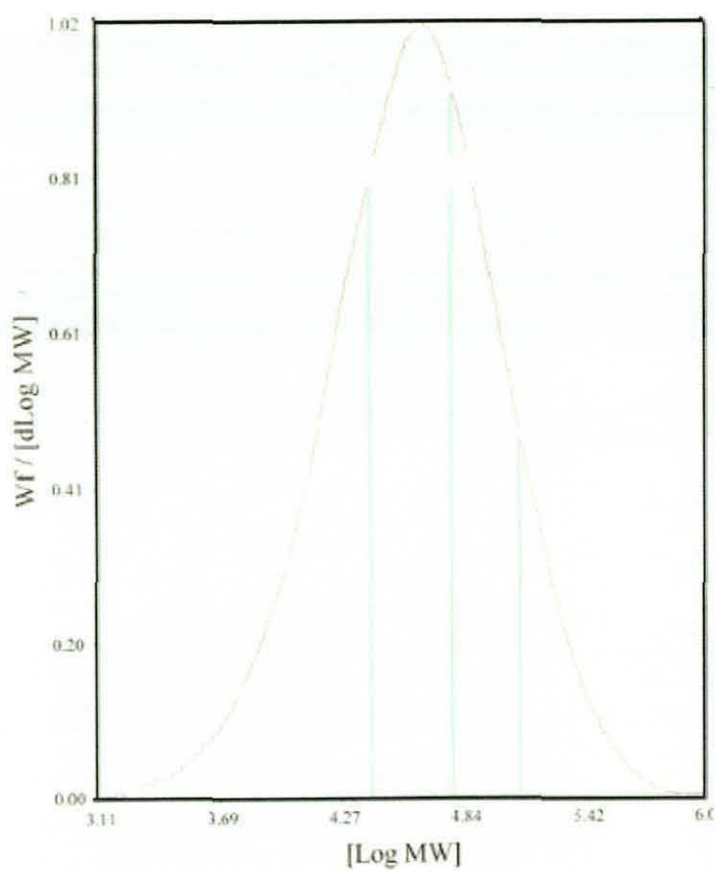


Figure 3.20 GPC chromatogram with high molecular weight PUDET2.5P

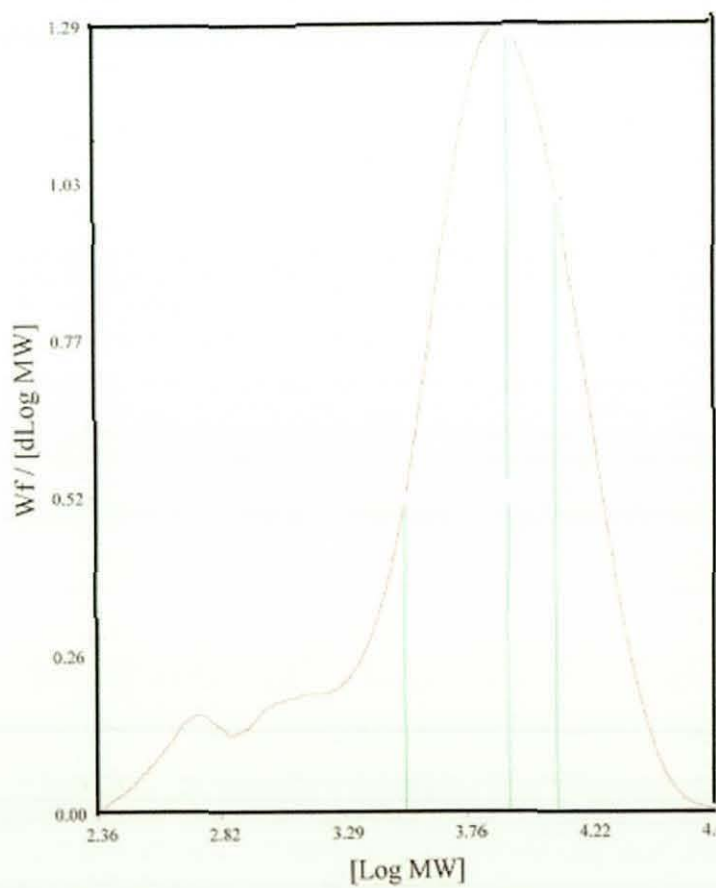


Figure 3.21 GPC chromatogram pf PUDET3.8P which illustrates the gradual development of bimodal molecular weight distribution at .

3.2. 4 Stress - strain curves for the IPDI- based polyether PUDs

Stress-strain curves of the dispersions with varying amount of DMPA are shown in figure 3.22. These curves are representative of typical stress-strain curves of flexible polyurethane of low hardness. The shape of the curves is consistent with slow increases in the initial modulus that occur on increasing DMPA content. The ultimate elongation at break (EAB) does not appear to be influenced by increases in the DMPA level. The elongation at break is partly determined by the molecular weight and by the chemical nature of the soft segments. The polyether used in the synthesis of WPUDs was a highly crystallisable PTMG 2900. It is well known that crystallisation of the soft segment on application of stress can limit the ultimate elongation ^[23]. An increase in the overall hard segment content will also limit the elongation at break of the polymer.

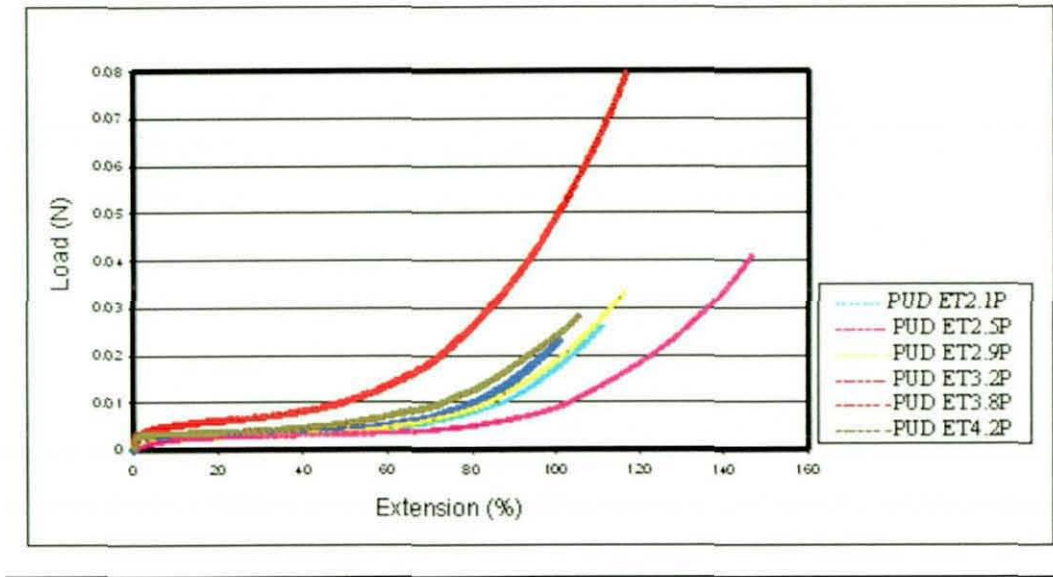


Figure 3. 22 Stress-strain curves of IPD-based polyether PUDs containing various levels of DMPA for the low strain region only.

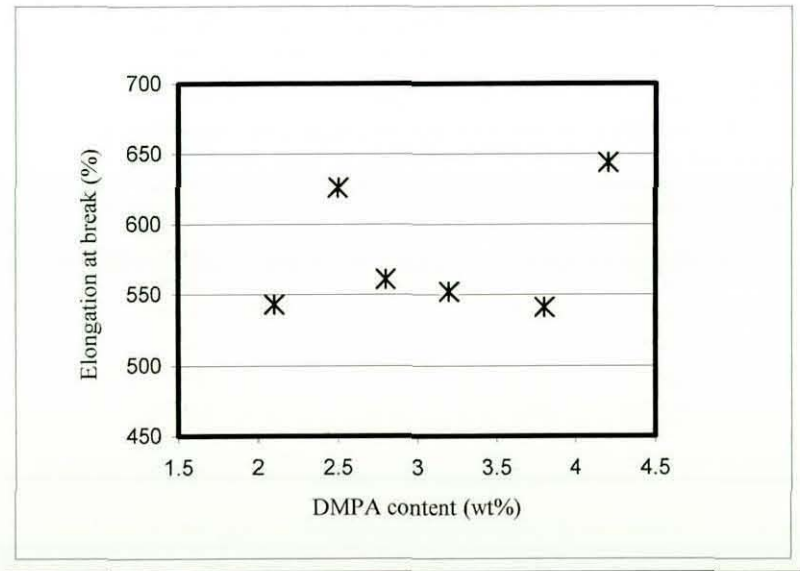


Figure 3.23 Effect of DMPA content on the elongation at break.

In general, therefore, the amount of DMPA incorporated in the WPUD formulation determines the type of dispersion that may be obtained. The level of DMPA controls the ease of dispersion, the stability of the final polyurethane dispersion, the dispersion particle size, and hence, its ability to form defect-free high quality films of the desired physical properties. In this work, it was found that the higher the DMPA content the easier it was to disperse the prepolymer. In cases where the level of DMPA was high and therefore a higher number of COO^- anions were present, the dispersions were readily achieved and remained stable after chain extension, giving rise to small particle sizes. The optimum level of DMPA for this study was determined as 2.9 to 3.2 weight percent. In contrast, in cases where a prepolymer of lower DMPA content i.e. 2 to 2.5 wt(%) was synthesised, the dispersion was found to contain large quantities of grit (microgel) and became unstable after 3 days. These dispersions also exhibited larger particle sizes. The changes in particle size with DMPA levels are presented in table 3.7 of this chapter. The optimum level of DMPA determined for WPUD at 2.9 to 3.2 wt% results in 24 to 26 wt % overall hard segment content which, as indicated by the trends in the physical properties in tables 3.9 of this chapter, yield hard, high modulus elastomers that are not suitable for use in soft elastomer applications. Another reason for the higher modulus is the use of a diamine as the chain extender that resulted in the formation of urea groups in the final dispersion. It is well known that solvent-based poly(urethane-urea) copolymers are high performance polymers which contain amorphous polyurea domains in their hard segments ^[18]. These urea hard segments, although relatively short, aggregate into domains that are quite rigid because of their high cohesive energy, thereby imparting greater toughness to the final material. Studies by Wang and Cooper ^[19] carried out on the film properties and characteristics of a series of polyether (urethane-ureas) showed that the presence of urea linkages gave rise to greater phase separation due to the higher cohesive energy and greater polarity of the urea groups compared to the urethane linkages and this often results in tougher, harder materials. In our study, a secondary diamine containing two bulky methyl groups was selected as the chain extender in an attempt to reduce the cohesiveness of the urea hard domains and to limit the hydrogen bonding, thereby generating a more flexible, softer material. However, a combination of ionic chain interactions and overall urea hard segment content meant that control of hardness was difficult to achieve.

3.2. 5 Stress relaxation measurements:

The measurement of stress relaxation at ambient temperatures for general purpose rubbers such as natural, butyl and polychloroprene have already been discussed in section 1.4.6.3. It has been demonstrated ^[68] that in cross-linked natural rubber the rate of relaxation fall progressively as the degree of cross-linking is increased in the vulcanised latex. In fact, Porter ^[285] observed that for any particular type of cross-links in NR, the rate of stress relaxation varies linearly with the inverse of the degree of cross-linking. That is, it varies directly with the average chain molar mass, $M_{c, \text{phys}}$ between neighbouring cross-links ^[68]. This applies equally to bulk rubber and latex vulcanisates.

However, where the network is not formed from covalent cross-links, the relaxation behaviour is different. For example, where the cross-links are readily exchangeable with one another or are otherwise labile (as when they are ionic or semi-polar in nature), substantial relaxation of stress may occur at room temperature over very short times. Similarly, in cases where the network is dependent upon the presence of domains of phase separated material, e.g. glassy polymers or internally hydrogen bonded polymers, considerable stress relaxation will occur if the material is capable of redistribution of stress in the rubbery matrix under stress. To examine this behaviour further, and to be able to conduct stress relaxation measurements of the polyurethane materials in this study, preliminary experimental work was carried out. In this introductory work a series of commercially available nitrile gloves and some in-house synthesised polyurethanes were tested for stress relaxation in order to gain an insight into the various relaxation processes that occur within these materials. The technique used and the results obtained from this preliminary work were then used to measure and characterise the relaxation processes that occurred in the WPU DS and bulk polyurethanes synthesised in this study.

3.2.5.1 Stress relaxation measurements of commercially available nitrile gloves.

Synthetic nitrile gloves are commonly used in industry for various applications including the healthcare industry where individuals have the suspected type I allergy arising from the natural rubber latex proteins. These synthetic nitrile rubber materials (XNBRs) are formulated such that they contain covalent sulphur cross-links as well as zinc carboxylate 'cross-links' in the final rubber film, formed from the methacrylic acid terpolymer of the carboxylated NBR emulsion and the zinc oxide added as part of the sulphur vulcanising system. To be able to conduct relaxation experiments on the XNBR rubbers, the latexes were cast into thin films and vulcanised in vacuum ovens at 80°C for a period of 8-10 minutes. The films were then allowed to reach equilibrium at ambient temperature (25°C) for a week before they were cut into Bongo test pieces according to the standard BS 903 part A41 (crosshead speed :1200mm/min). The test piece was then strained to 100% extension and the load (N) decay was recorded over a period of 10 minutes. The measurements were conducted at room temperature, and low extension (100%), short times (6 minutes). The results were compared to those of a natural rubber film which consisted of the same degree of sulphur cross-links. Table 3.10, and figure 3.24 show the stress relaxation graphs and data for both types of rubber. From the graphs in figure 3.24, it can be seen that for the four commercially available nitrile rubbers, the derived stress relaxation rates lie between 10-17 percent per decade. However, the stress relaxation of NRL film containing the same level of sulphur cross-linking indicates a relaxation rate of only 9.3 percent per decade. These relaxation rates are typical of lightly cross-linked soft rubbers.

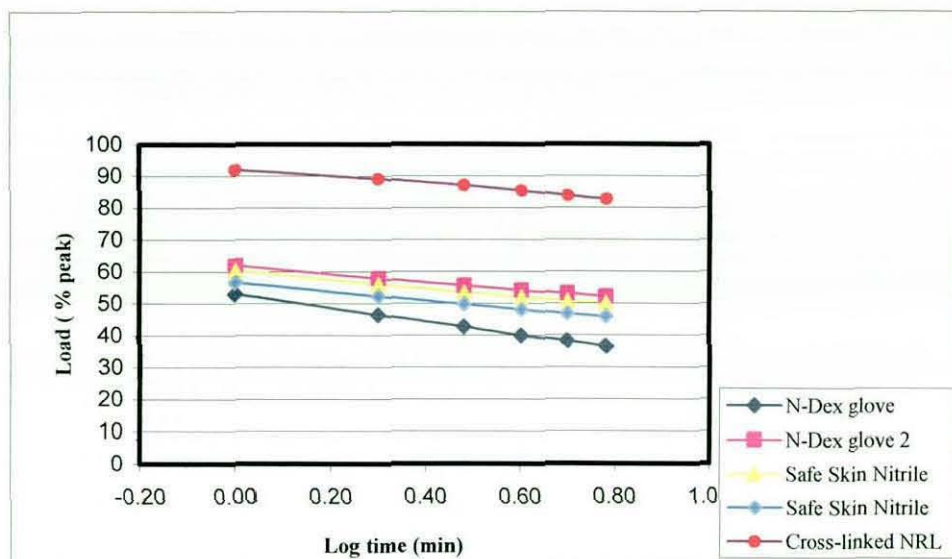


Figure 3.24 Stress relaxation behaviour of carboxylated nitrile rubber (XNBR) and natural rubbers film at 100% extension.

Table 3.10 Stress relaxation data for the nitrile and natural rubber films.

Rubber	Initial load (% of Peak)	Final load (N) % of Peak	Initial load drop (100 – initial load) (%)	Rate of stress relaxation (per decade)
Nitrile 1: N-Dex glove 1	53.1	36.6	46.9	16.5
Nitrile 2:N- Dex glove 2	62.1	52.3	37.9	9.8
Nitrile 3: Safe skin glove 1	60.6	50.3	39.4	10.3
Nitrile 4: Safe skin glove 2	56.8	45.9	43.2	10.8
Natural rubber	92.1	82.8	8.2	9.3

Another unusual behaviour observed in the nitrile rubbers was the high initial load drops at approximately 40%, which were clearly much larger than could be explained by inaccuracies in instrumental response and timing. The data suggest that these very large falls have their origin in a very rapid initial relaxation that takes place immediately after the application of load. Figure 3.25 shows the relaxation of a typical XNBR measured on an instrument capable of responding continuously from peak stress onwards. The abscissa represents time rather than log(time). From Figure 3.25, it is obvious that an initial very rapid relaxation occurs, leading to 50% loss of stress in the first minute. Relaxation slows sharply between one and two minutes, before settling down to a period of slow relaxation that is associated with the chemical cross-links within the rubber materials. This plateau section of the curve is representative of the resistance of the material to load due to the presence of sulphur cross-links.

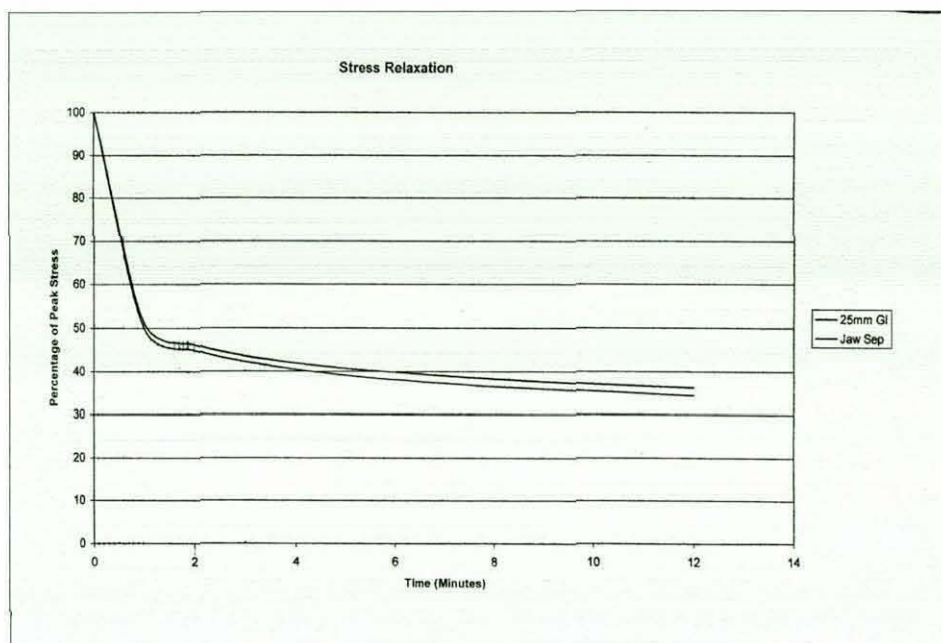


Figure 3.25 Continuous measurement of stress decay against time for typical nitrile rubbers

Re-plotting the stress values derived from figure 3.25 against log (time) gives figure 3.26 in which line **a** corresponds to the rapid initial relaxation, while line **b** represents the subsequent much slower relaxation. The slope of line **a** indicates a rate of nearly 80% per decade, while that of **b** corresponds to a rate of 13.4% per decade, a value similar to those of the nitrile rubbers of Figure 3.24. The initial load drop of 49% is at the high end of those for a covalently cross-linked rubber of the type given in Figure 3.24.

This initial period of very rapid relaxation can be ascribed to the presence of zinc carboxylate 'cross-links' in the rubber, formed from the methacrylic acid terpolymer and the zinc oxide added as part of the sulphur vulcanising system. Such cross-links are likely to have structures similar to those of ionomer rubbers which contain assemblies of ionic or semi-polar entities that are capable of rapid interchange with one another. When the data from figure 3.26 were plotted on a log scale, the normal linear plot, whose components could be separated and ascribed to different relaxation processes that occurs within a typical XNBR rubber, was obtained.

The results of the stress relaxation testing obtained from these nitrile rubbers which contain two types of cross-links, i.e. the sulphur and ionic zinc oxide based, suggest that under the conditions of ambient temperature, low extensions and short times, relaxation remains directly proportional to the logarithm of elapsed time. Additionally, the presence of ionic cross-links bring about a greater drop in the initial load recorded for the rubbery material.

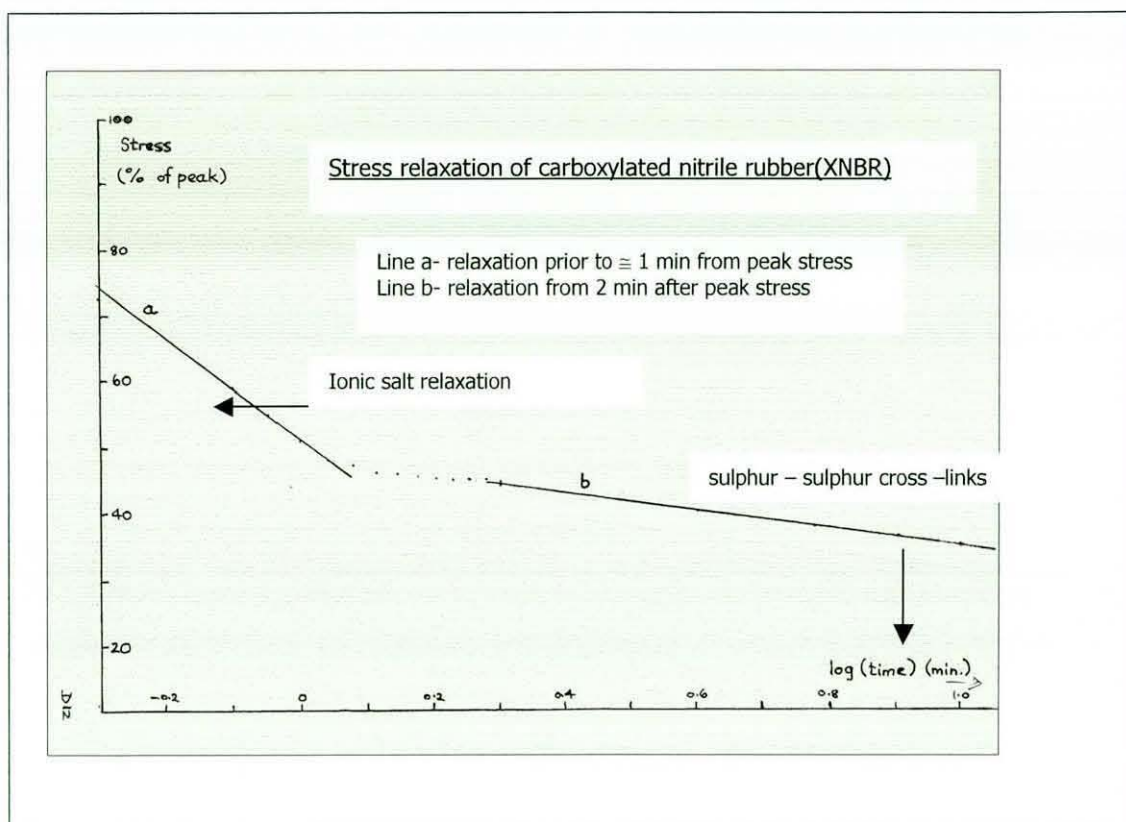


Figure 3.26. Re-plotting of the graph in Figure 3.25

It is therefore concluded that the relaxation rates of most rubbery materials can be derived in the same way by plotting load or stress against log (time) whether the network is formed by formation of chemical cross-links, or transient cross-links such as tiny crystallites or secondary chain interactions. Furthermore, from these tests it may be possible to identify the origin of the relaxations and relate to the particular process that may occur within the rubber during the timescale of the experiment.

To determine whether this is true for block copolyurethanes, this experimental procedure was also applied to a series of in-house synthesised polyurethane materials. The polyurethanes studied consisted of a covalently cross-linked polyurethane-urea, an aromatic thermoplastic polyurethane, as well as two polyester polyurethane elastomers that had exactly the same chemical composition, but one contained carboxylate salt pendent groups while the other was non-carboxylated. The overall chemical compositions of these polyurethane rubbers are given in table 3.11.

Table 3.11 Chemical Compositions of PU elastomers studied for their stress relaxation behaviour.

	Hard block	HS (wt %)	Soft block	Covalent cross-links	Carboxylate Salt
Aromatic TPU	Aromatic MDI/ BD	27	Ethylenebutylene adipate	None	N
Aliphatic PU-Urea	Aliphatic IPDI/ EDA / 1,2,3 propane triol	25.3	Poly (propylene glycol) (Acclaim 4200)	yes triols	N
Aliphatic TPU	Aliphatic IPDI/BD	29.0	1,4-Butane diol and neopentyl glycol polyester	None	N
Carboxylated Aliphatic TPU	Aliphatic IPDI/ NN'DMEDA	27.9	1,4-Butane diol and neopentyl glycol polyester	None	Y

Once again the results of stress relaxation measurement obtained at ambient temperature, low extensions and short times showed that the relaxation remained directly proportional to the logarithm of elapsed time for the urethane rubbers as well.

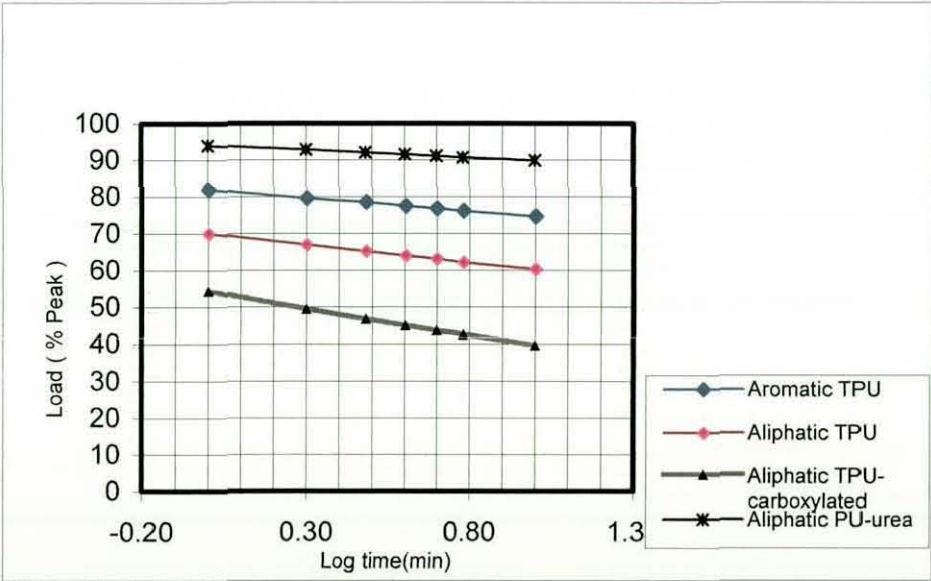


Figure 3.27 Stress relaxation behaviour of the PU rubbers of various chemical compositions.

The data from figure 3.27 was used to calculate the values of stress relaxation rate (SRR) and the initial load drop for each PU rubber. These are given in table 3.12. From the calculated values it appeared that the SRR and initial load drop are highly dependent on the chemical composition of the polyurethane. The most obvious feature is the different behaviour of the polyurethane having an ionogenic group (carboxyl) combined in the polymer and those that do not. The latter showed stress relaxation rates of <10% per decade, whilst the former show rates of approximately 15% per decade. It is proposed that the high relaxation rate was at least partly due to the presence of carboxylate salt group in this polyurethane. Support was given to this possibility by the fact that all the nitrile rubbers of figure 3.24 tested earlier, also showed main relaxation rates in the range 10 – 17% per decade. It is, therefore, reasonable to conclude that incorporation of a carboxyl group in a PU makes it relax more readily, both on the 1 to 10 minute relaxation, as well as relaxation during the first minute, (the initial load drop). The carboxylated PU film lost approximately 45% of the stress in the first minute after extension. This is again reminiscent of the behaviour of the carboxylated XNBR films illustrated in Figures 3.24 and 3.26, and was presumably due, likewise, to rapid exchangeability between the polar domains in the polymer. However, there was a difference in the XNBR films. The domains were of zinc carboxylate, whereas in the polyurethane films with no zinc present the domains were ionic carboxylates arising from the neutralisation of the acid with a counter ion, triethylamine.

Table 3.12 Stress relaxation rates and initial drop in load values of PU elastomer

Type of PU	Rate of stress relaxation (% per decade)	Initial load drop (100-initial load %)
Aromatic TPU	7.2	18.0
Aliphatic TPU	9.6	30.0
Aliphatic TPU (carboxylate salt)	14.7	45.7
Poly(urethane-urea)	4.1	6.0

It was apparent from Table 3.12 that ionogenic groups are by no means responsible for all of the initial load drop. The non-ionogenic aromatic TPU and the aliphatic TPU also showed initial drops of 18-30 % while the poly(urethane-urea) shows a drop of 6% only. The behaviour of the latter could only be linked to the presence of covalent cross-links in the latter, in a similar manner to natural rubber tested by Porter et al. ^[68]. The higher initial load drop could also arise from a structural feature such as the weaker hard domains of aliphatic urethane versus aromatic urethane groups ^[17,25], and much stronger cohesive urea linkages. The results of this work also indicated that covalent cross-linking was not always necessary in order to achieve a stress relaxation rate < 10%

per decade. The chemical nature and the proportion of hard blocks also determines the degree of inter-chain interactions in the elastomer and thus determine the network structure, where the hard blocks effectively act as cross-linking sites which give the material its elastomeric properties. Bayer and co workers^[6,16] showed that polyurethanes with the highest levels of modulus, tear and tensile strength can be obtained by the use of the most rigid, bulky and symmetrical diisocyanates. The low rate of stress relaxation and small initial load drop shown by the aromatic polyurethanes in this case can also be attributed to the presence of 4,4-methylenebis (phenyl isocyanate) that is capable of forming stiff and glassy or crystalline hard segments. It is, therefore, proposed that the extension and subsequent relaxation processes in an elastomeric polyurethane block copolymer, probably involves the orientation and restructuring of the molecular organisation initially present. Upon a limited elongation, stress induced crystallisation of the soft segments may occur. Not all of the soft segment in a block copolymer are capable of crystallising, either due to their chemical constitution or to their physical environment in the polymer matrix. Those soft segments that form crystallites will provide resistance to further extension because of the crystalline forces now present.

In the aliphatic thermoplastic polyurethane elastomers studied here, the polyester soft segments used consisted of neopentyl glycol which has a limited crystallising ability compared to poly(tetramethylene)glycol used in synthesising the aromatic thermoplastic polyurethane elastomer. The combination of a non-crystallising polyester soft segment and an aliphatic diisocyanate hard segment has meant a greater overall stress relaxation in the aliphatic thermoplastic polyurethanes. In the case of the aromatic thermoplastic elastomer, the combination of an aromatic MDI hard block and a stress crystallising soft block resulted in a stress relaxation rate of < 10% approaching that of a covalently cross-linked systems.

In the case of the poly(urethane-urea) elastomer, where the network consists of some covalent cross-links from the triol groups, and the highly rigid hard blocks arising from the urea groups, the stress relaxation rate, and the initial drop in load are quite similar to those obtained for covalently cross-linked natural rubber films shown in figure 1.6 in Chapter 1^[68].

3.2.5.2 Stress relaxation for IPDI-based polyether PUDs

To examine the stress relaxation behaviour of polyether-based WPUDs of differing ionic moiety concentration, a plot of load decay (% peak) versus log time(min) for each material was obtained and is shown in figure 3.28. From these plots the initial and the final loads were determined. The stress relaxation rate (SRR) of each material was estimated by calculating the gradient of the linear parts of the plots, and the initial fall in load from 100% was calculated from the intercept. These values are summarised in table 3.13.

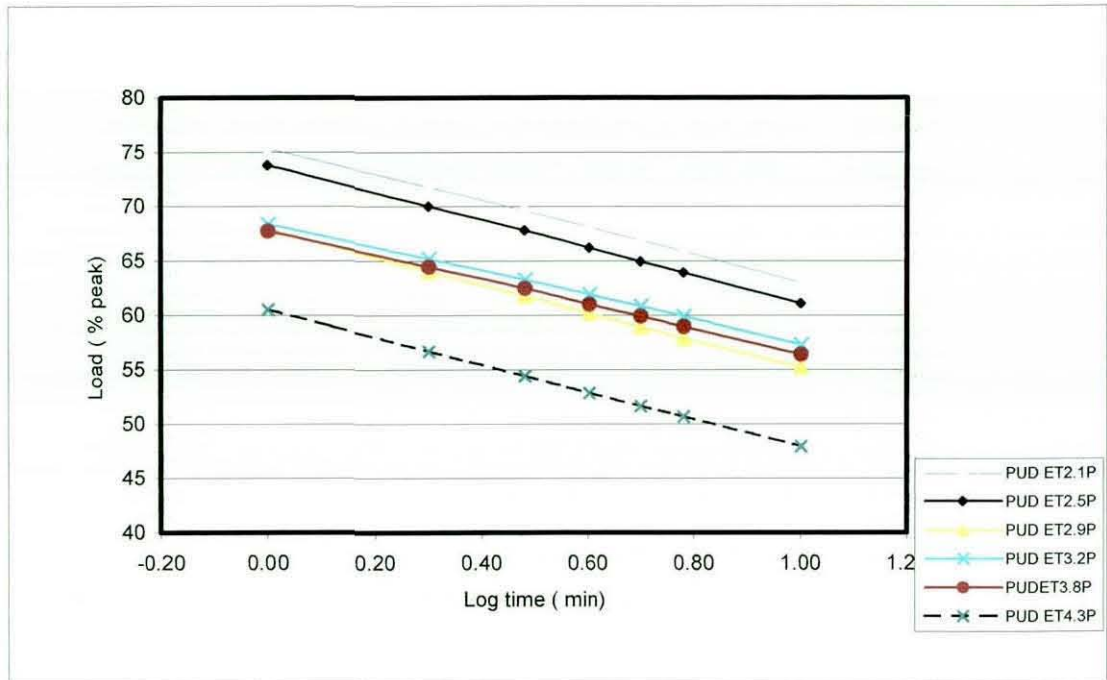


Figure 3.28 Stress relaxation curves for the poly(etherurethanes) with the IPDI / NN'DMEDA hard segment.

Table 3.13 Effect of DMPA concentration on load in WPUDs

PUD	Initial load (% of Peak)	Final load (N) (% of Peak)	Initial load drop (100 – initial load) (%)	Rate of stress relaxation (per decade)
PUDET2.1P	75.3	63.0	24.7	12.0
PUDET2.5P	73.8	61.1	26.2	13
PUD ET2.9P	67.9	55.3	32.1	13
PUDET3.2P	68.4	57.3	31.6	11.0
PUDET3.8P	67.8	56.5	32.3	11.0
PUD ET4.3P	60.5	48.0	39.5	13.0

Close examination of the plots obtained suggest that several processes contribute to the overall behaviour of WPUDs. The plots can be divided into two regions:

- The initial, non-linear region where there is a rapid decay of load within the first minute of the measurement starting.
- Slow but continuous, decay of load that occurs throughout the time scale of the experiment, i.e. 10 minutes.

This behaviour has previously been observed for polyurethanes [73,91]. For example when such measurements were carried out by Sing et al. [73] in order to study the thermal relaxation of polyurethanes, they also discovered their plots deviated from linearity initially and then approached linearity at extended times. They assigned the different regions in their plots to different viscoelastic processes that occur at different rates and different time scales.

Furthermore, it is well known that in cross-linked natural rubber films, the rate of relaxation falls progressively as the degree of cross-linking is increased in a vulcanised latex ^[68]. Similarly in cases where the network is dependent upon the presence of domains of phase-separated material, e.g. a glassy polymer or an internally hydrogen-bonded polymer, considerable stress relaxation will occur if the material is capable of redistribution in the rubbery matrix under stress. The preliminary experimental work, outlined in section 3.2.5.1, demonstrated this effect in studies with carboxylated NBR, as well as in selected polyurethane materials.

For the WPUDs being investigated here, the initial rapid decay must have its origin in the disruption of weak structural interactions that breakdown immediately the load is applied, with no ability to reform or resist the force being applied to the material. This behaviour may be associated with the breakdown of ionic interactions which in the case of WPUDs, arise from the presence of the ionic moiety, DMPA. From the results in table 3.13, it appears that the higher the level of ionic moiety in the dispersion the greater the initial fall in load. As the level of DMPA was increased from 2.1 to 4.3 wt%, the calculated drop in load within one minute of the application changed from 25 to 40%. Therefore there seems to be a linear relationship between the response of the polyurethane within the first minute and the level of the ionic moiety present in the WPUD. Figure 3.29 illustrates this effect. These effects were similar to those discovered for the nitrile rubbers, as outlined in section 3.2.5.1

The second part of the plot that provides the overall rate of stress relaxation, measured by the slope of the linear region, seemed to remain unaffected by changes in the DMPA concentration. It remains fairly unchanged except for both extreme concentrations, i.e. when the level of hard segment or ionic moiety is at minimum or maximum, that is at 2.1 and 4.3 wt%, respectively. The higher the SRR value, the lower the effective cross-linking as reported previously for vulcanised rubber latex films ^[68]. In the case of WPUDs, no covalent cross links were present and the rubber network was held together by hard domains, i.e. high cohesive energy urea linkages ^[19], as well as the ionic interactions of the ionic moiety. It was expected that as the level of hard segment increases, so would the size of the hard blocks giving rise to an improved degree of phase separation that yields effective tie points or cross-links between the polymeric chains. However, there also appeared to be an optimum level of ionic moiety level above which the degree of disorder was increased and the effective network disrupted. For this particular group of WPUDs, the optimum formulation lay between 3.2 and 3.8 (wt %) DMPA. From Figure 3.30, it can be seen that the value of SRR starts at 12.3, increases to 12.6 then fell to 11 and to 11.3 per decade, before it increased again at a DMPA concentration of 4.3wt% suggesting that the minimum SRR are shown by PUDs containing from 2.9 to 3.8 wt% DMPA concentration. Part of this effect, of course, is related to the much larger drop in the initial load observed for PUDET4.3P, which gave rise to a higher gradient for the plot obtained for this WPUD at 12.5% per decade.

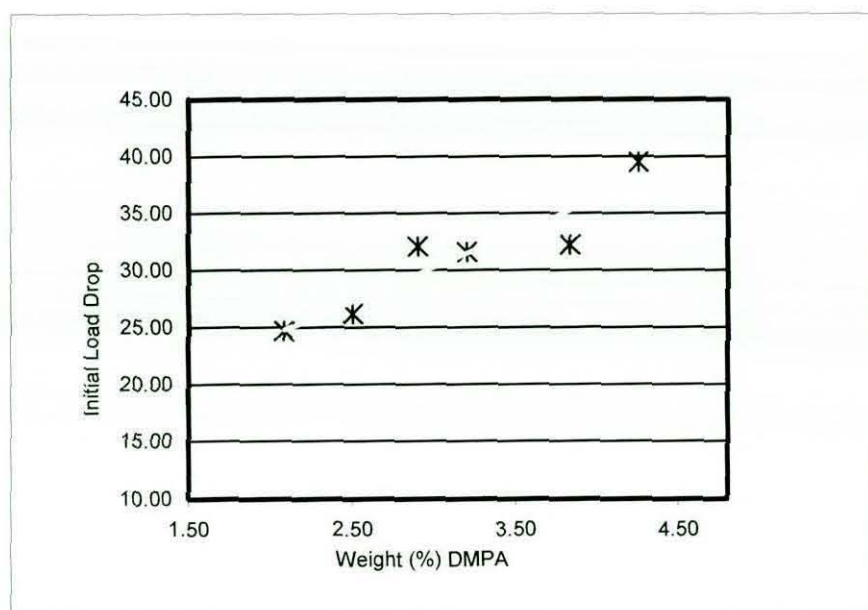


Figure 3.29 Effect of ionic moiety concentration on PUD initial load drop (%)

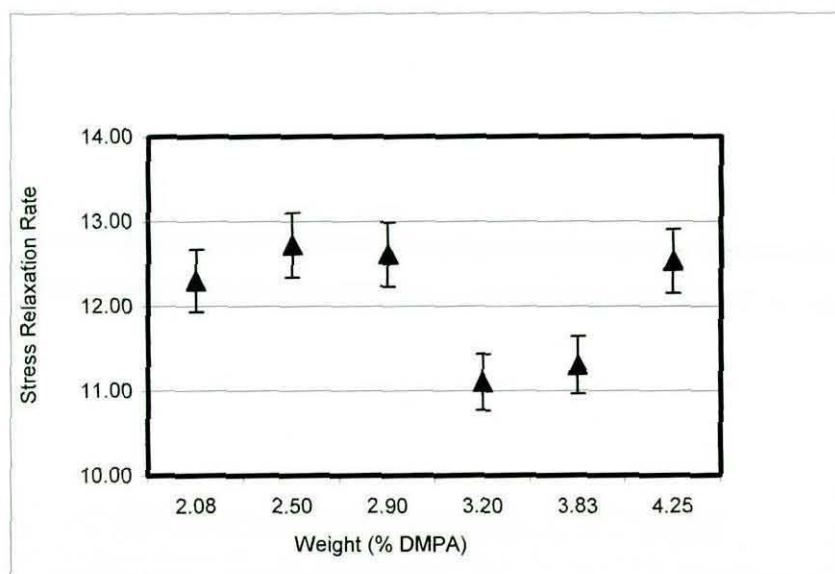


Figure 3.30 Rate of stress relaxation against DMPA concentration of PUDs

In conclusion, analysis of the stress relaxation results revealed that an increase in the overall hard block content of a PUD did not necessarily lead to improved elastic or rubbery behaviour. In fact, the experiments carried out in this study showed that an increase in wt % hard block from 20-29 wt (%) brought about by increasing mainly the ionic moiety, resulted in a lower initial load which was accompanied by a greater rate of relaxation up to a certain level of ionic moiety concentration. The cause of lower initial load was believed to be linked to the relaxation processes associated with the ionic moiety ^[68], and did not arise from the relaxation of the urea linkages of the polyurethane dispersion. The results in table 3.13 show that every 0.5 wt (%) increase in DMPA brings about a corresponding drop in the initial load, leading to the conclusion that it must be the ionic bonding in the PUD backbone that had been disrupted immediately after the application. After the initial drop, the behaviour of the elastomeric PUDs remained relatively unchanged since the SRR values did

not seem to differ widely, suggesting that this component of the relaxation curve was controlled by a different relaxation mechanism arising from changes perhaps within the urethane- urea linkages. The fact that PUDET3.2P, and PUDET3.8P show the lowest SRR seem to suggest that a level of 3.2 to 3.8 wt % ionic concentration may, in fact, lead to enhanced ionic cluster formation that augments the overall phase separation or cross linking effect, in PUDs, thereby reducing the relaxation rate shown by these two elastomers.

However, higher increases in the ionic moiety to 4.3 wt% as in the PUDET4.3P causes a deterioration of the overall phase separation and brings about a greater SRR. as indicated in table3.13. It is possible that the chemical composition of the urea hard segments would influence the SRR of a given polyurethane dispersion. Therefore, testing and analysis of the polyether PUDs of H₁₂MDI/ EDA composition might provide a further insight into the stress relaxation properties of these WPUD. This will be discussed in the subsequent sections.

3.3 Effect of change of the type of diisocyanate and chain extender on the physical properties of WPUDs.

3.3.1 Tensile properties of H₁₂MDI/ EDA- based polyether PUDs

Table 3.14 provides a summary of the physical properties exhibited by poly(ether-urethanes) synthesised from H₁₂MDI and ethylene diamine. In general, the H₁₂MDI/ EDA based polyether PUDs indicate comparable tensile strength, but much higher S100 modulus than their IPDI/ NN'DMEDA equivalents. However, lower elongations at break are exhibited by these PUDs. This behaviour could be attributed to the H₁₂MDI / DMPA and the H₁₂MDI/EDA hard blocks present in these WPUDs. It is also possible that a combination of H₁₂MDI/EDA leads to formation of discrete urea crystalline domains and a greater degree of phase separation than their IPDI, NN'DMEDA equivalents. The stress-strain curves for the polyether PUDs are compared in Figure 3.31.

Table 3.14 Tensile properties of H₁₂MDI/ EDA-based polyether PUDs.

Code	HS (wt %)	TS (MPa)	S100 (MPa)	EAB (%)
PUDET2.83H	26.0	50.3	4.5	540
PUDET3.3 H	30.0	42.7	7.3	430
PUDET4.1H	31.6	32.5	10.0	350

Note : average of 5 test pieces used for every measurement. One batch of dispersion prepared in each case only

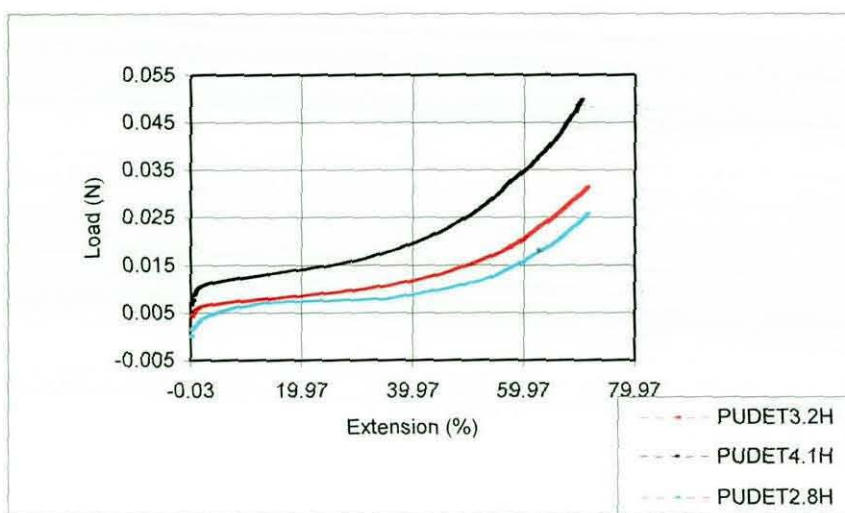


Figure 3.31 Stress-strain curves for the WPUDs with H_{12} MDI / EDA hard segments at low strain only.

There appeared to be a downward trend in tensile strength for the H_{12} MDI / EDA PUDs. A contributor to this could be the rapidly crystallisable hard segments, which as the level of overall HS increases and the hard segment increases in molecular weight, the hard segment chains increase in size thereby giving rise to a greater incompatibility with the growing polyurethane polymer chain. This is evident in the GPC chromatograms of the H_{12} MDI/ EDA based PUDs which clearly indicate a bimodal distribution of lower and higher molecular components. Figure 3.32 gives a typical GPC chromatogram for PUDET 3.3H.

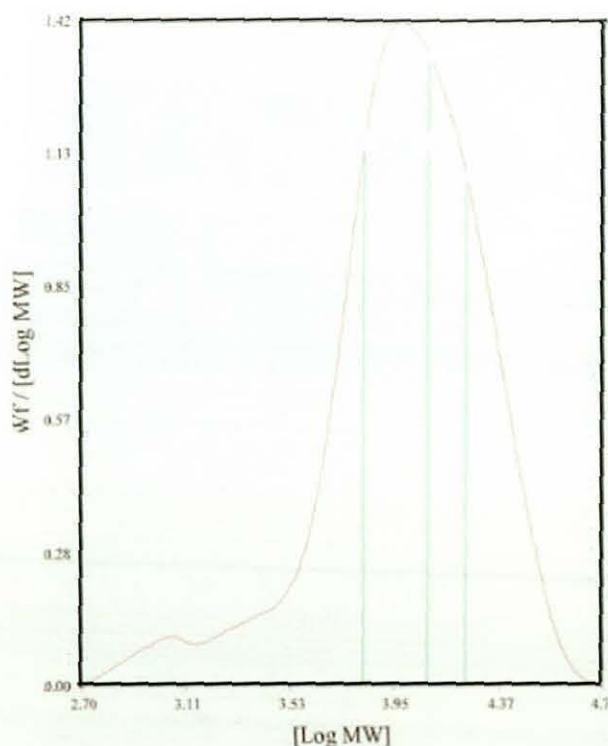


Figure 3.32 A typical GPC chromatogram for H_{12} MDI/ EDA polyether-based PUD at 3.3 wt% DMPA

3.3.2 Stress relaxation of H₁₂MDI/EDA based polyether PUDs.

Stress- relaxation measurements conducted on H₁₂MDI/ EDA polyether urethanes are summarised and compared with IPDI-based polyether PUDs, in table 3.15 and in figure 3.33. In the case of H₁₂MDI/EDA-based PUDs the higher the level of hard segment the lower the rate of stress relaxation but the higher the drop in the initial load. Overall, the H₁₂MDI/ EDA materials indicate lower rate of stress relaxation than the IPDI/NN'DMEDA-based PUDs. Table 3.15 compares the IPDI and H₁₂MDI materials.

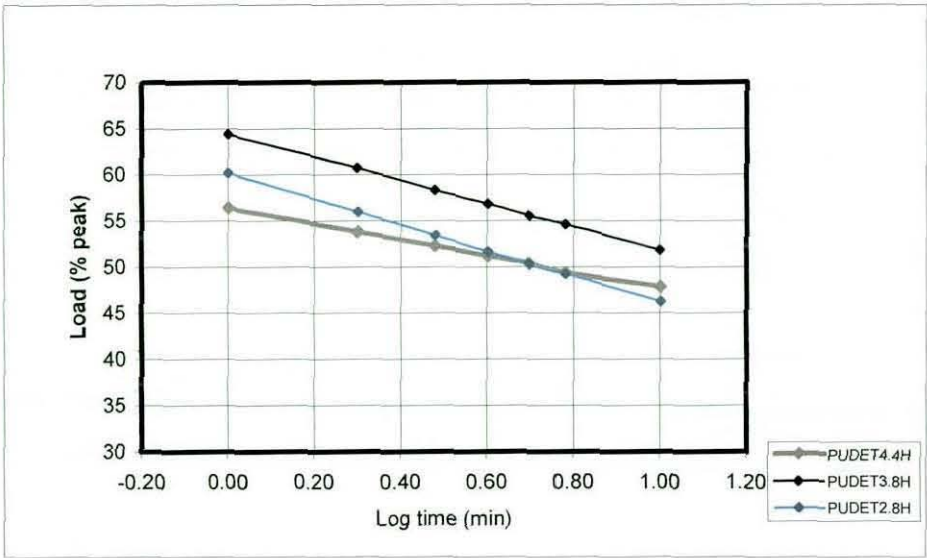


Figure 3.33 Stress relaxation behaviour of the H₁₂MDI/ EDA-based polyether PUDs

Table 3.15 Comparison of stress relaxation data for H₁₂MDI / EDA, with IPDI / NN'DMEDA-based polyether PUDs

PUD	Initial load (% of Peak)	Final load (N) (% of Peak)	Initial load drop (100 ~ initial load) (%)	Rate of stress relaxation (% per decade)
PUDET2.8H	60.2	46.3	39.8	14.0
PUD ET2.9P	67.9	55.3	32.1	13
PUDET3.8H	64.4	51.8	35.6	13.0
PUDET3.8P	67.8	56.5	32.3	11.0
PUDET4.1H	56.4	47.9	43.6	9
PUD ET4.2P	60.5	48.0	39.5	13

3.4 Polyester polyol polyurethane dispersions

3.4.1 Physical properties of polyester-based WPUDs

To determine the effects of the soft segment on the physical properties, a series of WPUDs were synthesised using poly(ethylenebutylene) adipate as the soft segment. This polyester has a molecular weight of 2000 and is made up of a 50:50 mixture of diols i.e. ethylene glycol and 1,4-butane diol. It has the ability to crystallise rapidly, which is thought to give rise to good physical properties.

For each type of diisocyanate and chain extender two reactions were conducted at two different levels of DMPA concentration i.e. 2.8 and 3.2 wt %. Table 3.16 compares the tensile properties of these polyester-based PUDs.

Table 3.16 Physical properties of polyester urethane with differing hard segment type

Code	HS (wt%)	TS (MPa)	S100 (MPa)	EAB (%)
PUDES2.8P	23.6	18.0	1.1	1050
PUDES3.2P	29.0	35	1.8	700
PUDES2.8H	30.1	34.0	2.4	600
PUDES3.2H	30.7	41.0	3.2	570

Note : average of 5 test pieces used for every measurement.

The most obvious difference was the reduction of the S100 value for these polyester WPUDs. In all cases, the polyester PUDs, regardless of the diisocyanate and chain extender type showed much lower S100 modulus but higher EAB than their polyether counterparts. One reason for this difference could be the greater degree of phase separation expected in the PTMG-based PUDs, as polyethers are known ^[19] to give rise to improved phase-separated polyurethanes in which the hard domains act as reinforcing discrete phases for the soft blocks ^[17,23,187].

Thermal analysis of these two groups of materials was expected to provide a greater insight. Stress-strain curves for polyester PUDs are given in figure 3.34.

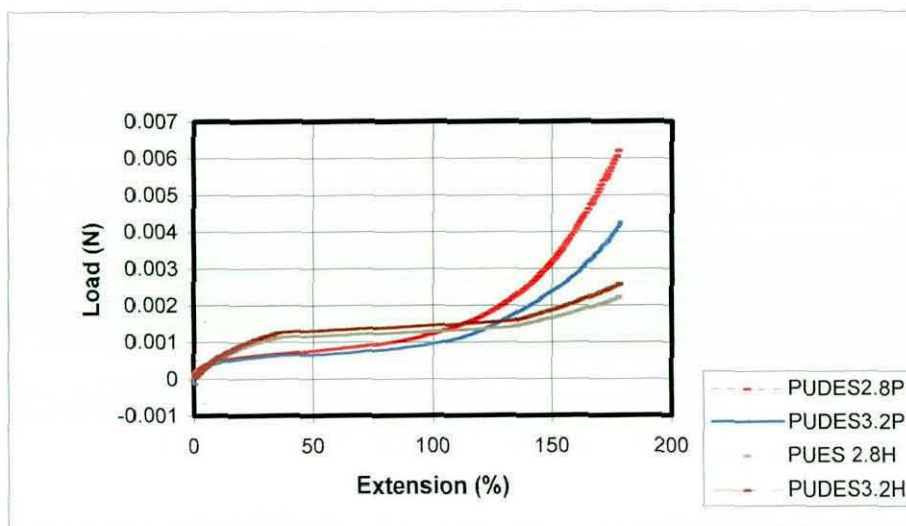


Figure 3.34 Stress-strain curves for the polyester based PUDs with differing hard segment contents at low strain only.

Examination of the molecular weight of these polyester PUDs by GPC, indicated in *general*, a broad distribution peak as indicated in figures 3.35 and 3.36. One reason for this behaviour may be the greater compatibility of the polyester soft segment with the urethane hard segments and, hence a more homogenous morphology than those shown by the polyether WPUDs.

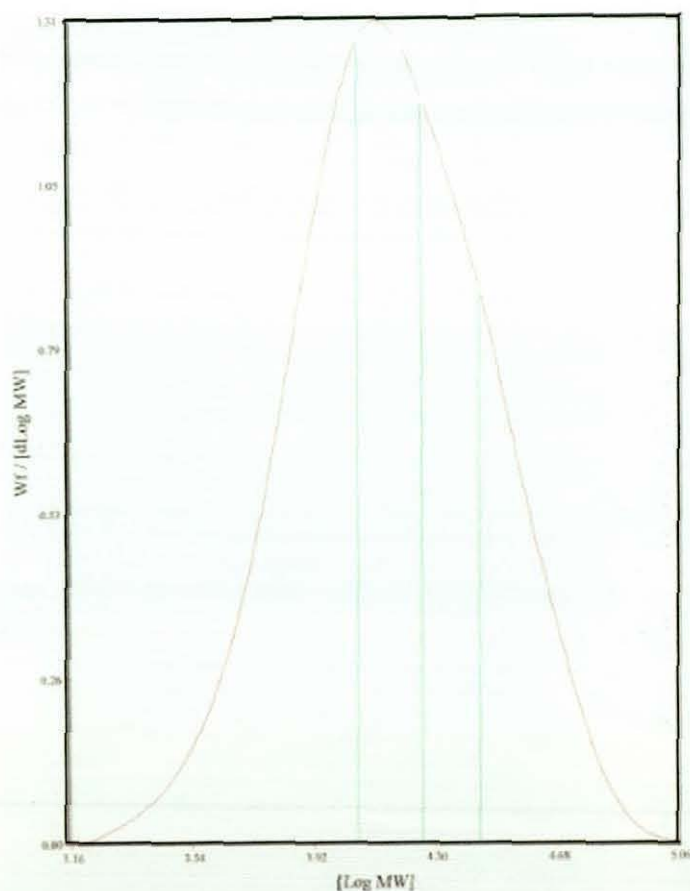


Figure 3.35 GPC chromatogram for IPDI-based polyester PUD at 2.8wt % DMPA.

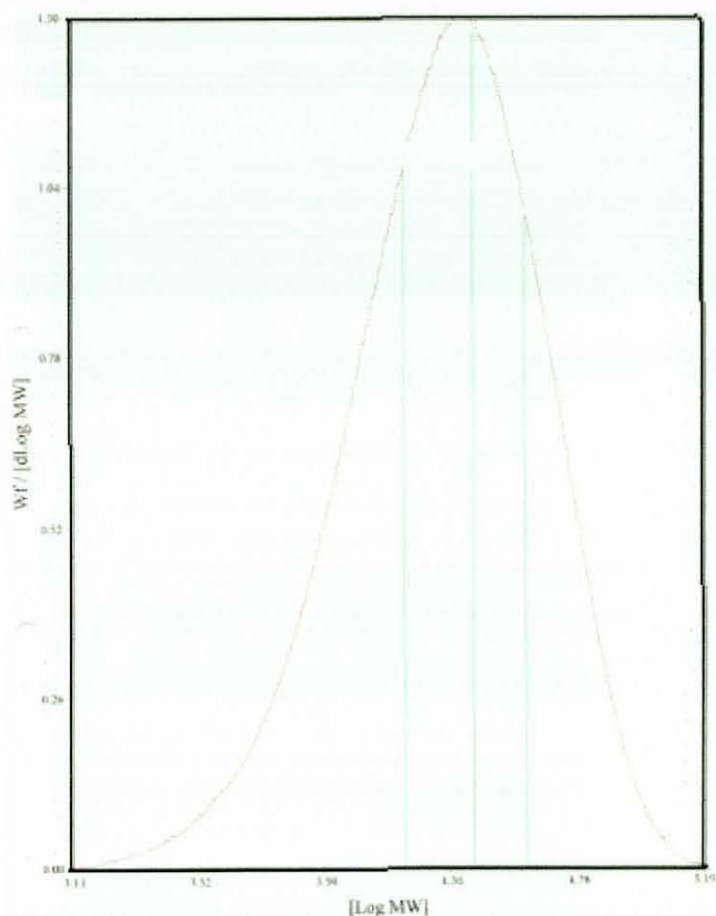


Figure 3.36 GPC chromatogram for H₁₂MDI-based polyester PUDs at 2.8 wt % DMPA

3.4.2 Stress relaxation in the polyester-based WPUDs.

From table 3.17 and figure 3.34, it appears that in all cases the presence of a mixed diol polyester soft segment has not only contributed to higher relaxation, but, more importantly, to a significant reduction in the initial load compared to their polyether counterparts. Within this series, the highest relaxation rate was indicated by PUDES2.8P. There could be several explanations for this behaviour. This may have had its origin in the chemical nature of the hard block, the overall weight percent hard segment and the presence of the polyester that is more compatible with the hard segment than a corresponding polyether ^[26-28]. In the polyether PUDs, the factor that determined the drop in load was the concentration of the ionic moiety. However, the stress relaxation data obtained for the polyester PUDs appeared to suggest that the degree of phase separation was the most significant factor in governing decay in the load, as well as the overall rate of stress relaxation of these PUDs.

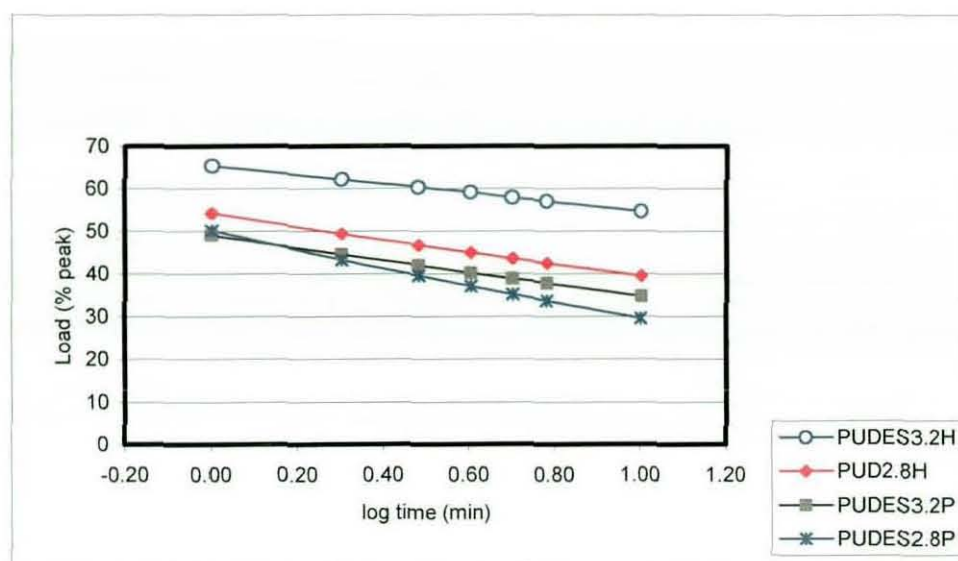


Figure 3.37 Stress relaxation behaviour of polyester-based PUDs with differing hard segment levels.

Table 3.17 Comparison of stress relaxation data for H₁₂MDI / EDA, with IPDI / NN'DMEDA based polyester PUDs.

PUD	Initial load (% of Peak)	Final load (N) (% of Peak)	Initial load drop (100 – initial load) (%)	Rate of stress relaxation (per decade)
PUDES2.82P	50.3	29.6	49.7	20.7
PUD ES3.2P	49.1	34.8	50.9	14.3
PUDES2.8H	54.3	39.7	45.7	14.6
PUDES 3.2 H	65.4	54.7	34.6	10.7

3.5 THERMAL ANALYSIS

3.5.1 Differential scanning calorimetry (DSC)

The polyurethanes synthesised in this study were expected to exist as microphase separated systems and exhibit complex thermal behaviour which was dependent on the starting materials that made up their chemical composition, and their thermal or process history. In the case of WPUDs synthesised in this work, all testing was carried out on room temperature cast-films, that were treated at the same elevated temperatures, i.e. 110°C for 20 minutes in a vacuum oven, and conditioned in humidity (50 % RH) and temperature-controlled rooms at 25°C for a period of a week, before being analysed by the DSC, to determine their morphology from the DSC and the extent of phase separation in each type of elastomer.

For the polyether WPUDs, the prepolymers were based on PTMG2900, a polyol that is known to be capable of extensive cold crystallisation at room temperature. A typical DSC thermogram for PTMG 2900 is shown in figure 3.38, which indicates a small T_g at -85°C, but an extensive multiple melting endotherm, which was the result of cold crystallisation. This begins at 23 °C and was complete at 40°C.

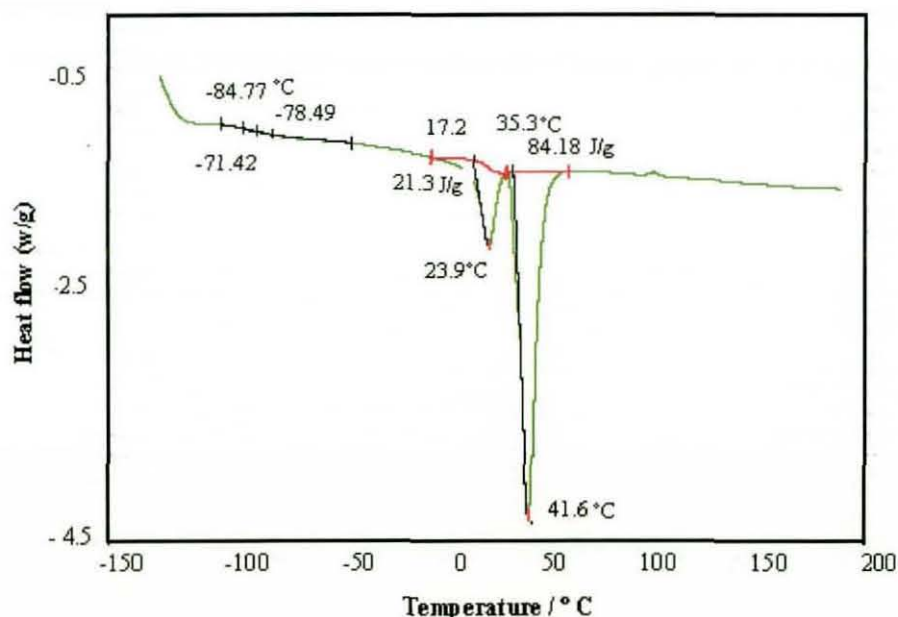


Figure 3.38 DSC thermogram for the pure PTMG 2900

For the polyester WPUDs, the polyol used was Bester 43H a poly(ethylenebutylene adipate) of 2000 molecular weight. This polyol is also capable of rapid crystallisation but has a T_g at -60°C, and a crystallisation exotherm at -11°C, followed by extensive melting transition at 13°C. Figure 3.39 gives the DSC thermogram for this polyester polyol.

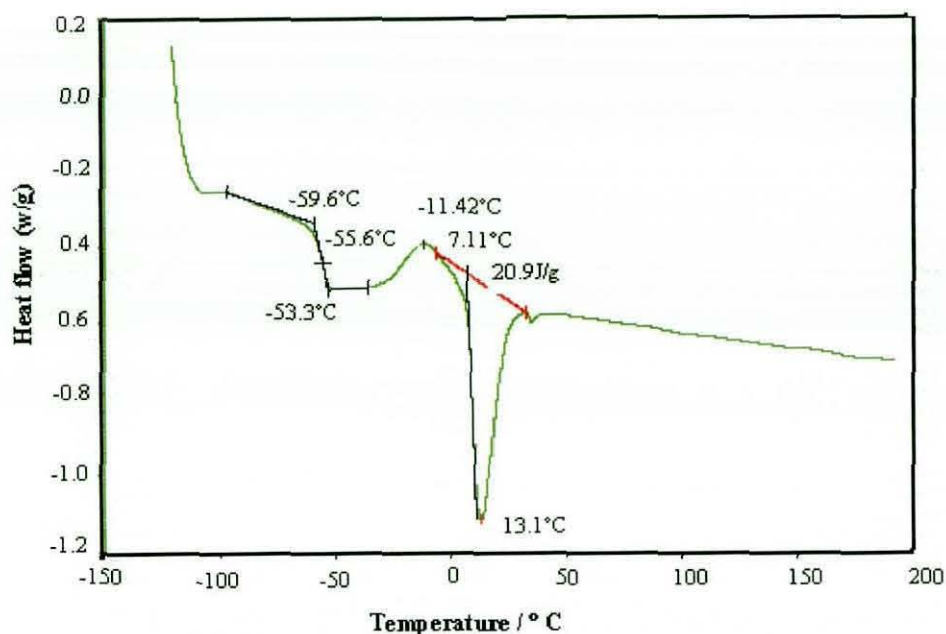


Figure 3.39 DSC thermogram of a pure polyester polyol.

3.5.1.1 Effect of DMPA content on the thermal behaviour of IPDI-based polyether PUDs.

Figures 3.40 and 3.41 provide the DSC thermograms for the series of polyether PUDs containing varying levels of DMPA and whose hard block is based on the secondary amine N,N'-dimethylethylene diamine and isophorone diisocyanate.

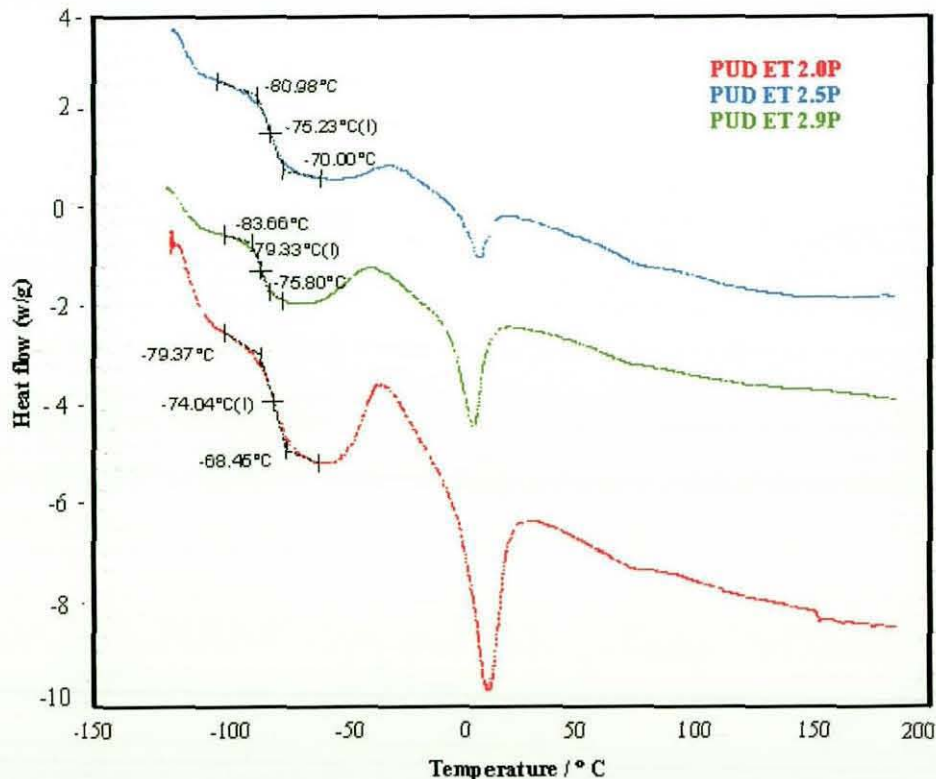


Figure 3. 40 DSC thermograms for the PUDET samples with 2.1, 2.5, and 2.9 wt% DMPA heated from -150 to 200°C.

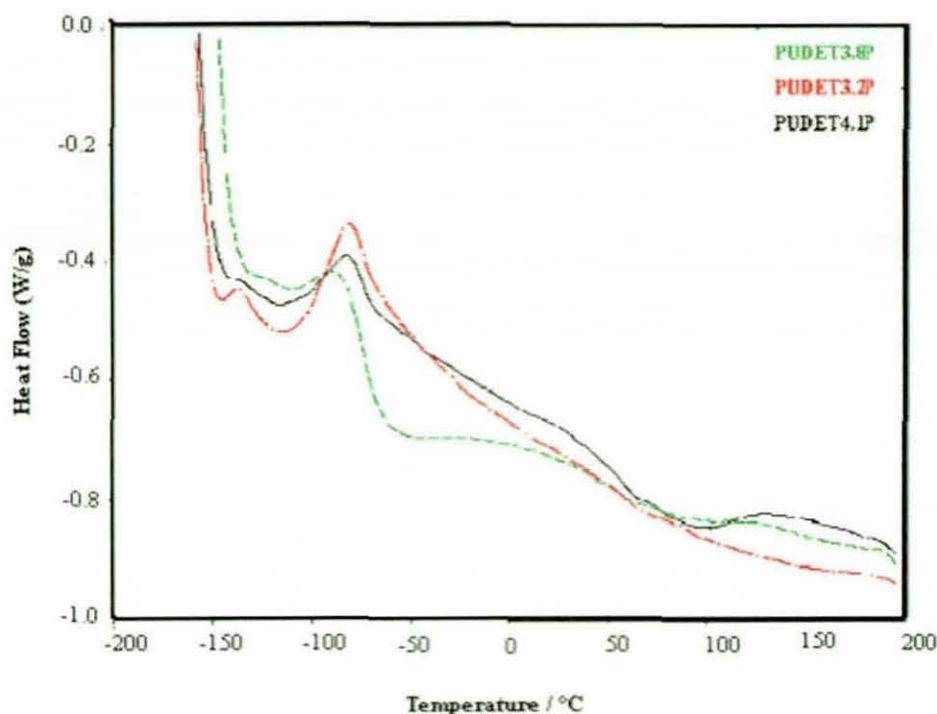


Figure 3.41 DSC thermograms for the PUDET samples with 3.2, 3.8, and 4.2 wt% DMPA. Heating from -150 to 200°C.

In general, the DSC thermograms showed two regions of activity: the low temperature region that started at the T_g and ended after the melting of the soft segments i.e. (-79 to 18°C), and the high temperature region which occurs following the soft segment melting endotherm and extends to higher temperature zones (from 18-70°C). The low temperature region represented the changes that occurred in the soft block as a result of heating, while the high temperature zone showed the response of the hard blocks to heating. These are discussed below in relation to the PUD compositions.

In all cases, the T_g exhibited by this series of PUDETs was higher than that of the polyol. This suggests a degree of mixing between the soft and hard blocks. In polyurethanes it is expected that an increase in the soft segment T_g will be brought about by the diffusion of short urethane hard segments into the soft regions ^[45-46]. This type of interaction between the two phases is expected to be greater in polyurethanes than poly(urethane-urea) due to the greater compatibility of urethane hard blocks with the soft segment ^[43, 46,49]. Also, all the DSC traces obtained for the PUDs under study indicate several endothermic peaks. These peaks have been observed by other workers ^[45], and thought to arise from the interaction of hard and soft blocks or from dissociation of the hard block components of the poly(urethane-urea). Their broad shape is a reflection of their polydisperse nature. In polyurethanes and poly(urethane-ureas), the hard segment from polymer chains have a tendency to align themselves together by the virtue of their hydrogen bonding ability, thus forming

the hard block aggregates. These hard segments vary in molecular weight and chain length. Therefore they give rise to hard blocks of greater degree of order. When the cast films were treated by the DSC, they showed various degrees of order breakdown at different temperatures i.e. T_I , T_{II} , and T_{III} , as had been described by Hesketh and Cooper^[44] in chapter 1, section 1.4.4.1. The lower endotherm T_I was associated with the disruption of short hard segments which were capable of aligning at about room temperature^[44], (known as storage annealing effects), and dissociate at some 20°C above the annealing temperature. The T_{II} , which appears as a very shallow, broad endotherm at about 100°C, arose from the disruption of hard blocks with a greater degree of order^[2,42,44-47,50]. In some cases, this endotherm has been attributed to the disruption of a microdomain structure, i.e. microphase separation temperature (MST)^[45-47].

From figures 3.40 and 3.41, it seemed that increasing the overall hard block content of the PUDET had a small effect on the position of the soft segment T_g , but it did influence the process of crystallisation, and consequently the size of the melting endotherm, as illustrated by the values of the heat of fusion. In PUDET2.0P, and PUDET2.5P, and PUDET2.9P, where the major component is the soft block, (i.e. isocyanate-capped PTMG2900), the crystallisation and subsequent melting of the soft segment aggregate are the prevalent features in the DSC thermogram. The only evidence for the two phase morphology is the small step-like change on the baseline at about 71°C. When the overall level of hard blocks was low, the T_g was low, as seen in PUDET2.1P and PUDET2.5P. This suggested minimum interaction between the two phases. However, for PUDET3.2P, PUDET3.8P and PUDET4.3P, where the levels of the hard block becomes significant, the T_g moved to higher temperatures, an indication of greater interaction between the soft and hard components. See table 3.18.

The changes in the thermal behaviour of polyether PUDs, with increasing hard block content are related to changes in the morphologies of these materials that were also reflected in the physical properties shown by these materials. As the level of hard block within the polyurethane increases, so did the size of the urethane / urea domains giving rise to more discrete domains capable of reinforcing the material resulting in polymers of improved physical properties, as indicated in Table 3.9 showing the physical properties. An increase in the level of hard segment brought about by increasing the level of DMPA and consequently the number of urea groups caused a change in the degree of soft segment crystallisation as it became limited until there were no longer distinct exothermic peaks. The reduction in the degree of crystallisation was brought about by the greater interaction between the hard phase component that prevented the free movement, and therefore the orientation of the polymer chains that was necessary for crystallisation to occur. Table 3.18 provides a summary of all transitions shown by the PUDET-P series. Another feature of the higher DMPA content and hence the hard segment content was the gradual appearance of a broad, shallow higher temperature endotherm for PUDET3.8P, and more so for PUDET4.2P that suggested a gradual development of a distinct hard block. Overall, an increase in the level of the ionic moiety, DMPA, appeared to create a disruption in the degree of order within the prepolymer which was predominantly PTMG2900 in composition.

Table 3.18 Characteristic peaks from differential scanning calorimetry (DSC) thermograms of the polyether-based PUDs with IPDI and NN'DMEDA hard segment.

Code	DMPA (wt %)	HS (wt %)	T _g (°C)	T _c (°C)	T _m (°C)	T _m (J/g)	T _{II} (°C)
PUD ET2.1P	2.1	21	-79	-27	18	13	71
PUD ET2.5P	2.5	23	-81	-25	14	5	71
PUD ET2.9P	2.9	24	-84	-30	12	11	63
PUD ET3.2P	3.2	25	-79	----			
PUDET 3.8P	3.8	28	-79	---			Shallow & broad peak
PUDET 4.3P	4.3	29	-75	----			

3.5.1.2 Effect of change of diisocyanate and chain extender on thermal behaviour of the polyether- based PUDs.

To examine the effect of change in the hard segment chemical structure, polyether PUDs with H₁₂MDI and EDA hard segments were also analysed by the DSC and compared to the PUDET P series see figure 3.42. The most noticeable difference between the two sets of DSC thermogram was the lower T_g at higher DMPA concentration i.e. 3.8 and 4.3 wt%, which was an indication of purer soft segment and improved phase separation. Also all of the H₁₂MDI/EDA-based PUDs showed a gradual formation of the higher endotherms at temperature regions of ≥ 70°C. One reason for this difference may be the greater polarity of H₁₂MDI/ EDA hard segments compared to the IPDI / NN'DMEDA case, which could have lead to more discrete hard domains. Once again, however, the crystallisation exotherm had disappeared but melting of the soft segment even though smaller in size, appears as quite distinct in these series of polyether PUDs. Another noticeable difference between H₁₂MDI/ EDA and IPDI/ NN'DMEDA PUDs was the development of distinct of T_{II} endotherms, which suggested a well-defined hard segment morphology. Figure 3.42 gives the DSC thermograms for the PUDET2.9H, PUDET3.8 and PUDET4.2H series. Overall at the given hard segment and ionic moiety concentration, a change from IPDI / NN'DMEDA to H₁₂MDI/ EDA appeared to improve the degree of phase separation in these polyether PUDs.

Table 3.19 Characteristic peaks from differential scanning calorimetry (DSC) data for the polyether-based PUDs with H₁₂MDI- EDA hard segments.

Code	HS (wt %)	DMPA (wt %)	T _g (°C)	T _c (°C)	T _m (°C)	T _{II} (°C)
PUD ET2.9H	2.9	24	-81	----	2.5	---
PUDET 3.8H	3.8	28.	-81	----	1.8	70
PUDET 4.3H	4.3	29	-82	---	12	70

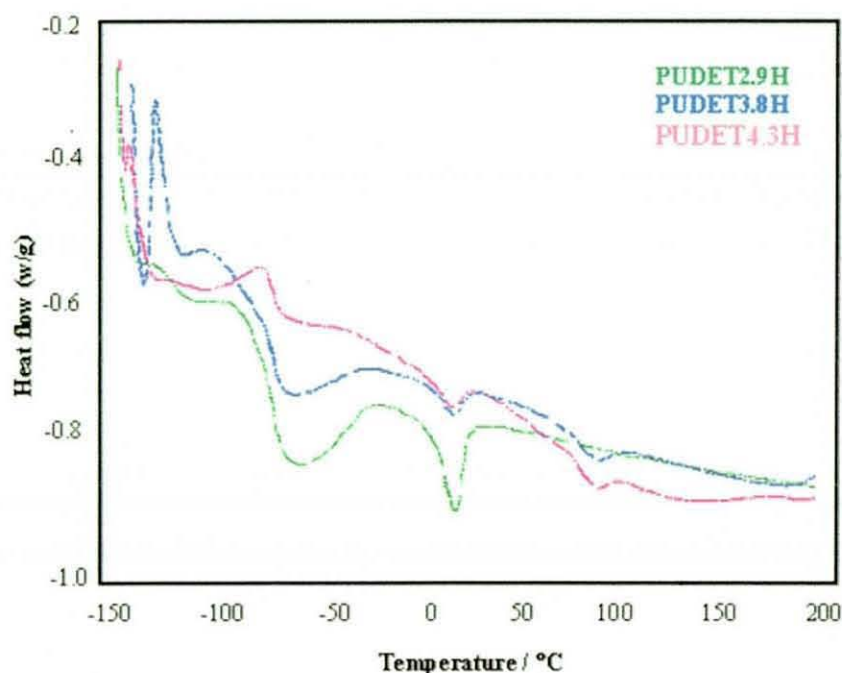


Figure 3.42 DSC thermograms for the H₁₂MDI/EDA-based polyether-urethanes

3.5. 2 DSC behaviour of polyester-based WPUDs

To examine the effect of change of soft segment on the T_g, and the overall morphology of the polyurethane dispersions, the polyester based dispersions (PUDES) of IPDI/NN'DMEdA and H₁₂MDI/ EDA hard segments were analysed by DSC. Figure 3.43 shows the DSC thermograms for PUDESs. All of these materials indicated a T_g at about - 40 to - 45°C, whereas the T_g of the polyester is measured at -60°C. The results are summarised in table 3.20. This marked difference between the T_g of the polyester polyol from which the PUDES were synthesised was an indication of a greater interaction between the urethane group and the carbonyl ester present in the soft segment. This was a well-known effect ^[26]. Furthermore, unlike the poly(ether-urethanes) which at a lower weight percent hard segment, showed crystallisation and melting that originated from the PTMG polyol sequences, in the case of polyester PUDs no evidence of an exotherm or a melting endotherm was detected. This was yet another indication of the mixing of hard and soft blocks that arose from a greater compatibility of the polyester soft segment with the urethane hard blocks. Comparison of the polyester with polyether PUDs DSC thermograms

clearly indicated a more defined morphology to be present in the polyether PUDs. This is supported by the improved physical properties shown by the PUDET regardless of the type of hard segments in comparison to their polyester counter parts. See tables 3.9, 3.14, and table 3.16 in sections 3.3 and 3.4.

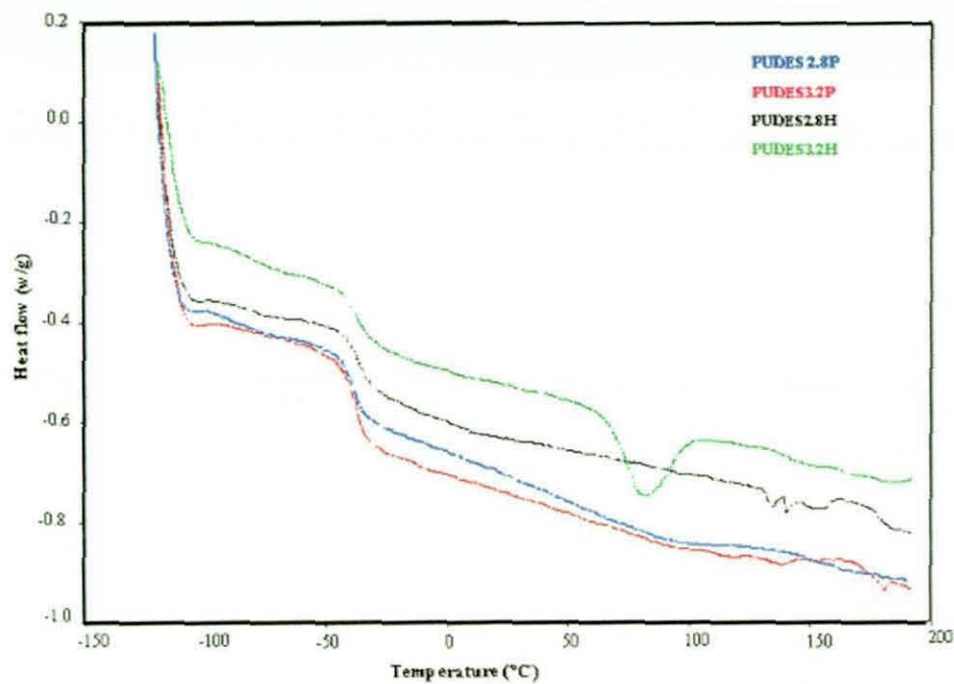


Figure 3.43 DSC thermograms for the polyester-based polyurethane dispersions.

Table 3.20 Characteristic peaks from DSC thermograms for polyester- based PUDs with different hard segments

PUD	DMPA (wt%)	HS (wt%)	T _g (°C)	T _I (°C)	T _{II} (°C)	T _{III} (°C)
PUDES2.8P	2.9	23.6	- 43	60	-----	-----
PUDES3.2P	3.2	29.0	- 44	----	125	175
PUDES2.8H	2.8	30.1	- 41	-----	-----	138
PUDES3.2H	3.2	30.7	- 41	60	-----	138

3.6 Dynamic mechanical thermal analysis

DMTA analysis was carried out on cast films conditioned using the same procedure employed to prepare the DSC films. The storage and loss moduli and $\tan\delta$ of each material were obtained and correlated with the tensile properties and possible structure of the polymers. Selected polyester and polyether PUDs and bulk polyurethanes, were compared for this purpose.

3.6.1 DMTA analysis of IPDI-based polyether PUDs

WPUDs are polyurethane-ureas and as such they are expected to be well phase separated materials due to the incompatibility of the urea hard blocks with the polyether soft segments. The DMTA loss and $\tan\delta$ plots as a function of temperature are discussed below. The storage modulus / temperature curves of a well phase separated block copolymer, that consists of two distinct phases, was expected to show two transitions occurring at the T_g of each block. In between the two transitions, a plateau is region often indicated ^[25], the size and shape of the plateau region is taken as an indicator of the degree of phase separation within the polymer ^[25]. The measure of $\tan\delta$ is a qualitative tool to determine the hysteresis, or heat build up in an elastomer during dynamic flex conditions. For a plot of $\tan\delta$ as a function of temperature as the hard segment is decreased, $\tan\delta$ peak height is increased indicating higher hysteresis of the elastomer associated with the presence of low molecular weight urethane chains in the soft polymer matrix, with little or no phase separation. The peak widths are also observed to increase, corresponding to the decrease in the hard block content of an elastomer. As with the DSC analysis, to begin with a series of polyether PUDs based on IPDI/ NN'DMEDA hard segments that contain different levels of the ionic moiety, were tested by DMTA to determine the effects of ionic moiety concentration on storage and loss moduli of WPUDs. Figures 3.44 and 3.45 show an overlay of elastic and loss moduli, as well as $\tan\delta$ for the polyether PUDs of different DMPA concentrations.

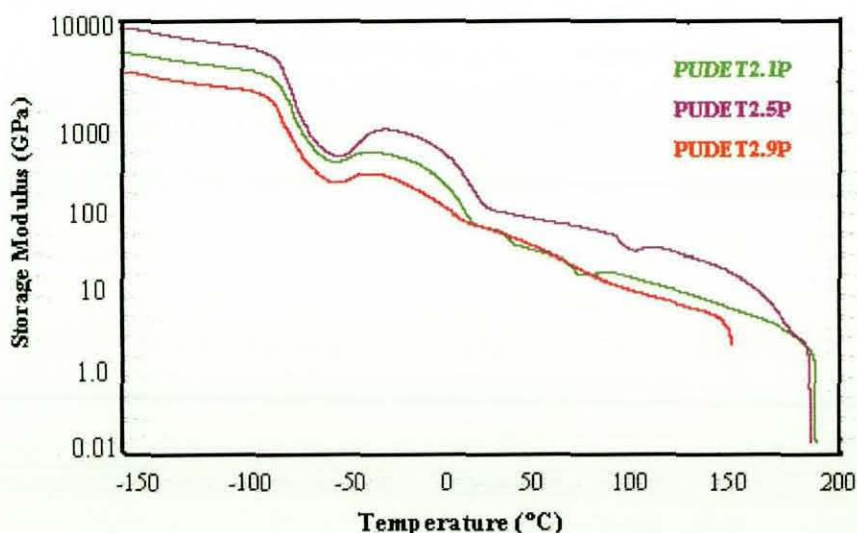


Figure 3.44 Storage moduli of IPDI/ NN'DMEDA-based polyether PUDs at low DMPA concentration

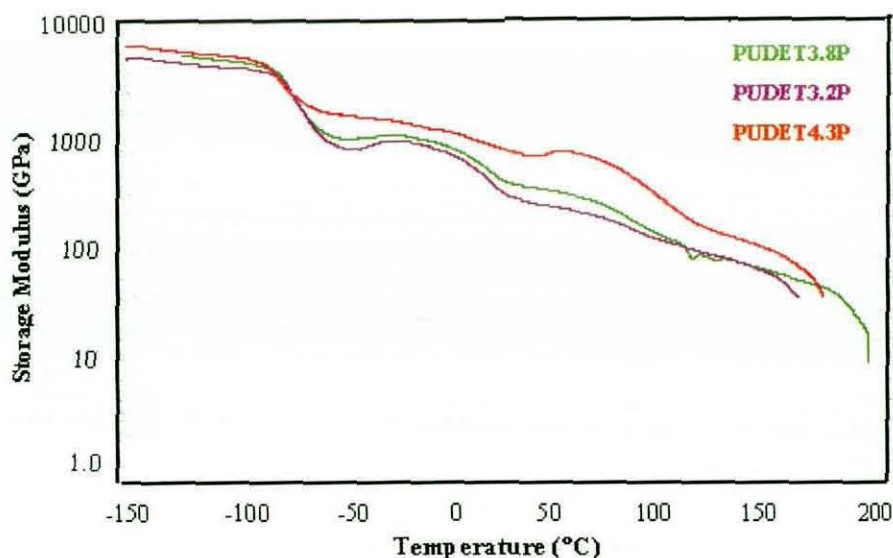


Figure 3.45 Storage moduli of IPDI/ NN'DMEDA-based polyether PUDs at high DMPA concentration

In general, the storage modulus (E') temperature curves for this series of WPUDs were typical modulus-temperature curves seen for a partially phase separated system in which the modulus was quite high at sub-ambient temperatures and below the T_g of the material, but upon heating, a dramatic drop was observed. The modulus then rises around approximately -22°C before it finally falls to zero. The rise at -22°C could be associated with the crystallisation and then melting of the polyether soft segments, as indicated by the DSC results. The expected plateau region with two distinct transitions at soft and hard block T_g was obviously small in size in the majority of WPUDs storage modulus-temperature curves. The DMPA concentration appeared to have little effect on the magnitude of the elastic moduli. The only exception was shown by PUDET4.3P, where the storage modulus did not decrease rapidly immediately after the melting of the soft segment, but persisted up to about 100°C .

This behaviour suggests that a DMPA concentration of 4.3 wt %, and an overall hard block content of 29.3 wt%, may lead to the onset of two-phase morphology in these materials, where the hard segments were of sufficient chain length to create the thermodynamic incompatibility required to give rise to a two-phase morphology. These results were also in agreement with the data obtained from DSC, in which the onset of higher temperature endotherms only became apparent at higher DMPA concentrations and higher overall hard block content. The initial value of the storage modulus at low temperature, also seemed to change as the level of DMPA and the hard block content increased. This increase was in agreement with the tensile property data obtained for these series of PUDs in which the S100 modulus appeared to increase as the weight percent hard block content within the material was increased. Analysis of the $\tan\delta$ curves showed two transitions, a major and fairly sharp one at -65°C , as well as a broad, smaller transition at about 22°C . The position of these transitions corresponded to the T_g and the melting of the crystalline soft segments. As the overall hard block content increased, however, a third transition at $80\text{--}100^\circ\text{C}$ began to appear

and develop in size, until it finally became a major peak in the case of PUDET4.3P, which had the highest DMPA and overall hard block content. This third transition may have its origin in the urea hard segments. Figures 3.46 and 3.47 provide the $\tan\delta$ -temperature curves at low and high concentrations of DMPA.

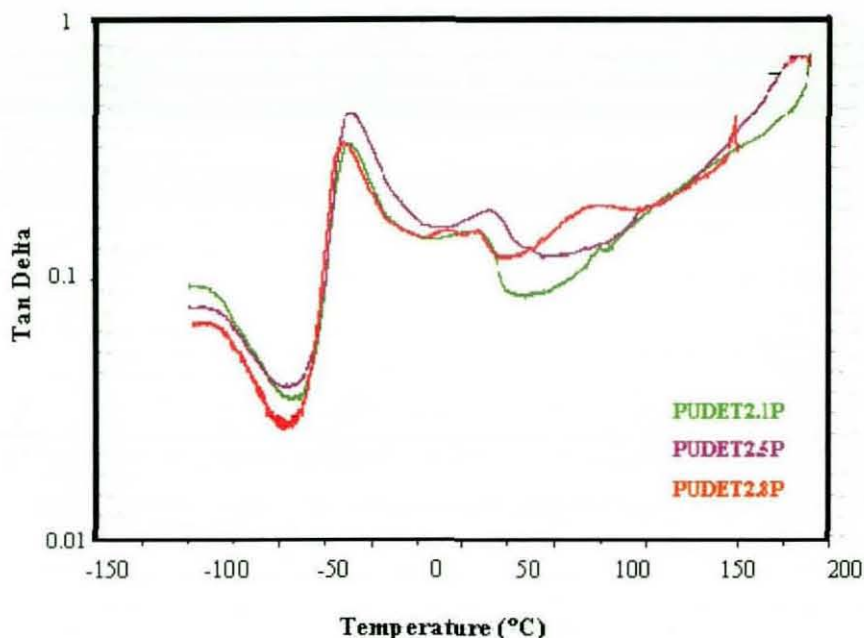


Figure 3.46 $\tan\delta$ -temperature for the IPDI/NN'DMEDA-based polyether PUDs at low DMPA concentration.

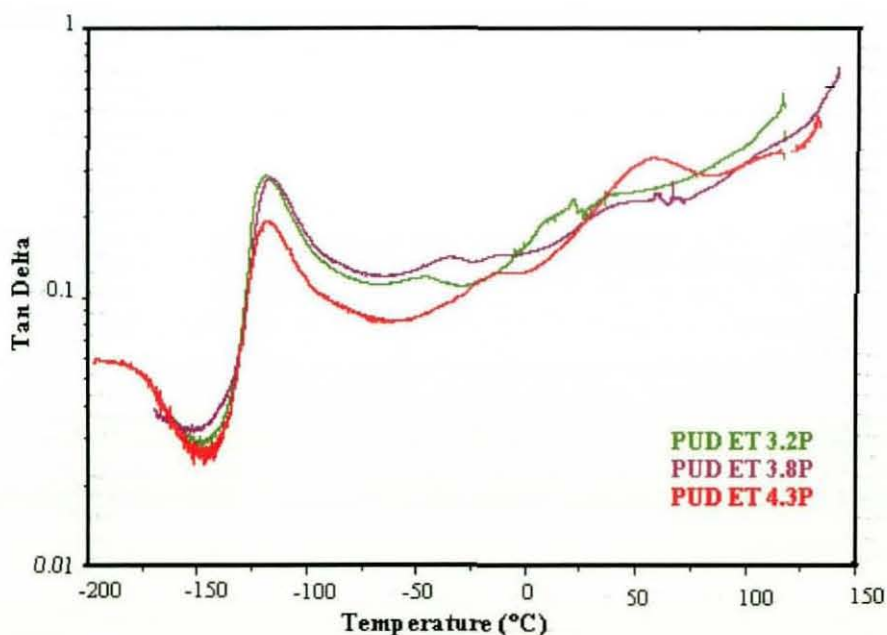


Figure 3.47 $\tan\delta$ -temperature for the IPDI/ NN'DMEDA-based polyether PUDs at high DMPA concentration.

The loss modulus curve (E'') followed the same trend as the storage modulus. Figures 3.48, and 3.49 showed an overlay of loss-moduli temperature curves for IPDI-based polyether PUDs. In general, the loss modulus curves, as a function of temperature for the PUDET IPDI series, showed a distinct peak at the glass transition temperature. However, as the level of DMPA within the material

increased the maximum peak of the loss modulus-temperature curve increased size, suggesting that high DMPA levels may contribute to greater hysteresis within the materials. This would be in agreement with the stress relaxation data that were obtained for the IPDI/NN'DMEDA PUDs, which indicated that an increase in the ionic moiety concentration was a major contributor to the initial rapid decay of the applied stress. In fact PUDET4.3P, which has the greatest initial rapid decay in the stress relaxation analysis, also showed the biggest peak in its loss modulus-temperature curve.

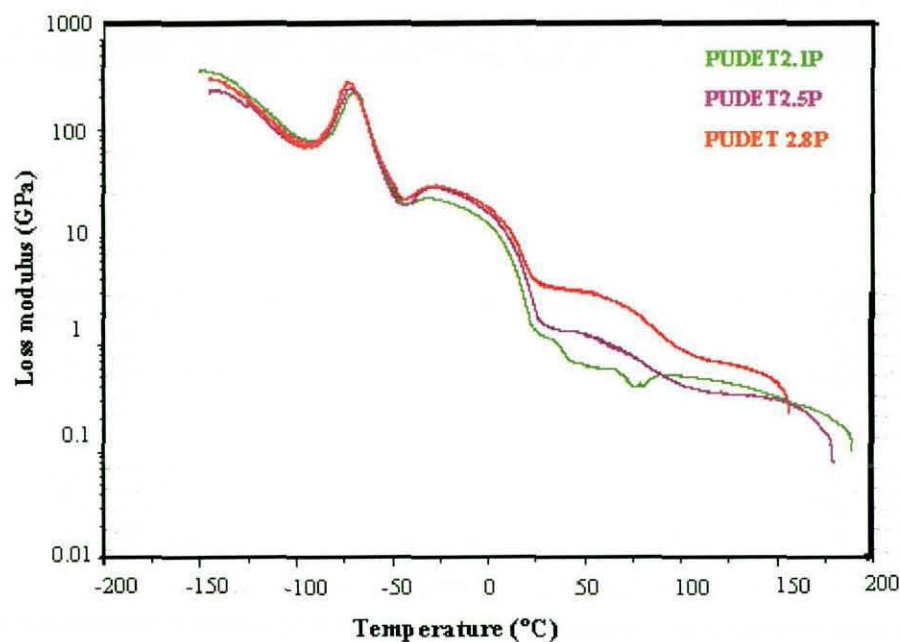


Figure 3.48 Loss modulus-temperature of IPDI/NN'DMEDA-based polyether PUDs at low DMPA concentration.

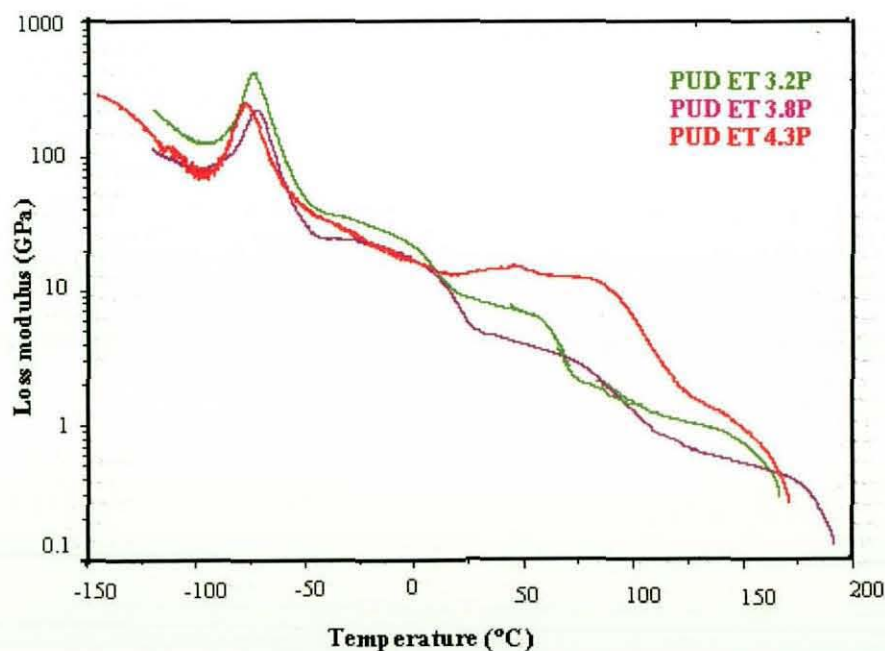


Figure 3.49 Loss modulus-temperature of IPDI/NN'DMEDA-based polyether PUDs at high DMPA concentration

3.6.2 Effect of change of diisocyanate and chain extender on DMTA behaviour of polyether-based PUDs.

The effect of soft and hard segment structure on the dynamic mechanical behaviour was also examined. Figures 3.50 to 3.53. show changes in storage modulus, loss modulus and $\tan\delta$ for the polyether PUDs based on H_{12} MDI and EDA as chain extender. In general, the DMA traces for H_{12} MDI / EDA-based PUDs indicate a greater degree of phase separation. The storage modulus-temperature curves for PUDET 2.8H, PUD ET3.2H and PUDET4.3H showed a well defined plateau that extends over several decades of temperatures. Although there are no distinct differences between the PUDETH materials as the moduli all start and finish at the same temperatures with no evidence of any other structural transitions at higher temperatures the values of storage modulus at any given temperature are higher for higher levels of DMPA and therefore overall hard segment contents. Some transitions were indicated at around 20-30°C, which could have their origin in the soft segment crystallisation and melting. Similar transitions were indicated in the loss modulus-and $\tan\delta$ temperature curves. The higher the DMPA and therefore, the overall hard segment content the broader the $\tan\delta$ peak. Figures 3.51 and 3.52 show the loss modulus- and $\tan\delta$ - temperature curves for the H_{12} MDI/ EDA-based dispersions. The greater degree of phase separation indicated by the DMTA analysis was in agreement with the tensile properties shown for these materials. The rate of stress relaxation for these polyether PUDs were lower and this in agreement with the size of $\tan\delta$ peaks shown by these materials.

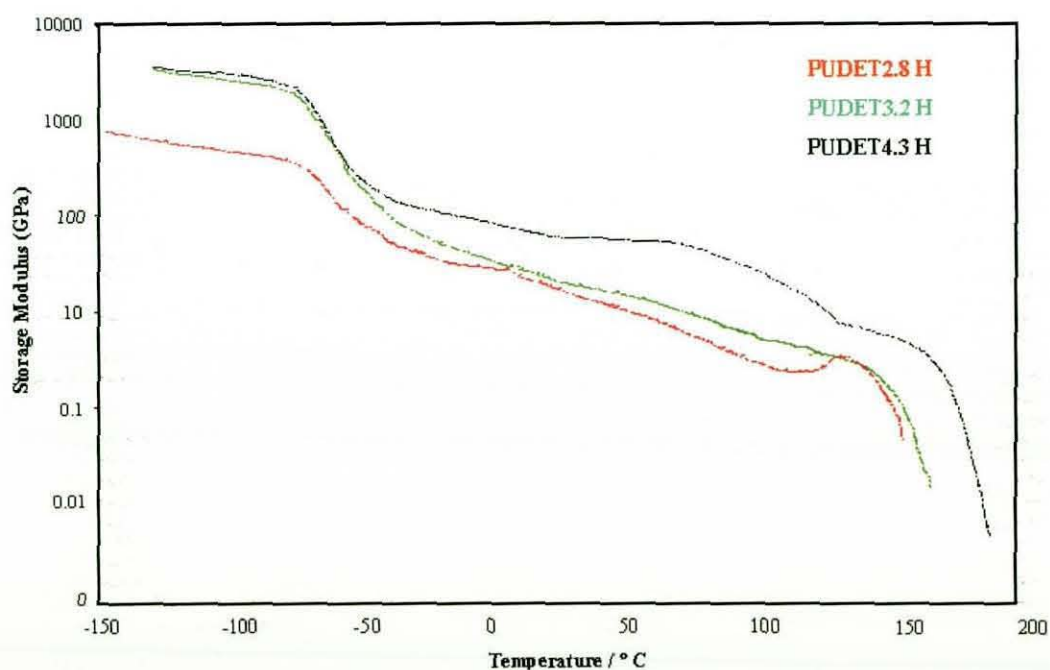


Figure 3.50 Storage modulus- temperature plots for the H_{12} MDI/ EDA-based polyether PUDs

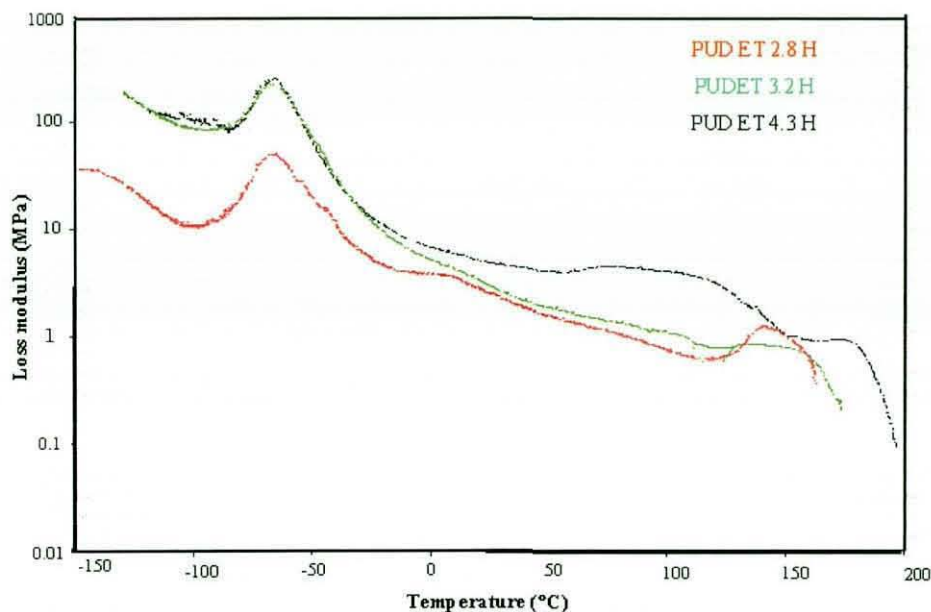


Figure 3.51 Loss modulus-temperature for the H₁₂MDI/ EDA-based polyether PUDs.

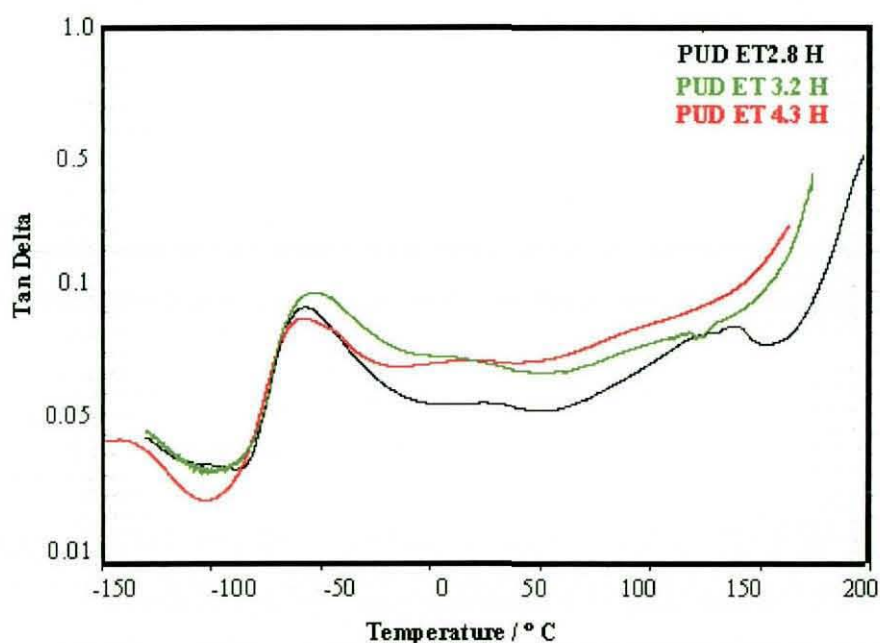


Figure 3.52 Tan δ -temperature plots for the H₁₂MDI/ EDA-based polyether PUDs.

3.6.3 Dynamic mechanical thermal analysis of polyester-based PUDs

To determine the effect of a change in the soft segment, polyester-based PUDs were also analysed by DMTA. Figures 3.53, 3.54, 3.55, give the storage, loss moduli and tan δ versus temperature curves for the polyester PUDs. Overall, the DMA plots of polyester PUDs were characteristic of polyurethane materials in which the hard and soft blocks are fairly compatible and there was a mixing of hard and soft blocks without achieving phase separation^[25]. The evidence for this was the elastic moduli- temperature curves. As shown in figures 3.53 to 3.55, where IPDI/ NN'DMEDA was used as the hard segment, as expected, the storage modulus had quite high values while the PUDs was still below its T_g at approx - 40°C. However, once the polymer went through its T_g the storage

modulus rapidly declines and no plateau was indicated until, finally, there was a small transition at approximately 25°C, possibly due to the melting of the polyester soft block phase. In contrast, where the hard segment was made up of H₁₂MDI/ EDA, some degree of phase separation is indicated, since elastic moduli-temperature curves clearly showed a short plateau. The greater the hard segment level, the more extensive was the modulus plateau. As the storage modulus is a quantitative measure of materials' elastic properties, and also an indicator of the hardness of the elastomers, it can be concluded that the polyester PUD are softer elastomers than their polyether counterparts. This was in good agreement with the physical properties shown by the two groups of materials, as indicated in tables 3.12 and 3.13.

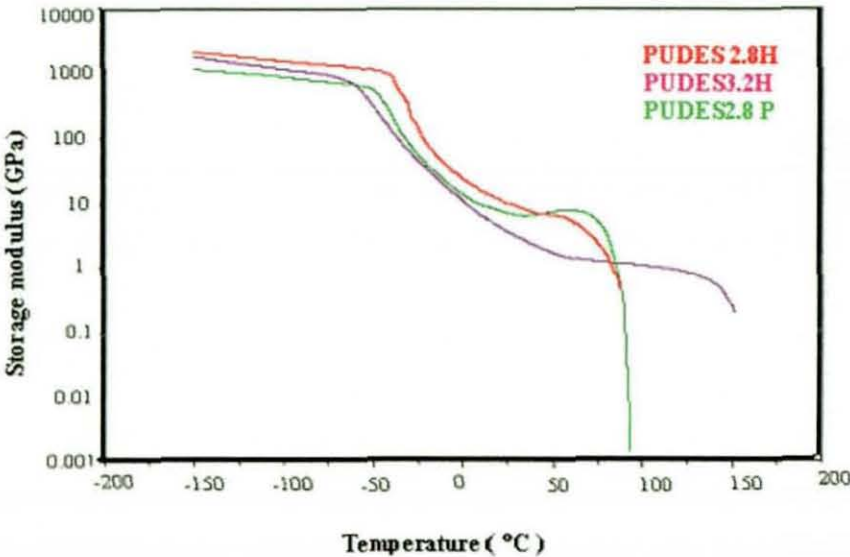


Figure 3.53 Storage modulus-temperature curves for the polyester-based PUDs with different hard segment types.

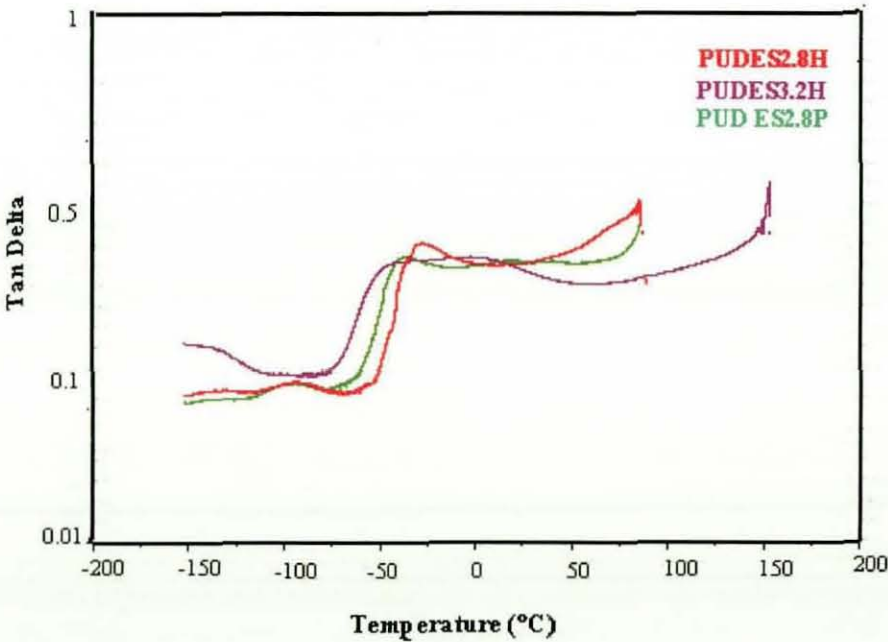


Figure 3.54 Tanδ-temperature curves for the polyester-based PUDs with different hard segment types.

In general, $\tan\delta$ -temperature curves for the polyester PUDs exhibit quite broad peaks spread over several decades of temperature. This was another indication of soft and hard block compatibility in these materials. The block copolymer morphology in the polyester-based PUDs has often been found to lead to diffuse phase boundaries due to interactions of ester carbonyl groups with the urethane ester groups ^[26-28].

The loss moduli and $\tan\delta$ curves both show a low temperature transition at about -100°C . A low temperature transition of this nature is often associated with crank shaft movements of ethylene groups in the polyester chain ^[75]. The loss modulus is a quantitative measure of energy dissipation in elastomers ^[19,23,25]. Low E'' values are indicative of low energy dissipation and low hysteresis, while high values of E'' are an indication of viscous flow. The values of E'' at room temperature can be related to hysteresis and correlated with the stress relaxation behaviour of the polyester PUDs. Figures 3.29 and table 3.13 of sections 3.4 clearly indicate a higher degree of stress relaxation in the polyester PUDs and particularly when IPDI/NN'DMEDA had been used in to make up the hard segment.

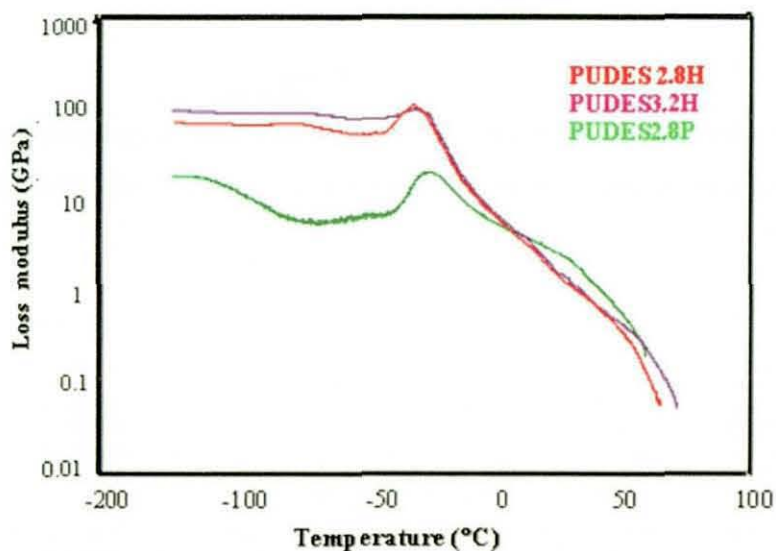


Figure 3.55 Loss-modulus temperature plots for polyester-based PUDs with different hard segment types.

3.7.1 *Polymerisation and dispersion characteristics*

Bulk polymerisation is a well established method of synthesising polymers; it is widely used in the polyurethane industry. Normally TPUs are produced using twin screw extruders ^[7] in which the raw materials are mixed and then cast on a moving belt where they are further reacted and turn solid. After the slabs have cooled and solidified, they are granulated before they being used in the desired application. The technique has long been used to generate polyurethanes including soft TPU elastomers, with a wide variety of properties. Bulk reactions are flexible, in that they allow the use of a wide range of monomers that impart specific features to the final polyurethanes. Because during the bulk polymerisation of polyurethanes since the chain extension is not carried out in water it allows the use of diol chain extenders, and hence formation of urethane materials(instead of urethane-urea) and, therefore it facilitates the syntheses of softer elastomers. Although many types of TPUs can be generated, for example hydrophilic TPU or adhesives, the deliberate synthesis of a TPU subsequently capable of being dispersed in water, such that it may ultimately be processable from water into soft articles such as gloves etc, is unknown. In this study to achieve dispersion DMPA was used as a reactant, and the chain extension process that was performed in the bulk was carried out using 1,4-butane diol (BDO) resulting in high molecular weight polymers. These were hydrophilic and could be dispersed in water via the ionisation of the pendent carboxylic acid group derived from the DMPA component in the PU.

The polymerisation of polyurethanes proceeds via a step growth reaction that characteristically shows a wide molecular weight distribution (MWD), giving a typical polydispersity of 2. Equally, it is well known that the two-step, or the prepolymer, method of synthesising polyurethane leads to a more defined morphology in the final PU film than a one-shot or one-step continuous reaction used in TPU manufacture ^[136]. Moreover the statistical nature of the step growth polymerisation and chain extension, means that when synthesising polyurethane dispersions, a variety of species of different chemical composition and chain lengths are produced. It has been shown by Dieterich ^[96,110] that when synthesising PU ionomers, a wide range of polymeric species of different chemical composition and chain length is obtained. These include polymer molecules with no ionic groups, water soluble electrolytes and polyelectrolytes in addition to the intended ionomer molecules. This wide spectrum of molecules contributes to the broad particle size and particle size distribution of PU ionomers^[96]. This effect is further encouraged when two types of extender are used and the polymerisation is performed in one step, as in the case of bulk PUs. To determine the effects of introducing the ionic moiety DMPA on the properties of bulk polyurethanes, a series of bulk polyether urethane with IPDI/ BDO hard segments and with different DMPA concentrations, were synthesised and tested.

3.7.2 Effect of DMPA on particle size of IPDI-based polyether bulk PUs

The relationship between particle size and DMPA content in bulk polyurethanes differed from that observed in PUDs. In the case of bulk polyurethanes, the particle size appeared to increase as the level of DMPA in the polymer was increased from 2.6 to 4.2wt %, though not with uniform increase. Table 3.21 summarises the particle size measurements obtained from bulk PUs and states the physical appearance of the dispersion. The bulk PUs of high DMPA content tended to rapidly absorb water during dispersion, resulting in a highly water swollen gel. In fact, only the lower DMPA - containing bulk PUs, such as BulkET2.6P, BulkET2.9P and Bulk ET3.2P produced stable dispersions, whilst BulkET3.8P and BulkET4.2P produced swollen gels. Examples of particle size distribution curves are given in figures 3.56 to 3.59. These results suggested that increasing the overall hard block content i.e. IPDI, DMPA and 1,4-butane diol content from 24 to 32 weight percent encouraged the formation of various species of different chemical composition. It is possible that on increasing the weight percent DMPA and IPDI in the BulkP3.8 and BulkP4.2, the probability of short chain polyelectrolytes and water-soluble electrolytes, as a result of reactions between PTMG/IPDI/DMPA, increased. These short chain polyelectrolytes could have acted as thickening agents absorbing large quantities of water during the dispersion stage. The behaviour may be compared to the thickening effects of non-ionic thickeners that are frequently used in the coatings industry. Additionally, the formation of greater quantities of short chains was expected to influence the morphology and the degree of phase separation of the films produced from the bulk PUs.

Table 3.21 Relationship between particle size and DMPA content in bulk polyurethanes.

Code	DMPA (wt %)	Average Particle Size (nm)	Viscosity (mPas)	Appearance / Texture
Bulk ET2.6P	2.63	202	35-70	White dispersion
Bulk ET2.9P	2.9	30	20-52	Very fine bluish dispersion
Bulk ET3.2P	3.2	119	35-56	White dispersion
Bulk ET3.8P	3.83	334	53-80	White dispersion
Bulk ET4.2P	4.2	616	----	Coarse gel Very opaque

3.7.3 Effect of DMPA content on the viscosity of IPDI-based bulk poly(ether-urethanes)

In order to obtain a dispersion from a bulk PU, the polymers had to be granulated and dissolved in tetrahydrofuran (THF) as a 15 % w /v (polymer/THF) solution, before adding a sufficient amount of water to achieve very low solids dispersions (5-8 %). Where the dispersion contained $\geq 3.8\text{wt \%}$ DMPA initially at low water content, a cloudy emulsion was obtained. However, as the level of water was increased the polymer/THF water/ mixture turned into a gel, and precipitated, creating two distinct layers.

3.7.4 Physical properties of IPDI-based bulk poly(ether-urethanes)

Since some bulk PUs could not be converted into aqueous dispersions, in order to determine the physical properties, the bulk PUs were cast from a polymer THF solution or from a mixture of water/ THF. The physical properties of the bulk PUs are given in table 3.22. In general, except for Bulk ET0.0P, a gradual increase in the tensile strength and S100 value was observed as the DMPA content was increased from 2.6 to 4.2 (wt %). Among these series of polymers, Bulk ET0.0P which was free of DMPA, showed the highest tensile strength and S100 modulus. These comparatively high physical properties shown by Bulk ET0.0P suggested an improved phase separated morphology compared to the bulk PUs containing DMPA. The higher S100 modulus suggested a more defined block copolymer in which the hard domains were discrete thereby creating a reinforcement mechanism.

Table.3.22 Tensile properties of Bulk PUs at various DMPA concentrations.

Code	DMPA (wt %)	HS (%)	TS* (MPa)	S100* (MPa)	EAB* (%)
BulkET0.0P	0	31.3	36.3 (sd=2.0)	2.5 (sd=0.05)	558 (sd=18.7)
Bulk ET2.6P	2.6	25.1	12.2 (sd=1.2)	0.6 (sd=0.03)	558 (sd=34.7)
Bulk ET2.9P	2.9	24.1	16.7 (sd=3.6)	0.9 (sd=0.08)	761 (sd=52.7)
Bulk ET3.2P	3.2	25.6	25.8 (sd=2.22)	1.5 (sd=0.03)	695 (sd=11.2)
Bulk ET 3.8P	3.8	31.5	24.2 (sd=5.3)	1.6 (sd=0.04)	742 (sd=53.7)
Bulk ET4.2P	4.2	29.5	30.8 (sd=2.6)	1.5 (sd=0.07)	1088 (sd=19.4)

*5 test pieces were measured in each case.

3.7.5 Effect of DMPA content on the molecular weights and tensile strength of IPDI-based (polyether-urethanes)

The effects of the ionic moiety concentration on the weight average molecular weight and the tensile strength of the bulk poly(ether-urethanes) with IPDI / BDO hard segments are given in figures 3.60 and 3.64, respectively. As the concentration of DMPA, and therefore, the overall hard segment was increased, there was a corresponding increase in the tensile strength, as seen in figure 3.64. When the weight average molecular weight was plotted against ionic moiety concentration, a similar trend to that observed in WPUDs was observed. The only exception from this behaviour is the bulk ET0.0P, this particular polyurethane was free from the ionic moiety. At a lower molecular weight of 111,600 g/mole it gave the highest tensile strength and modulus. It is possible this polyurethane possessed a greater degree of phase separation and a more defined morphology compared to the bulk ionomeric polyurethanes of this series. Figures 3.61-3.63 provide typical GPC chromatograms obtained for IPDI-BDO-based polyether bulk PUs. As with the polyurethane dispersions, it is apparent that as the concentration of DMPA was increased, the shape of the corresponding GPC chromatogram changed to a more defined bimodal distribution, illustrating the multi-component nature of the bulk polyurethanes, in which a range of polymeric species of different chemical compositions and molecular weight were present. This was in agreement with the particle size data obtained for these bulk PUs.

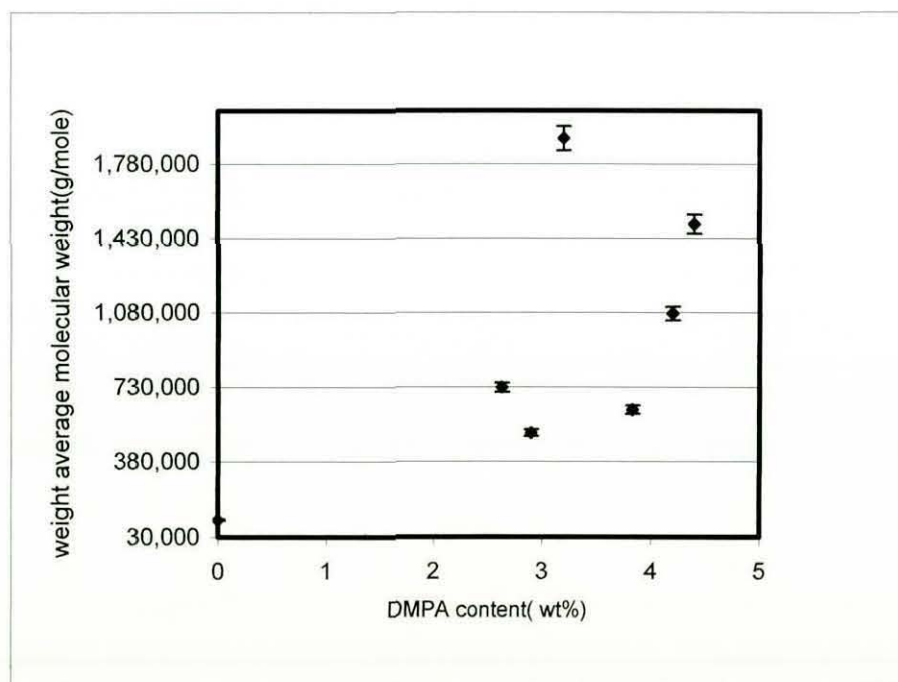


Figure 3.60 Effect of DMPA content on the molecular weight of IPDI-BDO based polyether bulk PUs.

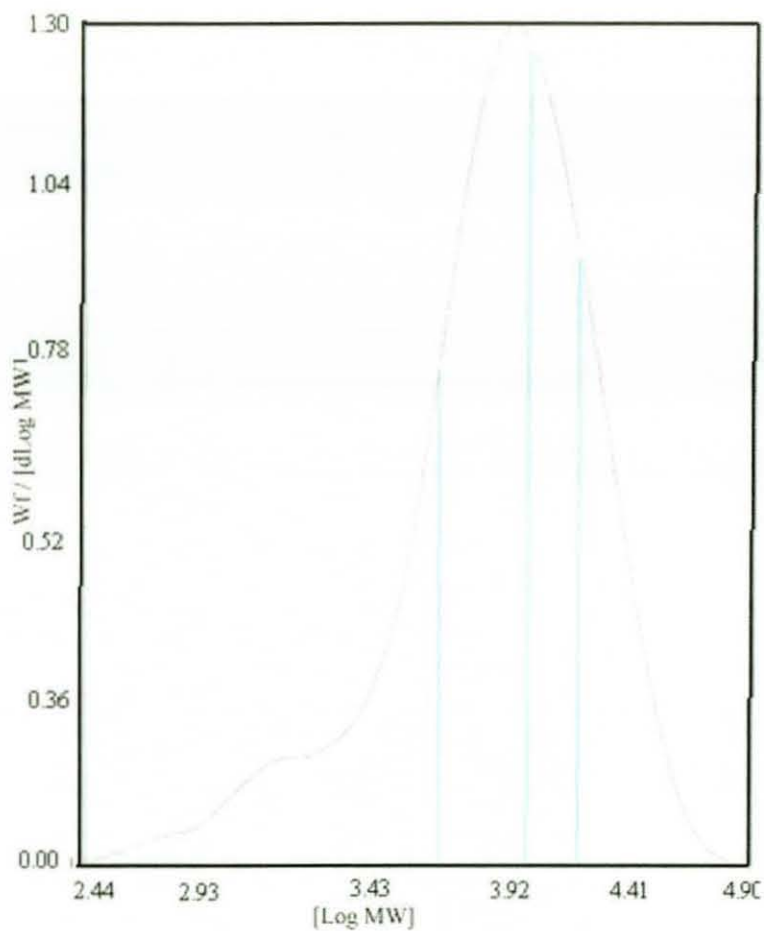


Figure 3.61 GPC chromatogram of IPDI-based polyether bulk PU at 3.2% DMPA content

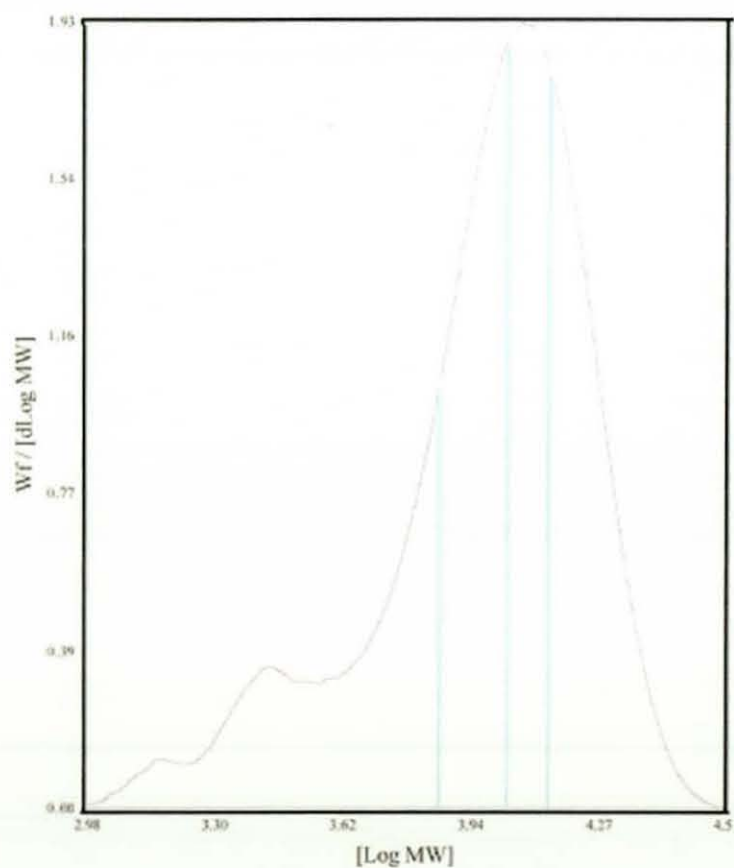


Figure 3.62 GPC chromatogram of IPDI-based polyether bulk PU at 4.2% DMPA content

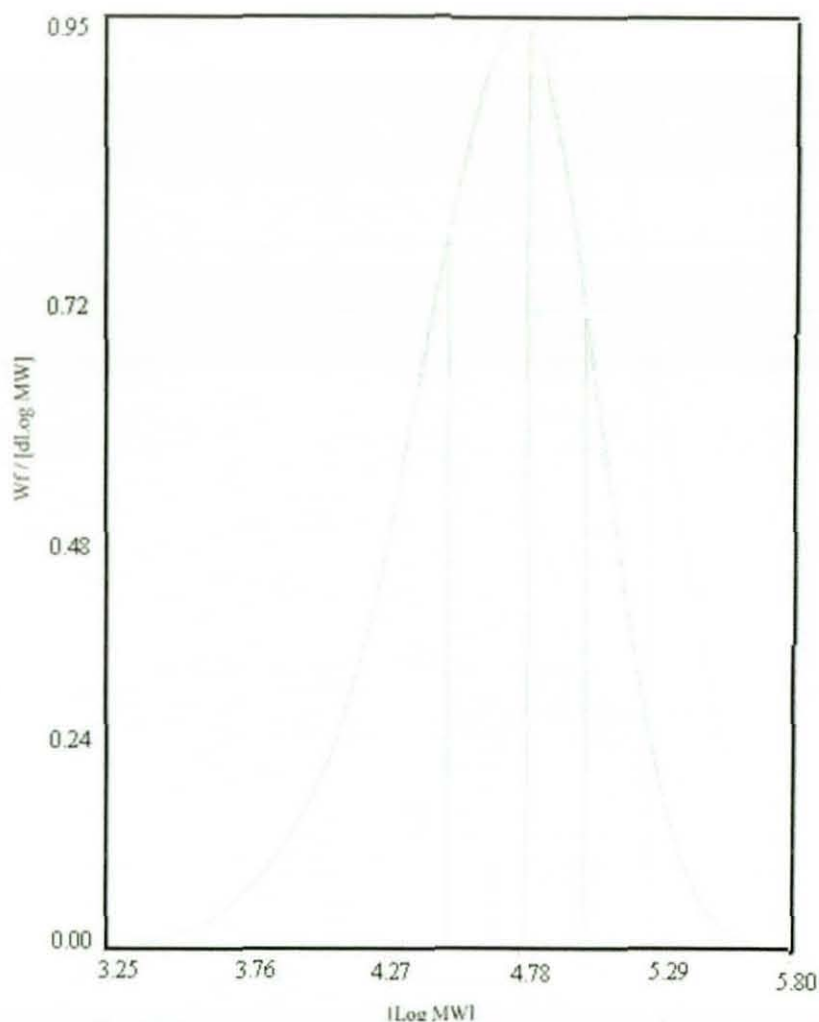


Figure 3.63 GPC chromatogram of the IPDI-based polyether bulk PU free from DMPA (bulk ET 0.0P)

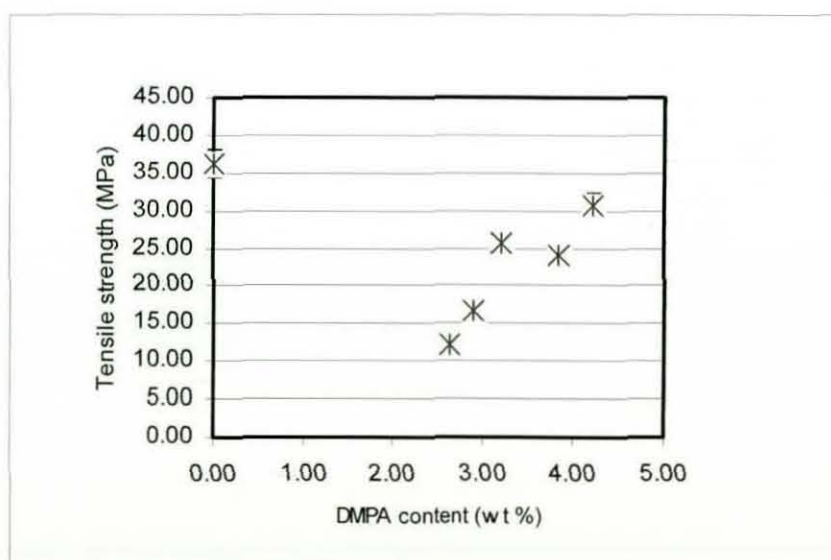


Figure 3.64 Effect of DMPA concentration on tensile strength of the IPDI/BDO-based polyether bulk PUs.

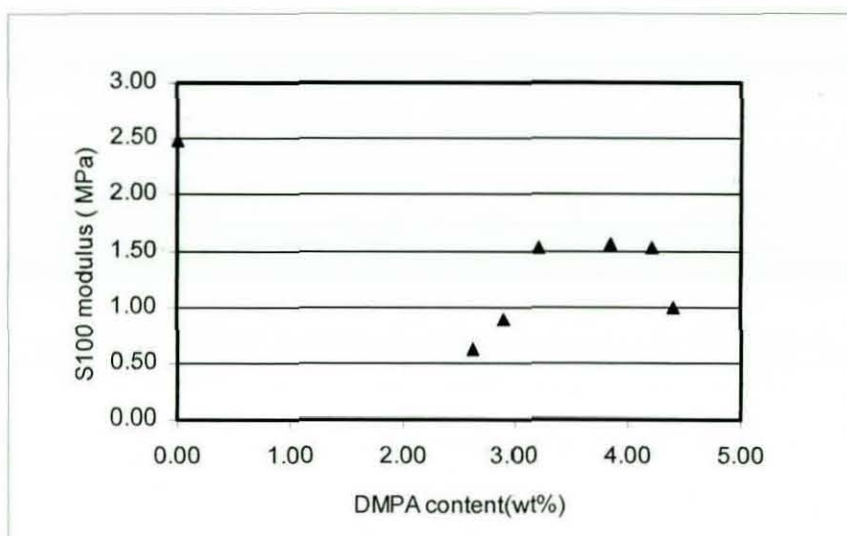


Figure 3.65 Effect of DMPA concentration on the S100 of the bulk PUs.

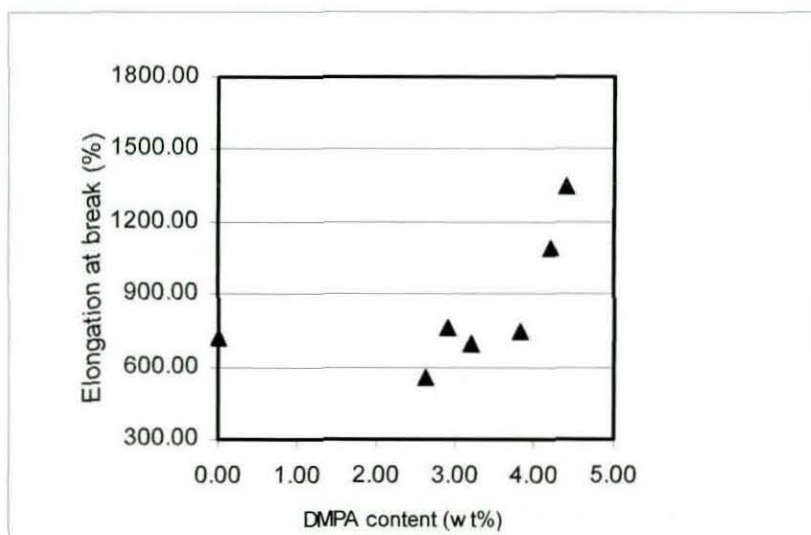


Figure 3.66 Variation of EAB of the bulk PUs with DMPA concentration.

Comparison of physical properties of PUDs and the bulk PUs of equivalent HS (wt%) and DMPA content of show ed that in general, the bulk PUs have much lower tensile strengths and S100 moduli, than their PUD counterparts of the same chemical composition. Table 3.23 compares the tensile properties of PUDs and bulk PUs of similar chemical composition.

Table 3.23 Comparison of the physical properties of polyether IPDI- based bulk PUs and PUDs of equivalent chemical composition.

Code	DMPA (wt %)	HS (wt%)	TS (MPa)	S100 (MPa)	EAB (%)
Bulk ET2.6P	2.6	25.1	12.2 (sd=1.2)	0.6 (sd=0.03)	558 (sd=34.7)
PUDET2.5P	2.5	22.6	51.0 (sd=3.7)	2.6 (sd=0.05)	630 (sd=15)
Bulk ET2.9P	2.9	24.1	16.7 (sd=3.6)	0.9 (sd=0.08)	761 (sd=52.7)
PUDET2.9P	2.9	24.3	41.0 (sd=3.8)	3.0 (sd=0.19)	560 (sd=35)
Bulk ET3.2P	3.2	25.6	25.8 (sd=2.22)	1.5 (sd=0.03)	695 (sd=11.2)
PUDET3.2P	3.2	25.5	39.2 (sd=4.0)	3.2 (sd=0.08)	550 (sd=18)
Bulk ET3.8P	3.8	31.5	24.2 (sd=5.3)	1.6 (sd=0.04)	742 (sd=53.7)
PUDET3.8P	3.8	27.9	51.4 (sd=13.1)	4.1 (sd=0.33)	540 (sd=44.7)
Bulk ET4.2P	4.2	29.5	30.8 (sd=2.6)	1.5 (sd=0.07)	1088 (sd=19.4)
PUDET4.3P	4.3	29.0	36.5 (sd=5.14)	5.2 (sd=0.17)	640 (sd=19)

Unlike the PUDs, where an increase in DMPA concentration brought about a large increase in S100 moduli, no significant increases in the bulk PU modulus were observed, and overall softer materials were obtained. As the amount of DMPA was increased from 2.6 to 4.2 wt %, S100 changed relatively little from 0.6MPa to a maximum of 1.6MPa.

3.7.6 Stress-strain curves for the IPDI-based polyether bulk PUs.

The stress-strain curves for IPDI-based polyether bulk PUs are given in figure 3.67. These curves are typical of polyurethane elastomers of low modulus. At low extension, all stress-strain curves showed the rubbery plateau characteristic of soft rubber materials. However, as the DMPA concentration or the hard segment content increased the size of the rubbery plateau became smaller. This was the trend, up to a DMPA concentration of 4.2 wt %. Small differences in the initial parts of the stress-strain curve could also be seen although the effect is not well defined. The shortest rubbery plateau and the highest initial modulus (S100) were clearly shown by the Bulk.ET0.0P that contained no DMPA.

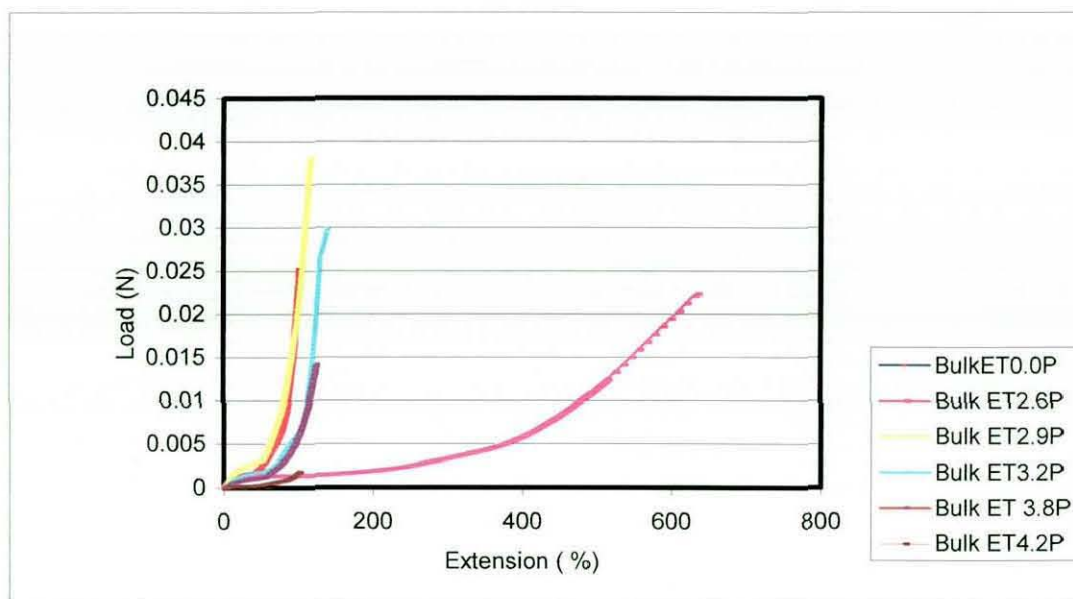


Figure 3.67 Load - extension curves of IPDI-based polyether bulk PUs as a function of DMPA concentration at low strains only.

3.7.7 Stress relaxation data for the IPDI-based polyether bulk PU

As in the case of the polyether-based PUDs in section 3.2.4, the load values at 100% extension for the bulk PUs containing different levels of DMPA was plotted and are shown in figure 3.68. The calculated rate of stress relaxation (RSR) and initial load drop shown by bulk PUs are summarised in table 3.24.

Table 3.24 Effect of DMPA concentration on the stress relaxation behaviour of IPDI-based polyether bulk PUs.

Code	Initial load % of Peak (N)	Final load % Peak (N)	Initial load drop (100 – initial load) %	Rate of stress relaxation (Per decade)
Bulk ET 0.0P	68.4 (sd=12.6)	54.7 (sd=19.3)	31.6 (sd=9.1)	13.7
Bulk ET2.6P	37.8 (sd=22.3)	16.2 (sd=26.0)	62.2 (sd=31.6)	24.4
Bulk ET2.9P	51.5 (sd=11.1)	28.4 (sd=9.7)	48.5 (sd=18..6)	23.1
Bulk ET3.2P	53.0 (sd=15.1)	34.0 (sd=11.1)	47.0 (sd=10.46)	19.0
Bulk ET3.8P	68.5 (sd=33.1)	51.7 (sd=19.2)	31.5 (sd=13.3)	17
Bulk ET4.2P	54.7 (sd=10.3)	34.2 (sd=13.5)	45.3 (sd=8.9)	20.5

In general, a significant initial drop in load and a greater RSR, were shown by the bulk PUs compared to their PUD counterparts. An increase in DMPA content was accompanied by an increase in the initial drop in the load. Similarly, the higher the DMPA content, the higher is the RSR. Among the bulk PUs, Bulk ET0.0P showed the lowest initial drop in load and relaxation rate. It was closely followed by Bulk PET3.2P. In contrast, BulkP2.6 indicated the highest initial load drop and RSR. It contained the lowest level of DMPA and the lowest hard segment content. This material also showed the lowest tensile properties (see table 3.22).

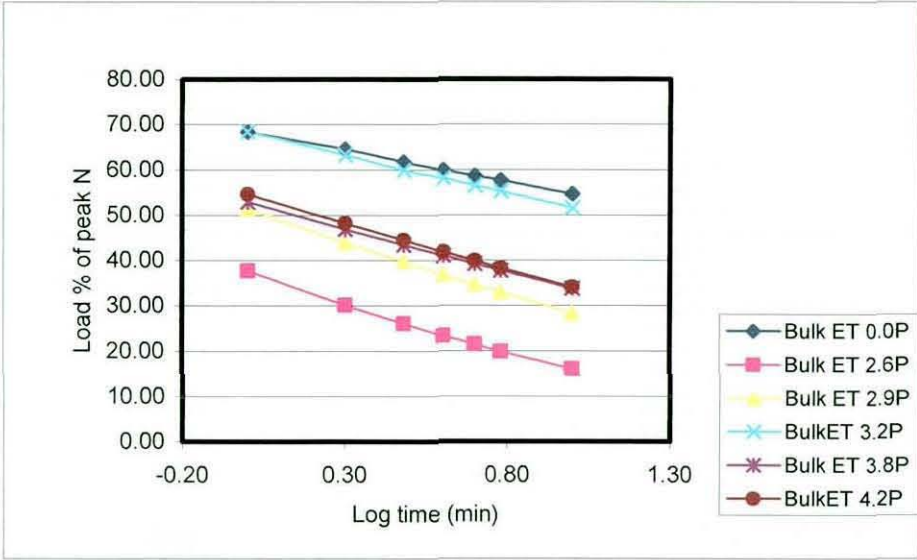


Figure 3. 68 Effect of DMPA content on the stress relaxation of IPDI-based polyether bulk PUs

3.7.8 Effect of change of diisocyanate type on the properties of IPDI-based bulk polyether PU

To determine the effect of change in the hard segment on the properties of polyether-based bulk PUs, the IPDI / BDO was replaced by H₁₂MDI/ BDO. Table 3.25 provides a summary of the tensile properties and the corresponding stress-strain curves, given in figure 3.69. From the tensile properties displayed, it appeared that a change in the structure of the hard block caused a significant change in the S100 and the tensile strength, of bulk PUs. The structure of H₁₂MDI yielded a PU system with a degree of toughness and strength higher than those based on IPDI. This difference in properties arose from the unique polymer morphology of segmented polyurethanes. The geometry of H₁₂MDI molecules has an effect on the arrangement of the polymer chains in the bulk material. This in turn can affect the polymer’s physical properties. H₁₂MDI is thought to yield small amorphous or semi-crystalline hard domains which consequently, resulted in greater strength and hardness of the polyurethane system ^[188].

Table 3.25 Tensile properties of H₁₂MDI- based bulk polyether PUs.

Code	Hard segment (wt %)	DMPA (wt%)	TS (MPa)	S100 (MPa)	EAB (%)
Bulk ET 3.2 P	30.3	3.1	25.8 (sd=2.22)	1.5 (sd=0.03)	695 (sd=11.2)
Bulk ET 3.8 P	31.5	3.8	24.2 (sd=5.3)	1.6 (sd=0.04)	742 (sd=53.7)
Bulk ET3.2 H	31.8	3.2	36.6 (sd=7.0)	2.96 (sd=0.2)	720 (sd=31.7)
Bulk ET 3.8H	32.7	3.8	42.2 (sd=9.8)	2.86 (sd=0.7)	640 (sd=57.0)

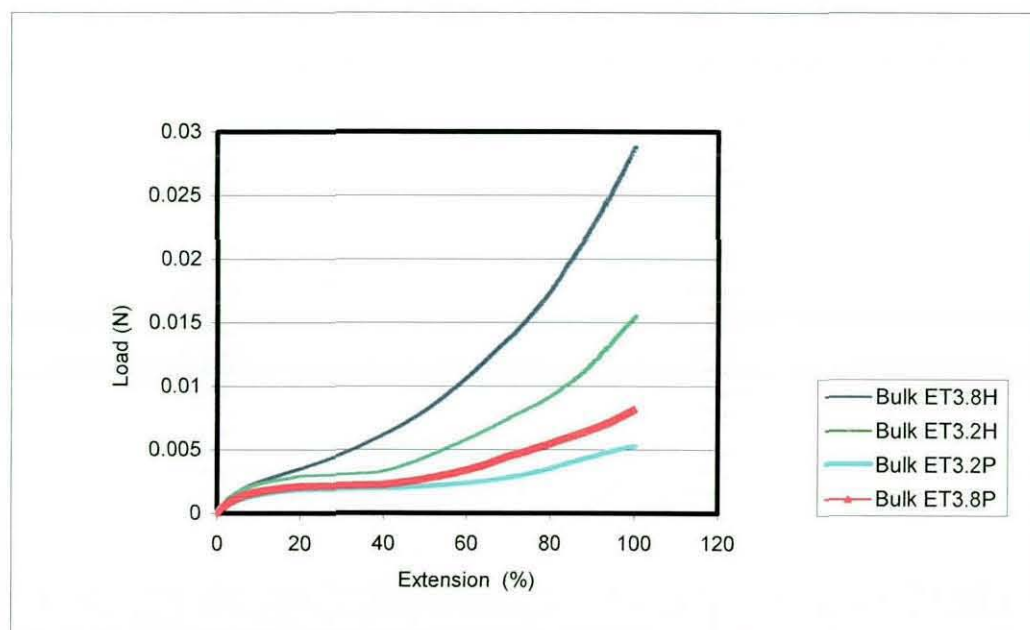


Figure 3.69 Comparison of load extension curves for the H₁₂MDI-based bulk poly(ether-urethanes) at low strain.

3.7.9 Stress relaxation behaviour of the H₁₂MDI/ BDO-based polyether bulk PUs

Figure 3.70 and table 3.26 provide the stress relaxation data for H₁₂MDI/ BDO-based poly(ether-urethanes). As in the case of IPDI-based bulk PUs, an increase in the level of DMPA brought about a reduction in the initial load and also an increase in the rate of stress relaxation. However, a change in the hard segment type did appear to provide a greater resistance to load, as illustrated by the lower RSR and initial load drop (%). An improved degree of phase separation may have been responsible for this behaviour.

Table 3.26 Comparison of stress relaxation behaviour of H₁₂MDI/BDO and IPDI-based polyether bulk polyurethanes.

Bulk	Initial load (% of Peak) (N)	Final Load (% of Peak) (N)	Initial load Drop (100 – initial load %) (N)	Rate of stress relaxation (per decade)
Bulk ET 3.2 P	68.5 (sd=23.7)	51.7 (sd=13.7)	31.5 (sd=10.3)	17
Bulk ET 3.8 P	53.0 (sd=17.8)	34.0 (sd=15.3)	47.0 (sd=,23..7)	19.0
Bulk ET 3.2 H	70.1 (sd=21.0)	60.8 (sd=8.4)	30 (sd=12.4)	9.3
Bulk ET 3.8 H	60.8 (sd=18.11)	47.9 (sd=25.5)	39.2 (sd=14.6)	12.8

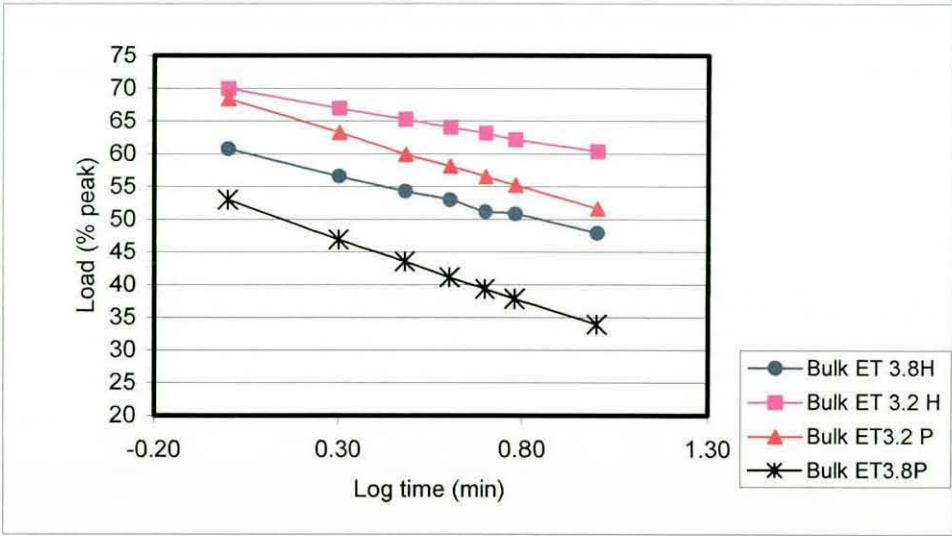


Figure 3.70 Comparison of the stress relaxation of the H₁₂MDI-based bulk poly(ether urethanes)

3.8 Polyester-based bulk polyurethanes

3.8.1 Physical properties and molecular weight of polyester-based bulk polyurethane

As in the case of polyurethane dispersions, the effect of a change in the soft segment chemistry on the properties of bulk PUs, was investigated by synthesising polyester polyol

polyurethanes using two different hard segments: H₁₂MDI/ BDO and IPDI/ BDO. These polymers also contained the ionic moiety DMPA as part of their chemical composition. Tables 2.4.9 and 2.4.10 of section 2.4.3.1 provide the composition breakdown for these materials. The physical property test results are given below in table 3.27.

Table 3.27 Tensile properties of bulk poly(ester-urethanes)

Code	HS (wt%)	DMPA (wt%)	TS (MPa)	S100 (MPa)	EAB (%)
Bulk ES2.8P	28.6	2.8	10.7 (sd=1.2)	1.46 (sd=0.05)	1180 (sd=53.4)
Bulk ES 3.2P	29.6	3.2	14.7 (sd=3.7)	1.47 (sd=0.08)	830 (sd=51.7)
Bulk ES 3.8P	30.6	3.7	23.6 (sd=6.3)	1.32 (sd=0.13)	820 (sd=34.8)
Bulk ES 2.8H	29.9	2.8	22.2 (sd=9.8)	1.3 (sd=0.07)	949 (sd=54.3)
Bulk ES3.8 H	34.2	3.8	30.2 (sd=9.7)	1.82 (sd=0.11)	840 (sd=18.8)

In general, the bulk poly(ester-urethanes) exhibited lower tensile properties than their polyether counterparts. Within the bulk polyester urethanes, the H₁₂MDI-BDO materials appeared to have higher tensile strength and S100 modulus values than the IPDI- BDO-based group. This was to be expected^[188]. The stress-strain curves for the IPDI-based polyester bulk PUs are shown in figure 3.71. The shape of the stress-strain curves of IPDI-based materials showed a necking and cold drawing effect. The cause of this behaviour was the inherent weakness of the soft segment poly(ethylenebutylene adipate) which was not capable of stress crystallisation which when in combination with IPDI-BDO based will have resulted in a loss of dimensional stability. This was in agreement with the properties shown by these materials at DMPA concentration of 2.8 and 3.2 wt%. The tensile strength of these materials were only 11, and 15 MPa, respectively.

For the H₁₂MDI/BDO-based polyester bulk PUs, the stress-strain curves were typical of soft materials of a rubbery nature. Although they indicated lower physical properties than their

IPDI/ BDO-based counterparts, no necking or cold drawing was observed. Figure 3.72 shows the stress-strain curves of the H₁₂MDI/ BDO-based polyester bulk PUs.

Overall, the use of the polyester polyol appeared to produce softer, weaker materials with limited elasticity, as indicated by the cold drawing of the IPDI / BDO-based PU of this category. This is probably brought about by incomplete phase separation. Unlike the polyester-based PUDs, in which the presence of a diamine chain extender and their higher polarity (compared to the polyester soft segments) provided a greater thermodynamic driving force for phase separation. In this case, the combination of 1,4-butanediol and the diisocyanate could only achieve limited phase separation, and for the IPDI/ BDO-containing polyesters lead to an even greater mixing due to the structural irregularity of IPDI. Consequently the formation of discrete hard domains dispersed in a soft rubbery matrix that enhance rubbery behaviour was inhibited. Also polyesters polyols was thought to hydrogen bond with the urethane groups and so encouraged segment mixing ^[26]. Another contributor to lower strength could be that the particular polyester used in this study was not capable of rapid stress crystallisation, and, therefore, did not promote higher strength in these elastomers.

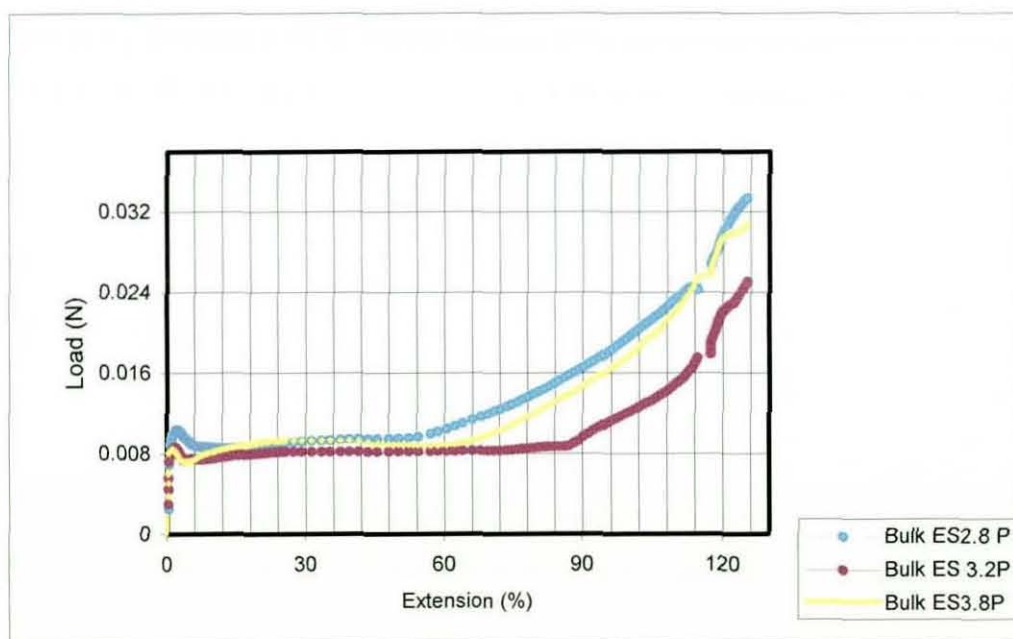


Figure 3.71 Load- extension curves for the bulk poly(ester-urethane) based on IPDI/ BDO hard segments.

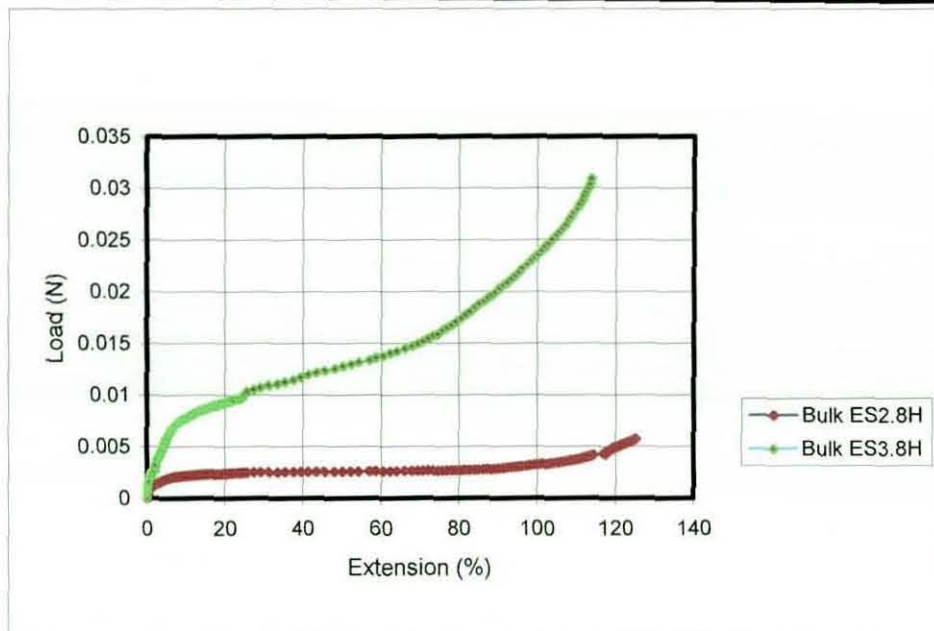


Figure 3.72 Load- extension curves for the bulk poly(ester-urethane) based on H₁₂MDI/ BDO hard segments.

3.8.2 Stress relaxation of polyester based bulk PUs.

The stress relaxation plots for the polyester bulk polyurethanes are given in figure 3.73. From this figure, the variation in the initial load and the rate of stress relaxation were calculated and summarised in table 3.28. Overall, IPDI-based polyester bulk materials showed extensive stress relaxation and much lower initial loads than their corresponding polyether-based counterparts. At lower hard segment and DMPA content, the IPDI polyester bulk polyurethanes showed a clear deviation from linearity. This was in agreement with the reduced properties and the cold drawing clearly exhibited in their stress-strain curves. The H₁₂MDI polyester bulk materials, on the other hand, although they show an improved rate of stress relaxation compared to their IPDI- based counterparts, exhibited a much lower initial load than the polyether-based polyurethanes. This behaviour was also in agreement with the properties shown. The results of stress relaxation tests carried out on the polyester-based elastomer PUDs, as well as the bulk polyurethanes, indicated that the degree of phase separation ultimately was the main factor in determining the rubbery behaviour in these materials. The chemical composition of each block and the resulting thermodynamic force that encouraged phase separation determined the overall rate of stress relaxation. The decay in load observed immediately following the application of load onto the elastomer and the start of the test, to some degree was controlled by the concentration of the ionic moiety present in the elastomer. However, the overall compatibility of the rubbery matrix and the hard domains also contributed to the stress relaxation rate in these polymers.

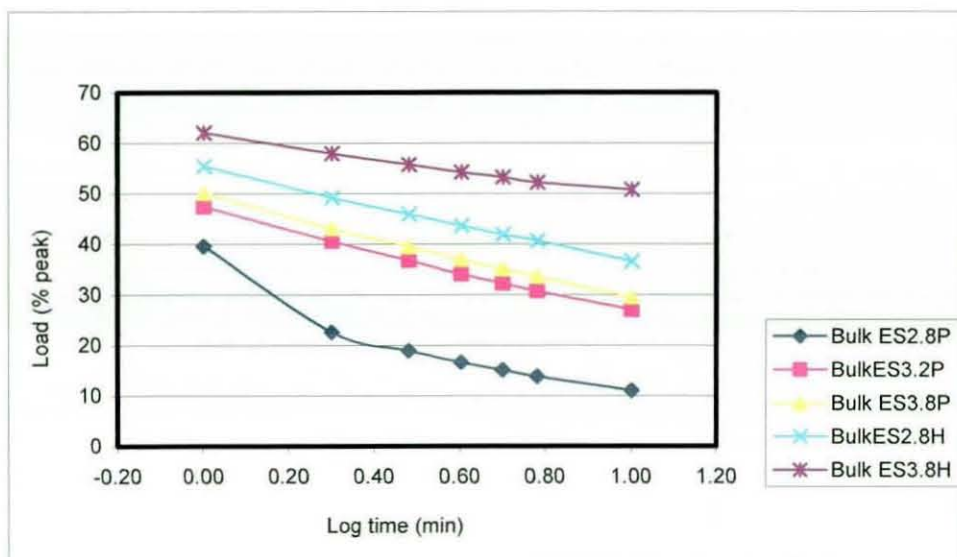


Figure 3.73 Stress relaxation behaviour of the bulk poly(ester-urethanes) based on IPDI or H₁₂MDI hard segments.

Table 3.28 Stress relaxation data for the polyester -based bulk polyurethanes with different hard segment structure.

Bulk	Initial load (% of Peak) (N)	Final load (% Peak) (N)	Initial load Drop (100 – initial load) (%)	Rate of Stress Relaxation (per decade)
Bulk ES2.8P	39.6 (sd=20.9)	11.1 (sd=3.2)	60 (sd=16.0)	28.5
Bulk ES 3.2P	47.5 (sd=16.3)	27.1 (sd=4.8)	52.5 (sd=17.4)	20.4
Bulk ES 3.8P	50.3 (sd=33.1)	29.6 (sd=6.8)	49.7 (sd=32.7)	20.7
Bulk ES 2.8H	55.5 (sd=19.8)	36.7 (sd=8.3)	44.5 (sd=26.4)	18.8
Bulk ES3.8 H	62.1 (sd=11.7)	50.9 (sd=25.4)	37.9 (sd=13.2)	11.5

3.9 Thermal analysis of the bulk polyurethanes

3.9.1 Differential Scanning Calorimetry

3.9.1.2 Effect of DMPA content on the thermal behaviour of the IPDI- BDO based bulk poly(ether-urethanes).

Cast films of bulk IPDI / BDO-based polyether polyurethanes were analysed by DSC. Each composition was subjected to a heating cycle from -150 to 200°C at $10^{\circ}\text{C}/\text{min}$.

For Bulk ET0.0P, which does not contain any DMPA, the DSC thermograms showed a distinct soft segment T_g , and a strong, distinct melting endotherm. Some evidence of a higher endotherm or hard block activity, was also noted. Bulk ETP0.0 represented a typical thermoplastic polyurethane behaviour associated with only one type of diol chain extender in its structure. The crystallisable component within its structure showed a clear T_g , and melting of its soft segment that originated from the PTMG 2900 polyol. If the Bulk ET0.0P was taken as the control material, it could be seen that, in general, as the level of DMPA in these polymers was increased from 0 to 4.2wt%, changes in the DSC thermograms were observed. At low levels i.e. 2.6 to 2.9wt % of DMPA, the overall behaviour appeared to be similar to that seen in the Bulk ET0.0P, except that as the level of the ionic moiety was increased the size of the melting transition slowly diminishes. The disappearance of the melting endotherm was indicative of deterioration in the degree of phase separation on addition of DMPA. Also at DMPA concentrations of 0 to 2.9wt%, the dominant contributor to the structure was the soft segment. Here the size of the hard blocks appeared to be limited. Figures 3.74 shows an overlay of the DSC thermograms of bulk ET0.0P, ET2.6P and ET2.9P.

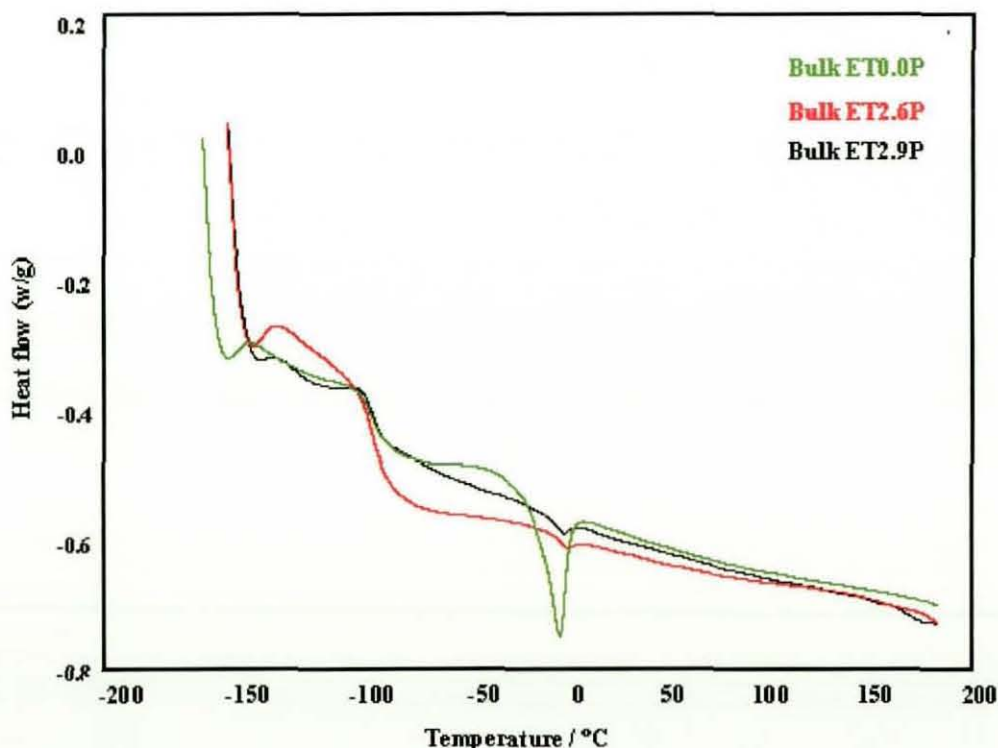


Figure 3.74 DSC thermogram for the IPDI/ BDO-based bulk polyether urethanes at low DMPA concentration.

When the DMPA concentration was increased to 3.2, 3.8 wt% and finally to 4.2 wt%, a change in the DSC traces was noticeable and higher temperature endotherm activity in the region of 100- 150°C were indicated. Figure 3.64 shows an overlay of DSC thermograms for the higher levels of DMPA. Although the presence of DMPA seemed to cause disruption in the crystallisation and melting of the soft segment, which is suggested by the reduction in size of the melting endotherm, it did, however, promote the formation of the hard blocks as indicated by the gradual appearance of higher temperature endotherms. The gradual disappearance of the melting endotherm from the DSC thermograms for the bulk ET3.2P, bulk ET3.8P and bulk ET4.2P suggested a greater degree of mixing and migration of short hard blocks of either DMPA-IPDI or IPDI-DBO into the soft segment region.

Generally, in polyurethane materials when the weight percent hard segment was increased, the incompatibility between the hard and soft blocks increased and the thermodynamic force for the phase separation was also increased. The increase in hard segment content also encouraged the formation of polydisperse hard segments of various compositions and chain lengths. It was expected that the shorter hard segment could diffuse in the rubbery matrix and cause an increase in the T_g , though this was not apparent in the bulk polyurethanes studied here. Table 3.29 summarises the glass transition and other endothermal activities observed in the DSC thermograms.

Overall, the DSC thermograms of the IPDI- based bulk PU suggested the presence of a limited two phase morphology in these materials. On annealing, the behaviour of these polymers could be changed. It was possible that on storage at ambient temperature for a sufficiently long time, or at appropriate annealing temperatures, the crystallisation of each component the hard and soft blocks, may have been induced. The hard block may then become able to realign and develop into a well-defined morphology giving rise to distinct exo/endothermic peaks.

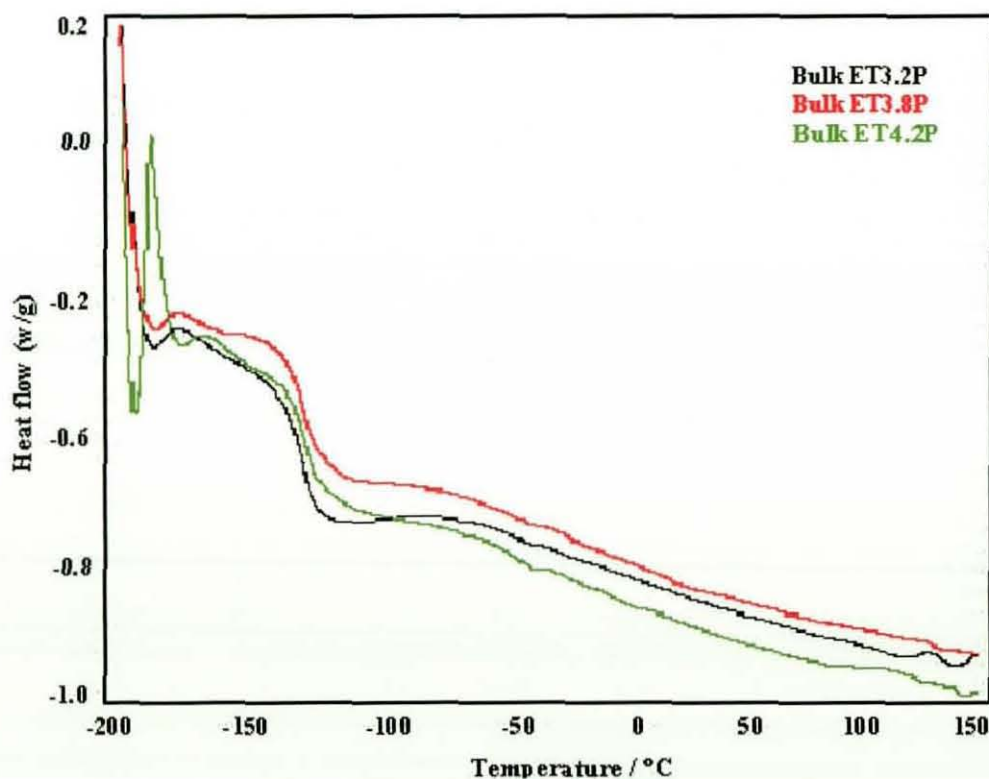


Figure 3.75 DSC thermograms for the IPDI-based bulk poly(ether- urethanes) at high DMPA content.

Table 3.29 T_g and thermal transitions shown by IPDI/ BDO-based bulk poly(ether-urethanes)

Code	DMPA (wt %)	HS (wt %)	T_g (°C)	T_i (°C)	T_{ii} (°C)
Bulk ET 0.0P	0.0	31.3	-83	13.3	----
Bulk ET2.6P	2.6	25.1	-82.4	17.0	----
Bulk ET 2.8P	2.8	24.1	-80.3	16.3	----
Bulk ET 3.2P	3.2	25.6	-81.1	41.0	
Bulk ET 3.8P	3.8	32.0	-83.2	--	147
Bulk ET 4.2P	4.3	30	-83	12.5	156

3.9.1.3 Thermal behaviour of H_{12} MDI-/BDO based bulk polyether urethanes

As can be seen from figure 3.76, a change from IPDI / BDO to H_{12} MDI / BDO hard segment does not appear to influence greatly, the DSC behaviour of the polyether-based bulk polyurethanes. In general, at equal levels of DMPA and hard segment, the materials, T_g remained unaffected although the higher level of DMPA did appear to give distinct endotherms in the high temperature region. This was perhaps due to the fact that H_{12} MDI-BDO or H_{12} MDI-DMPA were capable of producing more regular and distinct hard domains than their IPDI-based counterparts. Figure 3.76 provides a comparison of the DSC thermograms for bulk polyethers of IPDI-and H_{12} MDI-based hard segments. Table 3.30 provides a summary of T_g and endotherms observed from each material.

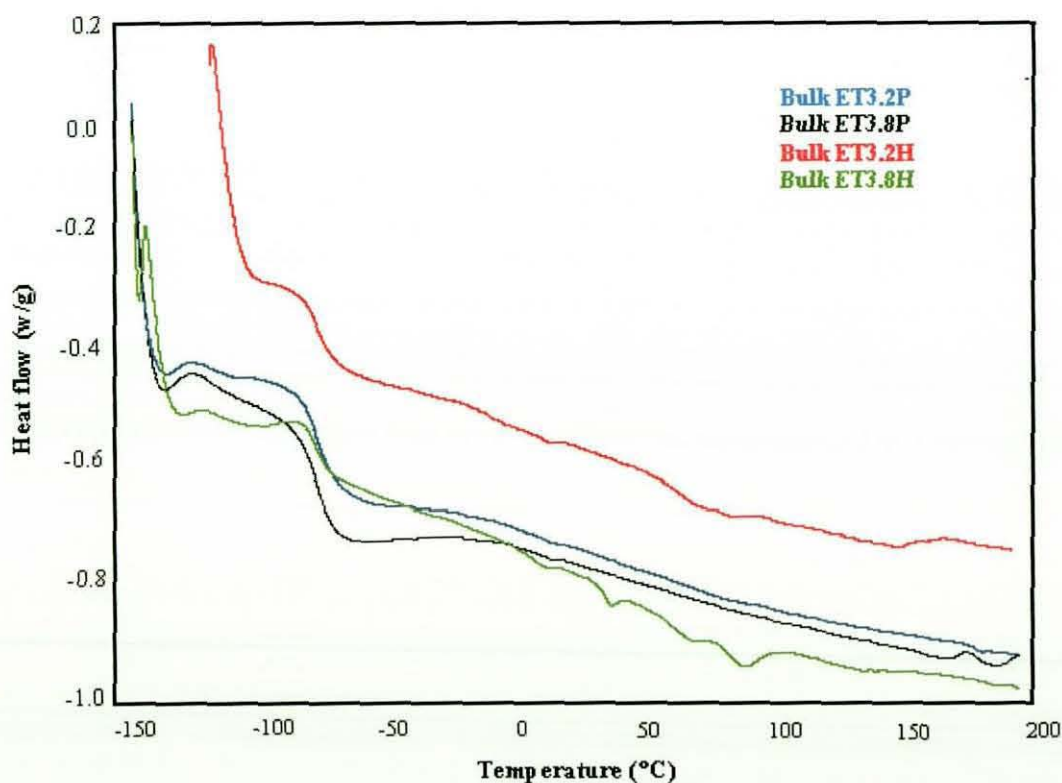


Figure 3.76 DSC thermogram of bulk H_{12} MDI-and IPDI-based bulk poly(ether-urethanes)

Table 3.30 T_g and thermal transition shown by IPDI/ BDO-and H_{12} MDI / BDO-based bulk poly(ether-urethanes).

Code	DMPA (wt%)	HS (wt %)	T_g (°C)	T_I (°C)	T_{II} (°C)	T_{III} (°C)
Bulk ET 3.2H	3.2	31.8	-83.2			
Bulk ET 3.8H	3.8	32.7	-84.0	12	81.2	145
Bulk ET 3.2P	3.2	25.6	-81.1			
Bulk ET 3.8P	3.8	31.5	-83.2			

3.9.1.4 Thermal behaviour of bulk poly(este-urethanes)

The effect of a change in the soft segment on the thermal behaviour of bulk polyurethanes was also analysed. As expected, the poly(ester-urethanes) showed a greater degree of segment mixing is well indicated by their T_g values. In all cases, the T_g of the poly(ester-urethanes) from -40 to 45°C appeared at higher temperatures than those of the pure polyester (-59°C), an indication of greater compatibility of the carbonyl groups in the urethane of the hard domains and the ester carbonyl group present in the polyol. Table 3.27 gives a summary of the T_g values and all endotherms. Figure 3.76 gives the DSC thermogram for the various bulk poly(ester-urethanes). The DSC results are in agreement with the properties obtained from the bulk poly(ester- urethanes), particularly in the case of Bulk ET2.8P, which showed the lowest tensile properties and the greatest rate of stress relaxation.

Overall, it may be concluded that presence of a polyester sequence in a bulk polyurethane or a polyurethane dispersion, resulted in limited phase separation, thus, leading to inferior physical properties.

Table 3.30 T_g and thermal transitions shown by IPDI/BDO- and H_{12} MDI /BDO-based bulk poly(ester-urethanes).

Code	DMPA (wt %)	HS (wt %)	T_g (°C)	T_c (°C)	T_m (°C)	T_{II} (°C)
Bulk ES 2.8P	2.8	28.6	-45		79.1	
Bulk ES 3.2P	3.2	29.6	-45		----	100
Bulk ES 3.8P	3.8	30.6	-46		81.1	
Bulk ES 2.8H	3.2	29.9	-41			128 - 164
Bulk ES 3.8H	3.8	34.2	-41		41.8	72

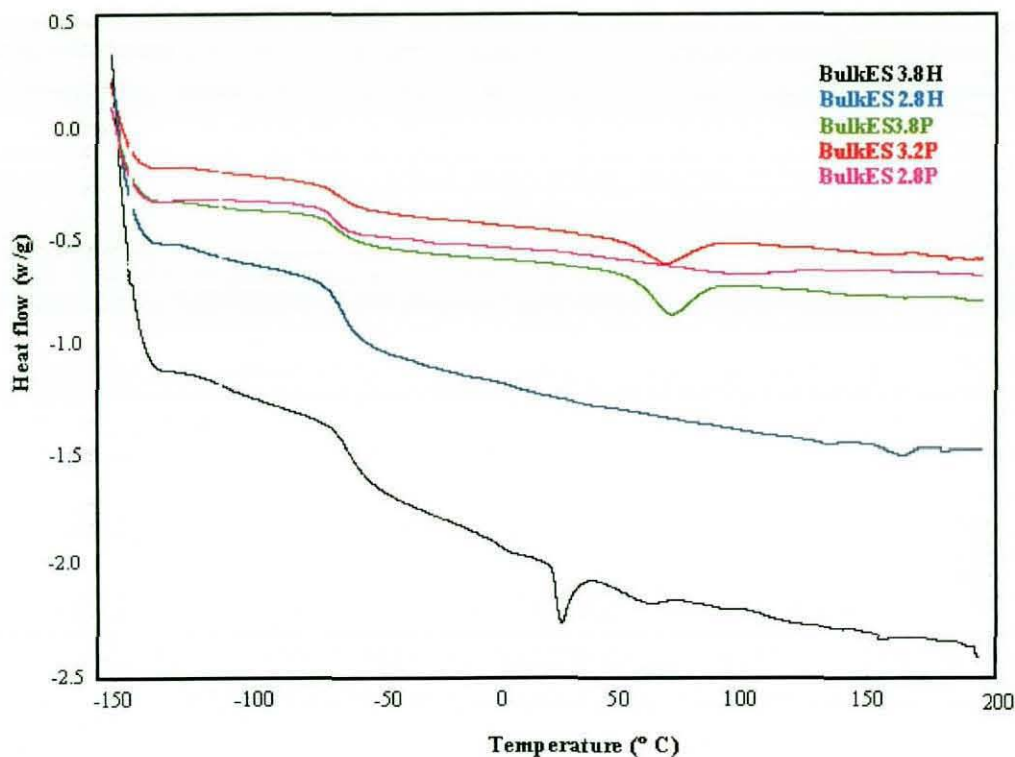


Figure 3.77 DSC thermograms of bulk poly(ester-urethanes) of IPDI or H₁₂MDI hard segment.

3.10 Dynamic mechanical thermal behaviour of bulk polyurethanes

3.10.1 Effect of DMPA content on the dynamic mechanical properties of IPDI- based bulk poly(ether-urethanes).

To determine the viscoelastic properties of bulk polyurethanes, DMTA testing was carried out. Initially, the effects of DMPA concentration on storage (E') and loss (E'') moduli was examined. As with the DSC analysis, the materials were grouped as low and high DMPA- containing categories. Figures 3.78, 3.80 and 3.82 show changes in the storage and loss moduli and $\tan\delta$ behaviours of these materials at low DMPA concentrations.

Analysis of the storage modulus-temperature plots show that Bulk ET 0.0P (figure3.78), clearly showed two drops in the modulus curves occurring at the two transitions temperature. From the DSC trace, figure3.74, the first drop in the E' corresponded to the T_g of soft segments and the second drop in E'' occurred at about room temperature, which corresponded to the melting endotherm observed in the DSC thermogram and was thought to arise from the soft segment melting. In between these two transitions, the storage modulus-temperature curves had two distinct but short moduli plateau, which clearly indicated the existence of a two-phase morphology. Upon the addition of DMPA, as seen in the DSC thermograms, the shape of the E' - temperature curves

gradually changed. The first plateau region that occurred between -80°C and room temperature became shorter and gradually disappeared. The gradient also became steeper, suggesting the destruction of the lower temperature morphology that was in existence in the Bulk ET0.0P polymer.

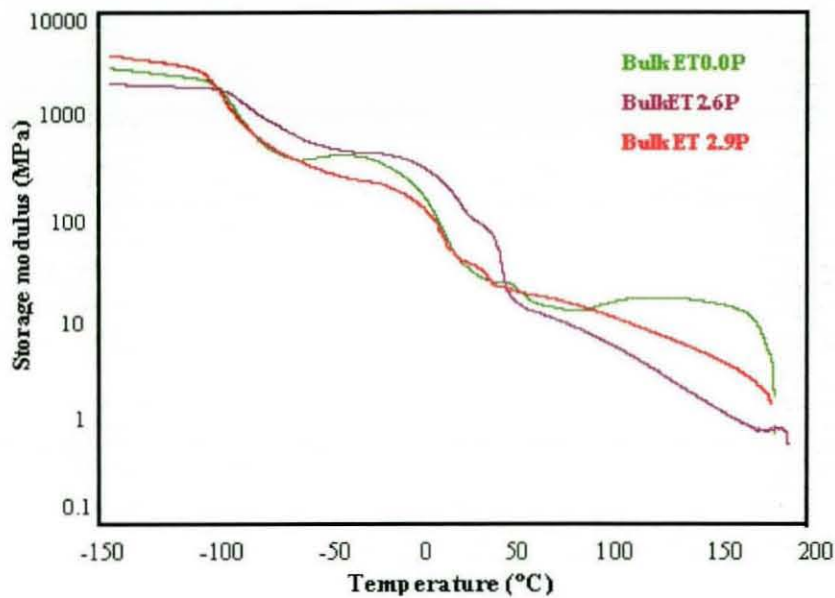


Figure 3.78 Storage moduli-temperature curves for the IPDI/BDO-based bulk poly(ether-urethanes) at low DMPA content.

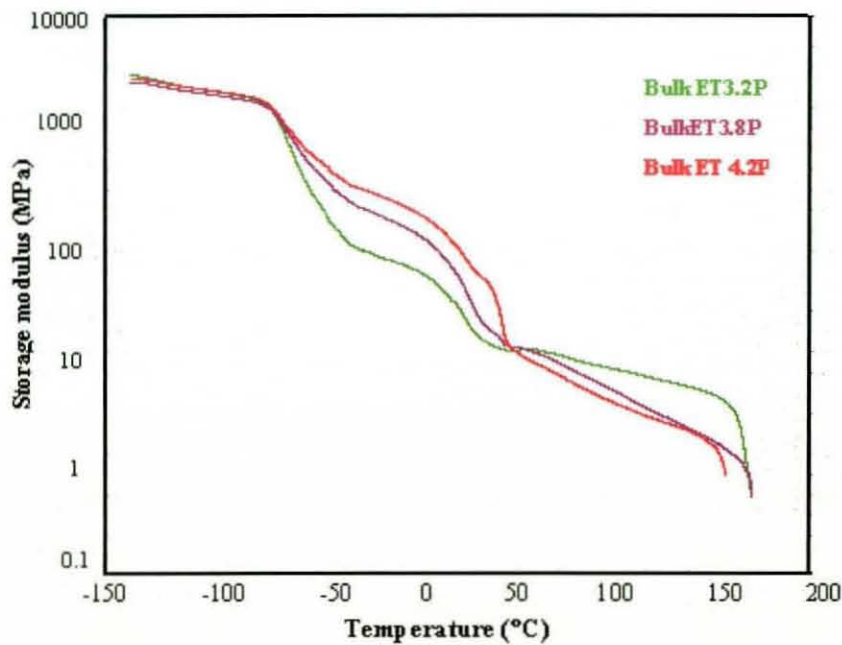


Figure 3.79 Storage moduli-temperature curves for the IPDI-based bulk poly(ether-urethanes) at high DMPA content.

When the level of DMPA is increased to 3.2 wt%, the predominant feature of the E' -temperature curves is the higher temperature region, and initial lower plateau is replaced by a steep drop of modulus at around room temperature. A second, and a more extensive, plateau however, begins to develop at the higher temperature suggesting the formation of more distinct and well-developed hard domains.

The $\tan \delta$ -temperature curves, at low DMPA, show similar trends at the various DMPA concentrations. The bulk ET0.0P shows a sharp $\tan \delta$ peak at the soft segment T_g , as well as minor transitions at higher temperatures. However, as the level of DMPA increases, the $\tan \delta$ peaks becomes broader and more diffuse. Figures 3.80 and 3.81 show the $\tan \delta$ -temperature curves.

At DMPA concentrations of 3.2 to 4.2 wt%, the $\tan \delta$ peak and the high temperature transitions arising from the development of the hard blocks appear to merge giving rise to diffuse broad peaks.

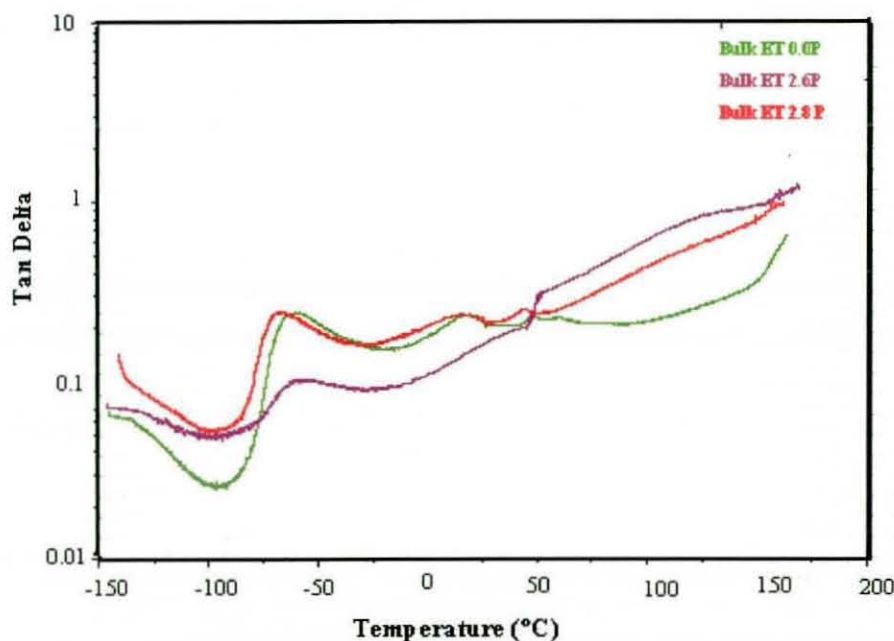


Figure 3.80 $\tan \delta$ -temperature curves for the IPDI/BDO-based bulk polyurethanes at low DMPA contents.

The measured loss modulus for these polyurethanes was an indicator of the viscous component within the material, and illustrated the effects of incorporation of the ionic DMPA moiety and its effect on the polymer morphology, and ultimately, the physical properties such as stress relaxation.

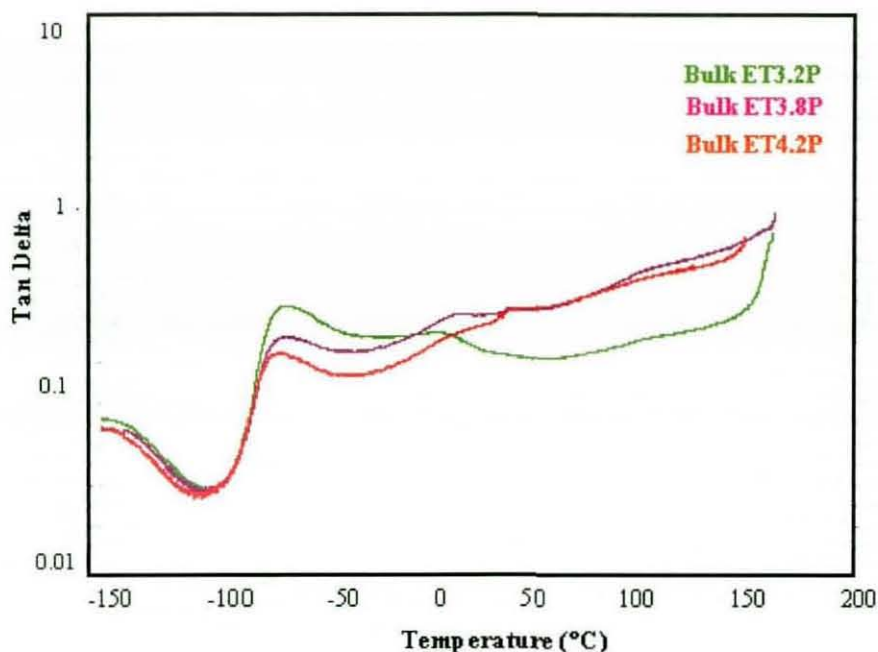


Figure 3.81. $\text{Tan}\delta$ -temperature curves for the IPDI/BDO-based bulk poly(ether-urethanes) at high DMPA contents.

Essentially, the loss modulus-temperature curves followed the same pattern as the $\text{tan}\delta$ and storage modulus-temperature (E') curves. As the level of DMPA was increased, and the main peak, which occurred at the T_g became more defined. The loss modulus-temperature curve for bulk ET2.6P gives the broadest peak extents from -25°C to 50°C . This suggested the existence of a random a copolymer with little or no domain morphology. This was particularly in agreement with the stress relaxation properties exhibited by this polymer.

The high drop in the load and the rate of relaxation exhibited by this polymer can be explained by the wide loss modulus peak, and the limited a two phase morphology exhibited by the loss modulus-temperature curve. The shape of the main peak in the loss modulus-temperature plot changes from a broad diffuse one to a more defined peak up to DMPA content of 3.2 %. Further increased in DMPA content, and, thus, hard segment content, appeared to broaden the peak, suggesting a change in the morphology. It appears that both bulk ET2.6P (lowest % DMPA) and bulk ET4.2P (highest % DMPA), favour a more mixed domain morphology.

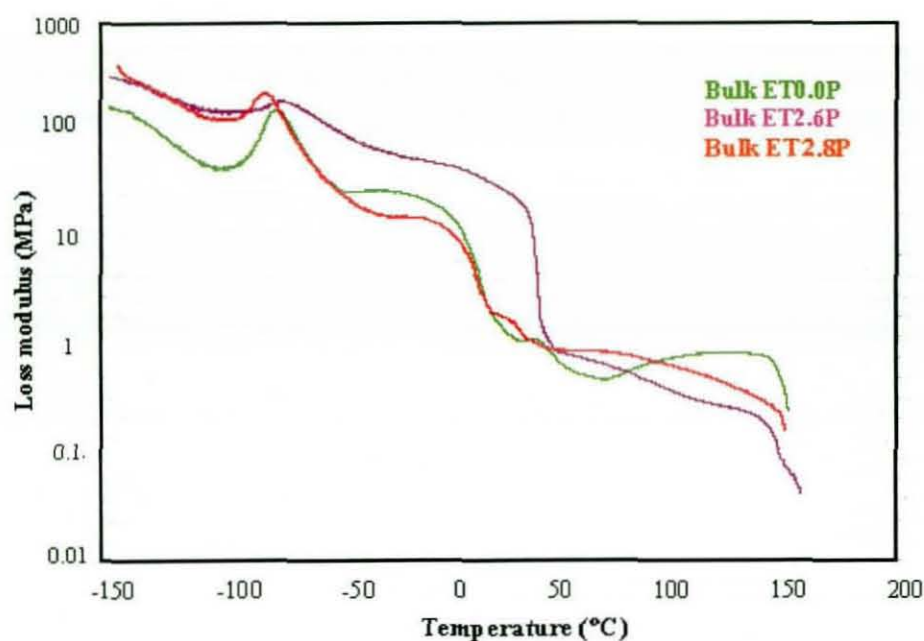


Figure 3.82 Loss modulus-temperature curves for the IPDI/ BDO-based bulk polyether PUs at low DMPA concentration.

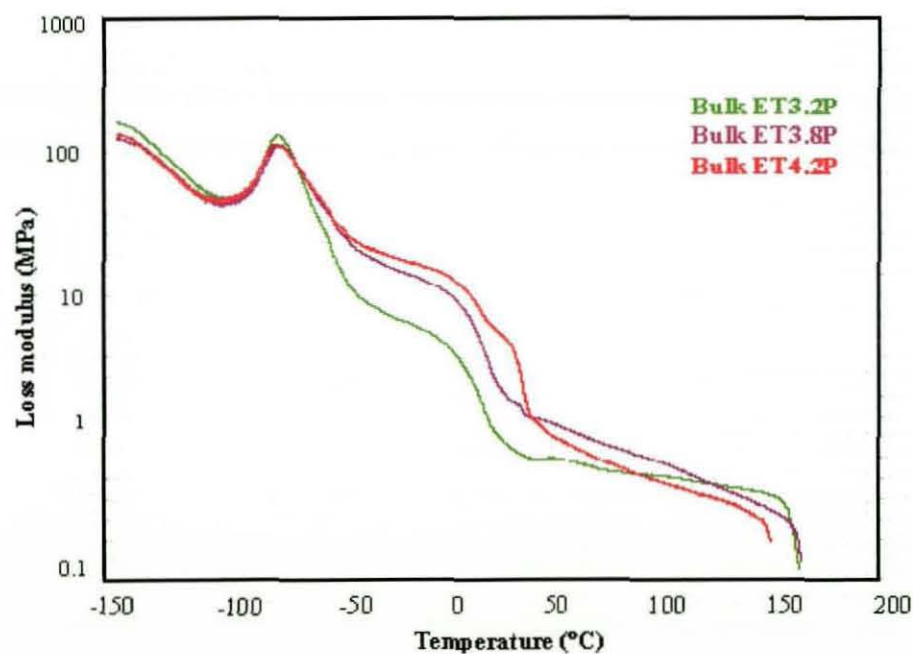


Figure 3.83 Loss modulus-temperature curve for the IPDI/ BDO- based bulk poly(ether-urethanes) at high DMPA concentration.

Figure 3.84 gshow the storage modulus-temperature curves for the H₁₂MDI/ BDO-based bulk polyether urethanes. At equal ionic moiety concentration and total weight percent hard segment, the effect of a change in the diisocyanate appeared to be an improvement in the degree of phase separation. For Bulk ET3.2 H, the E' temperature curves showed gradual step-wise changes indicating defined structural changes within the polymer. For Bulk ET3.8 H, several step-like changes in the storage modulus-temperature curves were detected, which were an indication of a well phase-separated structure^[17,25]. The presence of a two-block morphology was confirmed by the distinct transitions shown by the tanδ-temperature curves. These transitions were in agreement with the DSC behaviour shown by these polyurethanes. See figure 3.76.

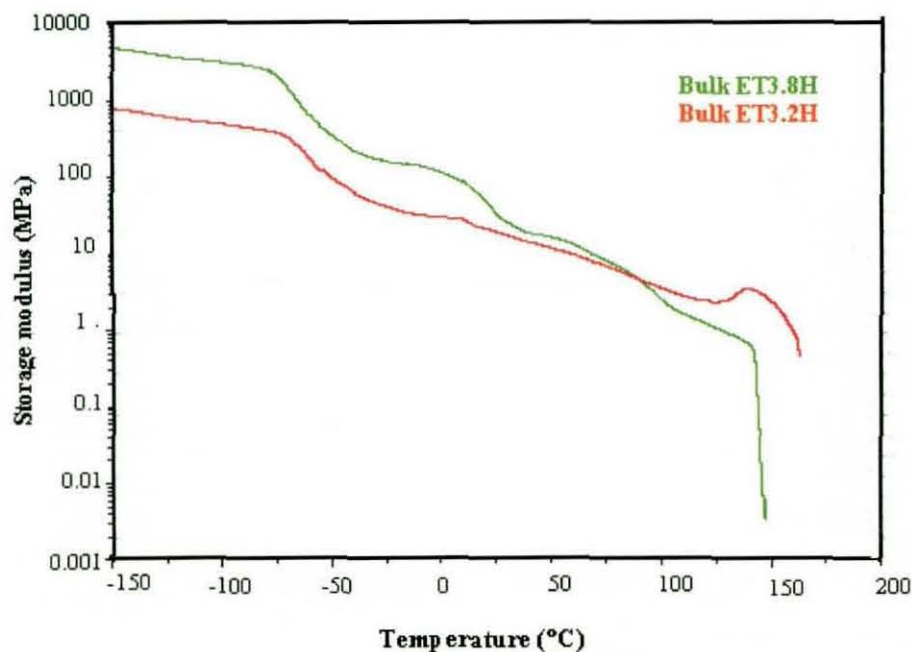


Figure 3.84 Storage modulus-temperature curves for the H₁₂MDI/BDO-based poly(ether-urethanes)

A similar trend was also shown by the loss modulus-temperature curves in which the higher level of DMPA and hard block content of H₁₂MDI type appeared to give rise to distinct domains within the polymer matrix. The DMTA data obtained for H₁₂MDI- based bulk polyether PUs suggested more phase-separated polyurethanes, in comparison to the IPDI system. This was expected and in agreement with the tensile strength, modulus and stress relaxation data obtained for the materials given in section 3.7.8.

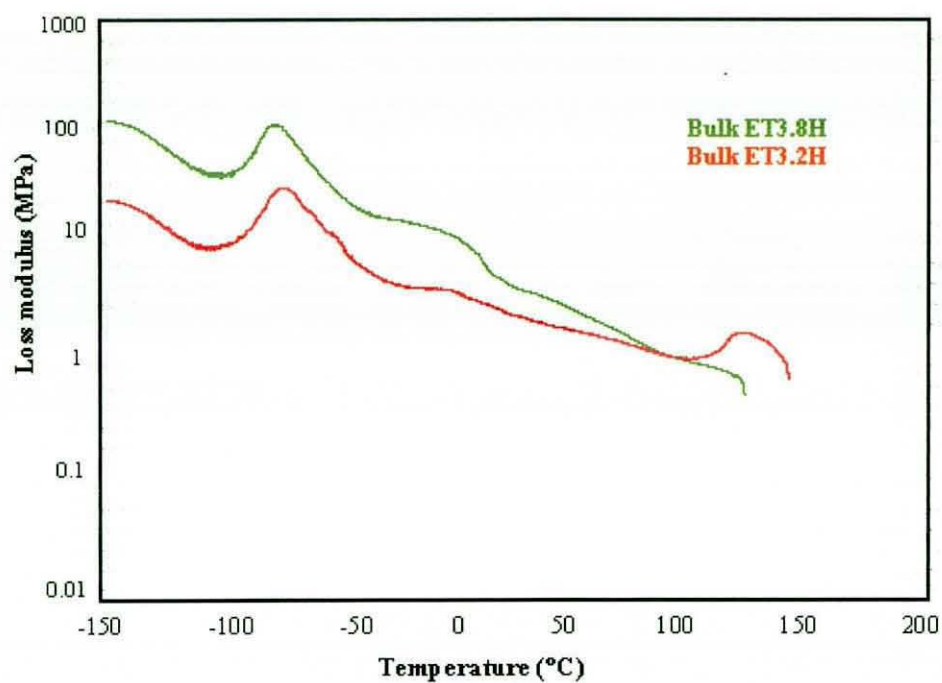


Figure 3.85 Loss modulus-temperature curves for the H₁₂MDI-based bulk poly(ether-urethanes)

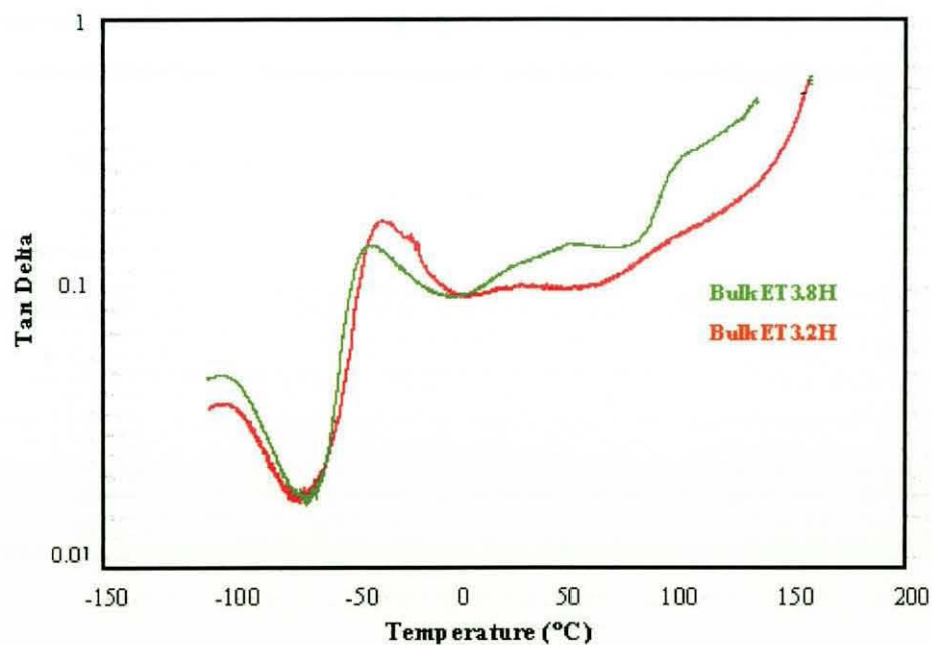


Figure 3.86 Tan δ-temperature curves for the H₁₂MDI/BDO- based poly(ether-urethanes)

3.10. 3 Dynamic mechanical behaviour of polyester-based bulk polyurethanes

Dynamic mechanical thermal analysis was also carried out on two representatives of the bulk poly(ester-urethanes): Bulk ES3.8H and Bulk ES3.8P. Figure 3.87 gives the storage modulus-temperature data for typical polyester bulk PUs. Unlike the bulk poly(ether-urethanes) the storage modulus-temperature curves were typical of a random copolymer with minimal chain interaction that could potentially act as pseudo cross-linking that has high storage modulus at low temperatures, but as it passes through its T_g the modulus begins to fall to low values. Some evidence of secondary structure was indicated by Bulk ES3.8P as its elastic modulus did show a small plateau from 50 to 100°C before dropping.

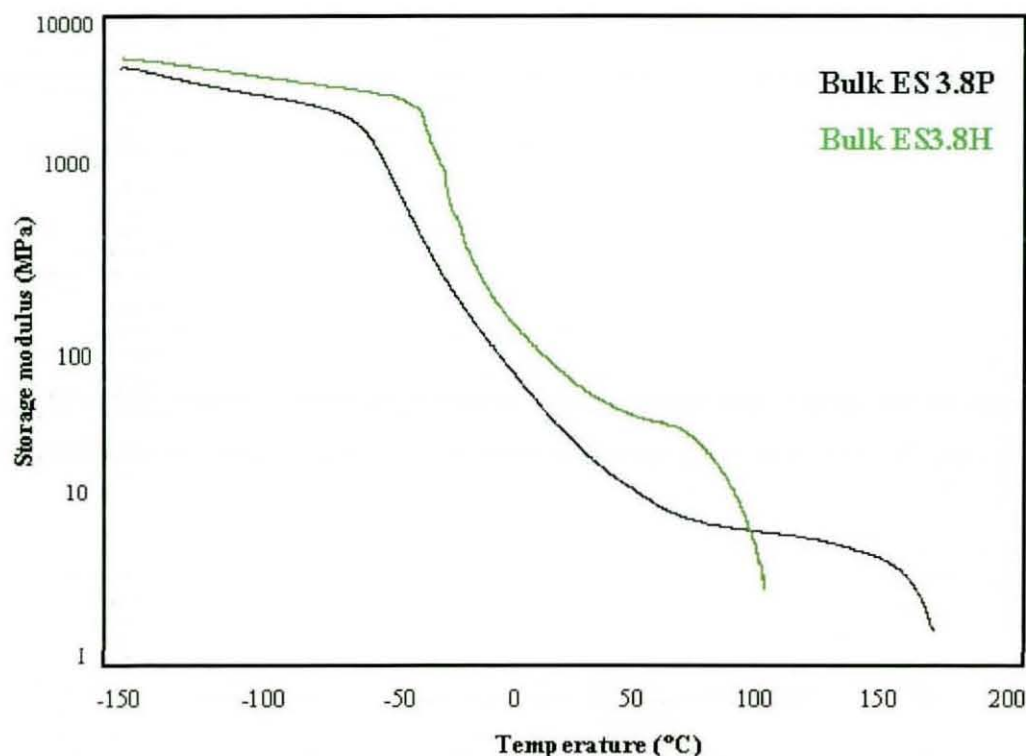


Figure 3.87 Storage modulus-temperature curves for the bulk poly(ester-urethanes) of different hard segments.

The $\tan\delta$ -temperature curve for both bulk poly(ester-urethanes) showed very broad peaks, and so an indication of segmental mixing. The Bulk ES3.8H curve showed low temperature transitions, which may have been due to crankshaft movements of the side chains of methylene groups in the polyester polyol. This evidence of low temperature segmental mobility could also be seen in the loss modulus-temperature curves. For the polyester-based bulk polyurethanes, the loss modulus-temperature showed extremely wide peaks which extend over several decades of temperature. Overall, the behaviour of these bulk PUs was typical of polyurethanes of low hard segment content with limited phase separation. This is in agreement with the physical properties exhibited by the bulk poly(ester-urethanes) which are summarised in tables 3.27 and 3.28.

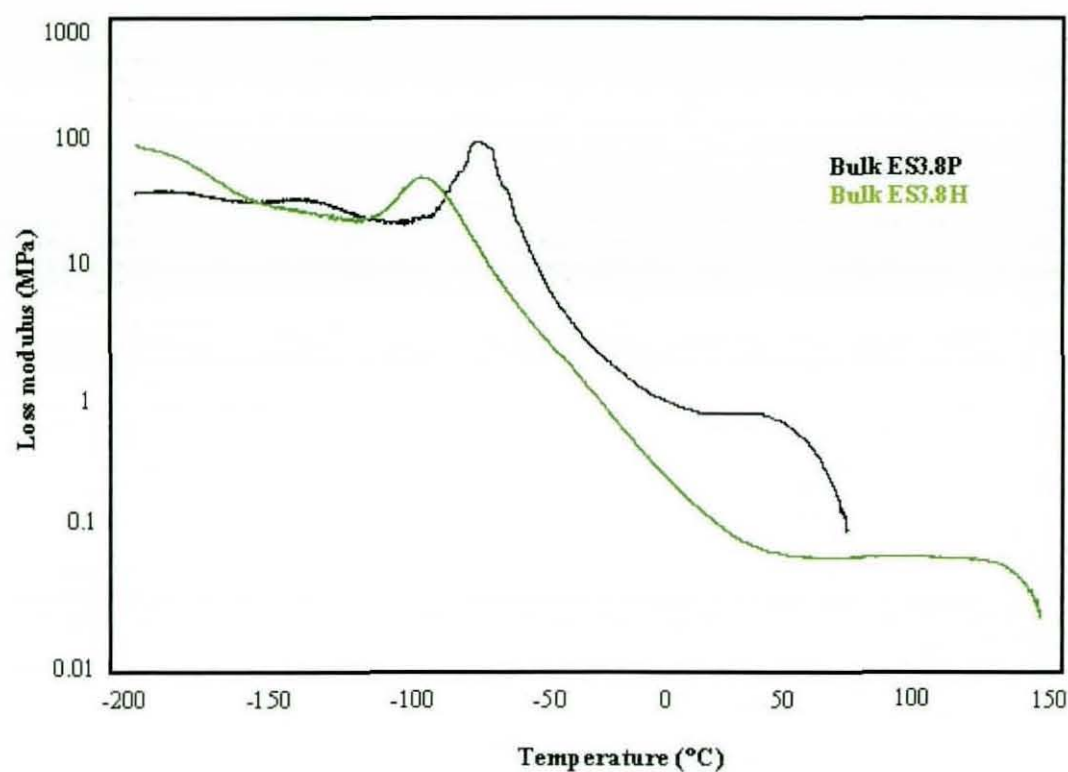


Figure 3.88 Loss modulus-temperature curves for the bulk poly(ester-urethanes) of different hard segments.

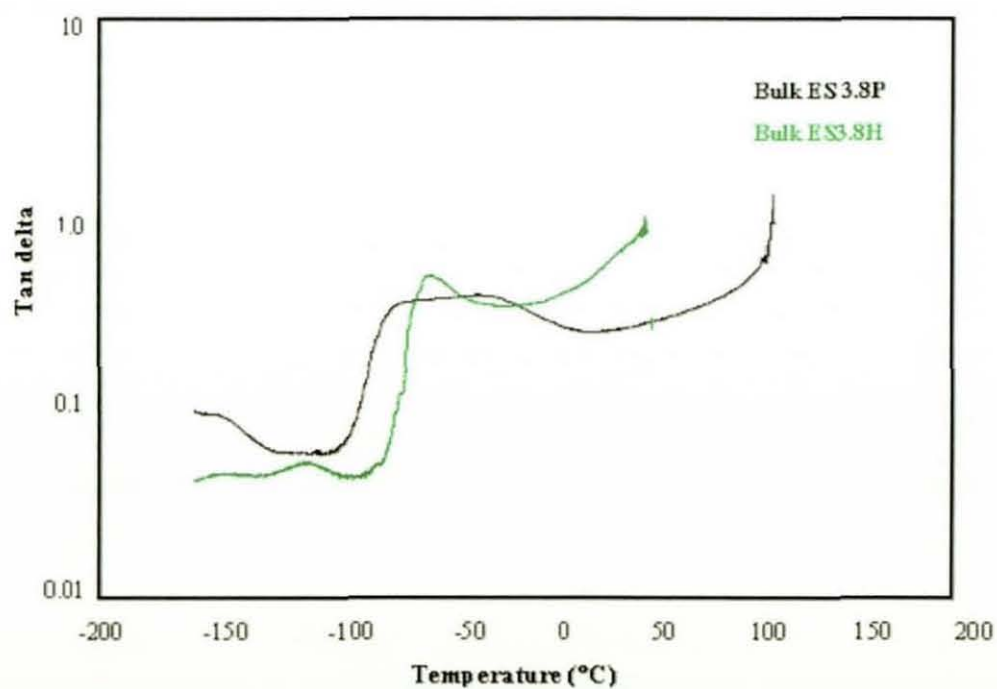


Figure 3.89 Tan δ -temperature curves for the bulk poly(ester-urethanes) with different hard segment.

CHAPTER 4

CONCLUSIONS AND FURTHER WORK

4. Conclusions:

The objective of this research was to determine the feasibility of synthesising water-based poly(urethane-urea) ionomers that have physical properties such as S100, tensile strength, elongation at break, and more importantly stress relaxation and recoverability properties, similar to those of vulcanised natural rubber films processed. These materials were meant for use in condoms, gloves and other of thin-walled soft elastic articles. The ideal physical properties for a soft elastomeric polyurethanes were given to be: tensile strength ≥ 25 (MPa), S100 modulus ≤ 1.5 , (MPa), and EAB $\geq 800\%$ ^[175]. The majority of the research was focused on the physical properties of the final films although some characterisation of the lateices was also carried out. The conclusions from each stage of the research is summarised below.

4.1 Synthesis

Initially some exploratory syntheses were conducted in which the effects of the chemical nature and the role of the co-solvent during the process of dispersion, and drying behaviour of a cast film were examined. Several conclusions were reached.

The chemical nature of the co-solvent, its viscosity and its boiling point, influenced the process of dispersion, the drying behaviour and the final, any film physical properties. The results showed that a low boiling co-solvent of low viscosity, such as MEK, gives rise to lower viscosity and smaller particles with a narrower distribution, compared to NMP having higher viscosity and a high boiling point. The use of a low boiling co-solvent facilitates the synthesis process as it acts as a diluent and allows for ease of dispersion. More importantly a low boiling co-solvent, such as MEK, volatilise during the drying and processing leaving no residues behind. The physical properties shown by films cast from NMP-based WPUDs were lower than those obtained from MEK systems. This was thought to be due to residual NMP in the films.

The prepolymer method of synthesising PU dispersions is well established. This method uses a diamine chain extender, with the chain extension process taking place in water. Side reactions of the isocyanate-capped prepolymers are expected and have been observed, and reported by various workers. The results of this study showed that the presence of diamines, regardless of their nature i.e. primary or secondary amines, still lead to final films of high tensile strength and high modulus with average elongation at breaks. Poly(urethane-ureas) synthesised in the study were shown not to have the characteristics, particularly the low S100 modulus, that are required for the processing and manufacture of thin elastic articles article. When examined for their stress relaxation behaviour, overall the poly(urethane-ureas) exhibit lower rates of relaxation. This behaviour may be attributed to the differences in the chemical nature of the urea hard blocks and their ability to enter into stronger, more cohesive hydrogen bonding interactions than polyurethane materials. The results of the current

study are in agreement with those discovered by previous workers who have compared the physical properties diol with diamine chain extenders.

The alternative method of synthesis, i.e. the conventional bulk method of manufacture of thermoplastic PUs was undertaken to determine the feasibility of developing water-dispersible PUs. These were synthesised in bulk to avoid the contact of the isocyanate-capped prepolymer with water and thus minimise the water side reactions while at same time allowing the use of diol chain extenders, which generally lead to lower S100 moduli films compared to their urea counterparts. The results of this study indicated that it is feasible to introduce an ionic moiety into a bulk reaction and achieve reasonably high molecular weight polyurethanes, that lead to soft films with average tensile strengths were acceptable elongation at breaks.

4.2 Molecular weight and GPC determination

Although the synthesis process was not monitored by taking samples during the synthesis, the molecular weight of the final films were determined by GPC. In both the cases of bulk polyurethanes and the WPUDs, molecular weight correlated with the tensile strengths of the films. Two observations were made. As the level of diisocyanate and the chain extender (ionic moiety / diol and diamine), were gradually increased, the shape of the GPC chromatograms changed. Also the greater the differences in the polarity between the soft and hard segments, the more defined the bimodal distribution. To demonstrate this effect, the Bulk ET0.0P that was synthesised free from an ionic moiety, when tested by GPC showed a single peak with no low molecular weight components. It is, therefore, reasonable to conclude that introduction of two types of chain extenders would increase the polydispersive nature of the final polyurethane material.

Additionally as the concentration of the isocyanate and the diol or diamines chain extender were to be increased, the likelihood of side reactions and the formation of lower molecular species would be encouraged. Generally these low molecular weight species tended to be more compatible with the polyether or polyester soft segment, diffuse into the rubbery matrix and acted as reinforcement fillers thereby influencing the S100 value of these materials. It is also reasonable to envisage that the low molecular weight species may have influenced the phase separation of the PU elastomer of this study, and therefore could have affected their strength, modulus and even viscoelastic properties. This phenomenon applies to both methods of synthesis.

4.3 Effect of ionic moiety

The ionic moiety appears to influence the dispersion characteristics, the physical properties and the thermal behaviour of the polyurethane materials. The concentration of the ionic moiety directly affects the particle size of a given WPUD and its viscosity. It was found that in order to obtain a

stable, water-based PU dispersion capable of producing a coherent transparent film of high tensile properties a minimum of 2.5 to 3.2 wt % ionic moiety concentration was required. The higher the level of ionic moiety, the smaller particle size and the greater the dispersion viscosity.

The concentration of the ionic moiety also influence the tensile properties of the final film and particularly the S100 modulus of the film. For a given polyurethane dispersion, there appeared to be an optimum concentration of ionic moiety that gave the best combination of physical and dispersion properties. For both groups of materials i.e. the WPUDs and the bulk PUs, this level appeared to be 2.5 to 3.2 wt%. Higher levels of ionic moiety concentration seem to disrupt the degree of phase separation, as indicated by increases in the T_g in the polyether-based PUD containing IPDI and NN'DMEDA hard segment. The addition of higher levels of ionic moiety also further encouraged the formation of low molecular weight species as shown by the GPC chromatograms. This could be another reason for the disruption of phase separation process.

The presence of the ionic moiety significantly influenced the stress-relaxation behaviour of a water-borne bulk polyurethane and to a lesser extent the stress relaxation of poly(urethane-ureas).

The ionic moiety concentration seems to control the initial load drop in all the materials investigated in this research. The rate of relaxation, however, seems to be controlled by the effective pseudo cross-linking, or the degree of phase separation in the polyurethane

4.4 Effect of change in the hard and soft segment molecular structure

Characterisation by DSC and DMTA yielded evidence that the polyurethanes studied, were partially phase separated. At lower ionic moiety concentration, the DSC traces showed soft segment T_g s close in value to that of the pure polyol and clear evidence of the soft melting. Little evidence of hard domain endothermal activities was detected at low hard segment concentration for either type of materials. However, a gradual increase in the ionic moiety concentration brought about the development in the hard segment morphology which became obvious by the appearance endothermal activities, T_I , T_{II} and at times, even T_{III} on the DSC thermograms.

An increase in the ionic moiety seemed to influence the soft segment crystallisation and this was evident by the disappearance of the melting endotherm from the DSC traces. A clear difference between the polyester and the polyether-based materials was observed. In all cases the DCS thermograms of polyester-based materials showed limited evidence of any endothermic activities arising at higher temperatures, and increases of ionic moiety led to upward move of the soft segment T_g .

The overall dynamic mechanical properties of the polyurethanes analysed, were representative of partially phase separated systems with mixing of both types of segments in the matrix due to the smaller sizes of the hard blocks. The modulus curves showed two transitions where the modulus

changed markedly over a narrow temperature range at the T_g of the soft segment, T_m or T_g or dissociation the of hard segments.

Between the two transitions, a plateau region of lesser change in the modulus with temperature, was observed. The loss modulus, E'' is a quantitative measure of energy dissipation in the elastomer. Low values of E'' are indicative of low energy dissipation, low hysteresis and consequently, low heat build up. For the polyurethane materials studied in this research, the loss modulus values were high at low temperatures, but decreased as the temperature increased. The $\tan \delta$ plot as a function of temperature for a well phase separated block copolymer, may show several peaks. The $\tan \delta$ -temperature curves of the polyurethanes analysed exhibited fine differences, that reflected the subtle structural differences that existed in these materials. Structural changes that corresponded to a soft segment T_g , soft segment crystalline melting, hard segment T_g and hard segment melting or dissociation were detected for both types of PU materials analysed.

Once again as the ionic moiety concentration was increased, the shape of the DMTA curves changed too. Although all materials showed a rubbery plateau on the storage moduli-temperature curves, the shape and the size of this plateau were found to be different in each case and influenced by the molecular structure of each block. Materials that showed a high temperature peak on the $\tan \delta$ curve, also indicated a rubbery modulus that extended over a much higher temperature range, suggesting the presence of an enhanced secondary structure that resisted a catastrophic fall in the modulus up to high temperatures. This was particularly evident in PUDET 3.2P, and Bulk ET3.2 P, and was attributed to the presence of a strong hard segment structure and an improved degree of phase separation, that acted as effective pseudo cross-links that stabilised the modulus over a wider temperature range.

In general comparable stress-strain data were obtained for the two groups of polyurethanes examined. Differences in S100, elongation at break and tensile strength values were found to closely relate to the chemical structure and the size of the hard and soft blocks.

Overall, polyether-based polyurethanes and polyether-based poly(urethane-ureas) appeared to be stronger materials and showed evidence of a block copolymer morphology when analysed by DMTA and DSC.

In contrast, when the soft segment was based on a polyester polyol, the resultant films showed lower overall tensile properties, and a limited degree of phase separation, as illustrated by the increases in the T_g of these materials when measured by the DSC, as well as the single peak indicated on their GPC chromatograms.

5. Further Work

5.1 Synthesis

The bulk method of synthesis was only briefly examined in this study to determine its feasibility. However, having established that it may be possible to avoid the use of diamines and so chain extension in the presence of water, it is believed that there may be an opportunity to further explore the possibility of developing a soft elastomer with high recoverability properties using this process.

Although this technique may seem to be suited for industry, such as the one that has sponsored this research, it could also provide possibilities in other industrial sectors, where the use of nitrosamine or protein free materials are essential.

It is recommended that a wider range of ionic moiety, a wider range of diisocyanates, and polyols should be explored. Examples of these are use of sulphonates as the ionic moiety. Also use of a tetramethylene xylene diisocyanate TMXDI is expected to give lower modulus materials as it does not favour hard segment alignment. Additionally chain extenders such as 1,2-benzene dimethanol, 2-hydroxybenzylalcohol, could be used to further control the strength and the modulus of the polyurethane rubber. It is further recommended that some custom made, innovative raw materials and precursors are used to allow for formation of covalent cross-linking in order to improve the stress relaxation of the materials and produce a polyurethane or poly(urethane-urea) rubbers that are similar in stress relaxation behaviour to natural rubber. Examples of these materials may be hydroxyl-terminated polyisoprene soft segments or chain extender diols, containing unsaturation groups such as trans but-2-ene-1,4-diol.

5.2 Molecular weight

It is recommended that the synthesis process be monitored by FTIR/NMR spectroscopies and absolute molecular weight measurements, or other powerful analytical tools to facilitate a greater understanding and identification of the most dominant type side reactions, that are likely to occur during the synthesis process.

5.3 Stress relaxation

The method of measuring stress relaxation was only briefly researched and applied in this study. It is proposed that polyurethane latices of various chemical compositions, including ones with the potential for covalent cross-linking, are produced and tested. Additionally the effect of other methods of non ionic emulsification on initial load drop and the rate relaxation, should be determined.

5.5 Thermal analysis

In this study, only a limited amount of DSC and DMTA analyses were conducted. In order to obtain a greater insight into structure-property relations, annealing exercises could be carried out on selected materials to determine the effect of processing parameters on final film properties.

DMTA could be used to in conjunction with stress relaxation measurement in order to further enhance understanding of the process and predict materials performance in use.

The DSC analysis could be combined with another tool, such as X-ray scattering, to determine alignment and morphology of ionic and hydrogen bonded hard blocks. It will also be of use to investigate the effect of soft segment crystallisation and its role in determining the degree of phase separation.

5.6 Particle characterisation

As the materials prepared and studied in this research were synthesised in water, or were synthesised in bulk a dispersed in water, it is essential that an in-depth analysis of particle morphology be conducted. This should be linked to the chemical structure of the starting raw materials. The effect of particle size on the film formation and the film mechanism must also be studied.

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