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The Structure-Property Relationships of Water Dispersed Polyurethanes Based on Tetramethyl Xylene Diisocyanate

by

Adisai Rungvichaniwat

A doctoral thesis
submitted in partial fulfilment of the requirements
for the award of
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Supervisor: Dr. R.J. Heath, Ph.D.
Institute of Polymer Technology and Materials Engineering

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Abstract

Novel water dispersed polyurethanes based on tetramethyl xylene diisocyanate (TMXDI), polycaprolactone or polytetramethylene glycols and aliphatic diamine chain extenders were synthesised. 2,2 bis(hydroxymethyl) propionic acid (DMPA) and triethylamine (TEA) were used respectively, as potential carboxylic anionic emulsifying centres and neutralising agent in the resulting aqueous phase to form pendent quaternary ammonium salts. These were necessary to provide high hydrophilicity to the polyurethanes, sufficient to make the polyurethanes easily dispersed in water without the assistance of organic solvent.

The effect of isocyanate building block ratio, carboxylic acid (DMPA) emulsifier block ratio, aliphatic amine chain extender types and variations in soft segment molecular weights were investigated.

The resulting urethane-urea copolymers dispersions (UUCDs) were characterised by their appearance, pH, viscosity, surface tension, particle size and distribution. The amount of DMPA used in UUCDs preparation was optimised between 0.08 to 0.2 (DMPA equivalent molar block per total equivalent molar block ratio of TMXDI/polyol/DMPA/Chain extender based polyurethanes), to obtain stable milky white dispersions of high solids content. The concentration of pendent carboxylic acid group was found to have a significant effect on pH, viscosity and particle size.

In subsequent examination of solid properties, the UUCDs were converted to coherent solid films by casting, or by precipitating to powder which was injection moulded into sheet. Cast films were examined by Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analysis (DMTA), Fourier Transform Infra-red (FT-IR) analysis and tensile behaviour (300% modulus, tensile strength and elongation at break). In a later limited programme, a single formulation of UUCDs as injection moulded sheets was examined only by DSC, DMTA and tensile properties.

Properties of the solid cast thermoplastic UUCDs were mainly influenced by hard segment content and molecular weight of soft segment (polyol). General trends of modulus, tensile strength, glass transition temperature, secondary transition temperature, degradation temperature and hydrogen bonding showed increases with higher hard segment content or lower molecular weight of soft segment respectively. It is possible that higher pendent carboxylic acid emulsifier content in the urethane-urea copolymers structures decreases their thermal stability.
From these studies of injection moulding behaviour and the evaluation of the performance of selected urethane-urea copolymers materials obtained from the water based dispersion polymerisation process show that useful products can be obtained. It was found that increasing injection temperature, injection speed and mould cooling times result in inferior tensile behaviour of urethane-urea copolymers. It was also found that the properties of injection moulding specimens are inferior to the specimens obtained by the casting technique, probably resulting from degradation.
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Chapter 1 Introduction: New Polyurethane Systems

1.1 Polyurethanes

Polyurethanes are a family of polymeric materials which can be formulated to produce a wide range of hard, rigid to soft, elastic products with versatility and outstanding properties. They find use in a wide variety of forms such as films, foams, fibres, plastics, surface coatings, adhesives and elastomers. Most remarkable of their properties are excellent abrasion resistance, good low temperature flexibility and good impact strength.

The term polyurethane is used for convenience rather than accuracy since not only are urethane groups contained in the polymer structure but also other groups such as ester, ether, urea, biuret, allophanate, amide, etc., may also be present. However, the urethane groups are generally the main primary groups in the backbone structure.

1.2 A brief history of polyurethanes

The history of urethanes goes back to 1849 when Wurtz first synthesised an aliphatic isocyanate by reacting organic sulphates with cyanates (1.1) but most of development of polyurethanes started in the 1937 with the work done by Prof. Otto Bayer and co-workers in Germany.(1.2) In 1941, the first urethane products were marketed as Perlon U, a fibre forming polymer, and Igamid U, for plastics moulding use.(1.3) and by 1952 the Vulkollan class of castable polyurethane elastomers had been established and marketed.(1.4) However, most of the research and development were based on cellular polyurethanes.

It was not until the 1960s that solvent based polyurethanes gained wide acceptance as coatings and adhesives. However, with the emergence of environmental and workplace related legislation in the last 20 years, pressure to limit or ban excessive amounts and certain types of organic solvents, used as part of polyurethane coating systems, has placed great emphasis on the development of water based systems. By the end of the 1980s water based polyurethanes were the predominant form of polymers used in the coating industry.
The movement towards the use of water dispersible polyurethane system was initially slow but since the 1960's several formulations and processing techniques have been invented to permit the preparation of these materials. However, the main process for producing water based polyurethanes still employs a relatively large amount of organic solvents. This leads to higher production costs and a potentially unsafe working environment. In application, the main advantages of water dispersible polyurethanes include ease and economy of application, with conventional equipment, no limitation on working life, comparatively easy control of end product quality since no further polymerisation is required in the fabrication stage and finally, relatively low viscosity of latex at relatively high molecular weight of polymer. The disadvantages of water based polyurethanes are longer coating times and high energy requirement for water removal in the film forming stage.

There are certain advantages in producing types of polyurethanes which are available in both latex and solid forms. Water dispersed polyurethanes may appear to offer many opportunities for development. They have advantages over the solvent based polyurethanes with respect to environmental issues and offer commercial benefits. Polyurethane dispersions can be cast to form solid films, as surface coatings or dip coatings, or precipitated directly to powder form without going through the conventional bulk oligomerisation and granulation technique. This will offer advantages in energy and time consumption. The resulting polyurethane powders can then be further processed to much thicker sections using conventional casting techniques.

Very little systematic work has so far been carried out to understand and evaluate the necessary qualities needed of water dispersed polyurethanes, either for their use as surface coatings, dip coatings or adhesives or as powders, produced from water dispersed systems to be used as solid, elastomeric mouldings. Little work has also been carried out on the understanding of the basic structure-property relationships for these materials.

Polyurethane systems are derived from a wide range of components and endless possibilities exist to make structures suitable for a variety of end products. It is of great commercial and industrial importance to have a fundamental knowledge of the interaction between the structure, composition, morphology of polyurethanes and their relationships to strength, toughness, abrasion resistance, etc., if proper
use is to be made of this new type of polyurethane system in the manufacturing industry in future.

1.3 Objectives of the research programme

The original objectives of this research programme were as follow:

a) To synthesise a number of anionically water dispersed polyurethanes which were stable latices of high solids concentrations, using low or no amounts of organic solvent in their preparation. These latices were to be used for castings or surface coatings.

b) To synthesise formulations under the following conditions in order to understand their influence on the resulting polyurethane properties:
   i) the effect of an isocyanate reaction block ratio (i.e. the equivalent molar block ratio of isocyanate to active hydrogen containing compounds),
   ii) the effect of an internal emulsifier and its reaction block ratio,
   iii) the types of chain extenders
   iv) the types of polyols and their molecular weight.

c) To carry out a comprehensive study of the properties of both latices and cast solid films. It was felt particularly necessary to have a good knowledge of the phase interactions and polyurethane morphology, as they are related to these properties.

The properties of latices determined were:
   • pH,
   • viscosity,
   • surface tension
   • particle size and distribution.

The properties of solid cast film determined were:
   • thermal properties (i.e. glass transition temperature, secondary transition temperature and degradation temperature)
   • hydrogen bonding
   • tensile properties (i.e. 300% modulus, tensile strength and elongation at break)

d) In the latter stages of the programme, it was realised that stable polyurethane powders could be prepared directly from their latices. A study was therefore
undertaken of the melt process properties, preparation and subsequent mechanical properties of the moulded polyurethane.

Schematic outline of the objectives of the research programme is presented in Figure 1.1

Figure 1.1 Summary of the research work plan
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Chapter 2 General Background Chemistry & Preparation of Polyurethanes

2.1 The general background of polyurethane science

Polyurethanes were discovered by Prof. Otto Bayer, of I.G. Farbenindustrie AG in Leverkusen, Germany in 1937, probably as a competitive response to the work by Carothers at Du Pont, USA on the polyamides. (2.1) The history of polyurethane development has been documented by a number of authors. (2.2 - 2.6)

2.1.1 Basic reactions of isocyanates

The most importance group of reactants in polyurethane chemistry are the isocyanates, which have the following general formula:

\[ R-(N=C=O) \]

Isocyanates are very reactive and versatile materials that can combine with nucleophilic reactants to produce a range of reactions which are employed to build up polyurethane molecules. The reactivity of an isocyanate group is mainly determined by the pronounced electro-positive character of the carbon atom in the cumulated double bond sequence consisting of nitrogen, carbon, and oxygen. The positive charge at the carbon atom is obvious if one considers the resonance structure; the radical (R) with the NCO group will also influence this reactivity:

\[
\begin{align*}
R-\overset{\cdot}{N} = C = O & \leftrightarrow R-\overset{\cdot}{N} = C - O^- \\
\end{align*}
\]

The negative charge can be delocalized into R, if R represents an aromatic radical. This explains the distinctly higher reactivity of aromatic isocyanates over aliphatic or cycloaliphatic isocyanates. Substituents on the aromatic ring will influence the positive character of the NCO group, i.e. electron withdrawing substituents at the para or ortho positions, increase the reactivity of the NCO group, electron donating substituents lower its reactivity.

An isocyanate will react with a so-called active hydrogen containing compound, these include hydroxyl compounds (form urethane), amines (form urea), water
(form amine and carbon dioxide), carboxylic acid (form amide, carbon dioxide, urea and acid anhydride), urethane (form allophanate) and urea (form biuret). Of less importance are the dimerization, trimerization and carbodiimide reactions. Details of each reaction are followed:

(a) Reaction with hydroxyl compounds

\[
\text{R-NCO} + \text{HO-R'} \rightarrow \text{R-NH-CO-O-R'}
\]

Isocyanate Hydroxyl compound Urethane

This is the reaction to give the basic urethane structure, occurring at room temperature without catalyst within a few hours with primary hydroxyl compounds. With catalysts such as tertiary amines, or organotin salts, the polyurethane reaction is initiated within a few seconds at 20 °C.(2.7) However, many industrial polyether polyols are not miscible with aromatic isocyanates (e.g. MDI) and tend to quickly phase separate before reaction is completed. Secondary hydroxyl groups react more slowly with isocyanates. Tertiary hydroxyl compounds react with isocyanates to produce unstable compounds which decompose at room temperature into olefin, amine and carbon dioxide.(2.8)

(b) Reaction with amine compounds

\[
\text{R-NCO} + \text{R''-NH}_2 \rightarrow \text{R-NH-CO-NH-R''}
\]

Urea

This reaction is mostly used to promote chain extension or crosslinking following the polyurethane process. The reaction of unhindered isocyanates with primary amines at room temperature without additional catalyst is considerably faster than the reaction with primary alcohols. The reactivity of amines increases with the basicity of amine, with aliphatic amines reacting faster than aromatic amines.

(c) Reaction with water

\[
\text{R-NCO} + \text{H}_2\text{O} \rightarrow (\text{R-NH-COOH}) \rightarrow \text{R-NH}_2 + \text{CO}_2
\]

Unstable carbamic acid

\[
\text{R-NH}_2 + \text{R''-NCO} \rightarrow \text{R-NH-CO-NH-R''}
\]

Disubstituted urea
This reaction is responsible for the production of carbon dioxide gas used in the formation of flexible polyurethane foams. In this reaction, the primary polyaddition product is a carbamic acid. Since the carbamic acid is unstable, it decomposes to carbon dioxide and the corresponding amine. The amine subsequently reacts with isocyanate forming a urea. However, for the production of bubble free castings or coatings, the isocyanate-water reaction is undesirable. The isocyanate-water reaction occurs slowly at room temperature in the absence of catalysts. It is catalysed by its reaction product, urea, and very strongly by tertiary amines.\(^{(2.7)}\)

(d) Reaction with carboxylic acid

\[
\text{R-NCO} + \text{R'-CO-OH} \rightarrow (\text{R-NH-CO-O-OC-R'})
\]

Mixed anhydrides of carboxylic and carbamic acids, which are unstable at room temperature

\[
\text{R-NH-CO-R'} + \text{CO}_2 + \text{R-NH-CO-NH-R} + \text{R'-CO-O-OC-R'}
\]

Amide Urea Acid anhydride

Major product Minor product

The reaction rate is dependent on the acid strength. Carboxylic acids are somewhat less reactive than primary alcohols or water. This reaction occurs slowly at room temperature and is catalysed by tertiary amines, cobalt, ferric, and nickel compounds. It is generally an undesirable reaction in polyurethanes, which leads to hydrolytically unstable polymers, containing acid anhydride groups that easily degrade in the presence of water.\(^{(2.7)}\) It is also contributes to carbon dioxide formation leading to bubbles in solid polyurethanes.

(e) Reaction with urethane

\[
\text{R-NCO} + \text{R'-NH-CO-O-R''} \rightarrow \text{R-N-CO-O-R''}
\]

Urethane Allophanate

The reaction of isocyanate with urethane occurs very slow at room temperature without the aid of catalyst. However, in the presence of lead and strongly alkaline compounds, the reaction will occur at room temperature within a few minutes.
Stannous, dialkyltin, cobalt, copper compounds or strong tertiary amines cause the allophanate formation to occur within a few hours at 70 °C.\(^2,9\)

(f) Reaction with urea

\[
\text{R-NCO} + \text{R'}-\text{NH-CO-NH-R''} \rightarrow \text{R''-N-CO-NH-R'}
\]

Without catalysts, this reaction occurs very slowly at temperatures below 90 °C. Organotin catalysts are most effective in the promotion of biuret formation. Both allophanate and biuret reactions are important since they create branching and crosslinking in the polyurethanes, forming network structure.

(g) Dimerization of isocyanates

Isocyanate molecules can react with each other to form dimers (i.e. uretidinediones). Aliphatic isocyanates are not known to undergo this reaction but most aromatic isocyanates dimerize; this is inhibited by ortho substituents. Because of their thermal instability at higher temperature, uretidinediones can be reversed back to isocyanate. They are of interest in creating blocked isocyanate allowing an isocyanate to function only at elevated temperatures. Mixtures of isocyanates which containing NCO groups of different reactivity, can be separated by selective dimerization. Isocyanates dimerize significantly only in the presence of pyridine, triethylamine or complex metal alkoxides.
(h) Trimerization of isocyanates

Molecules of isocyanates can also react together to form trimers (i.e. isocyanurates). Both aliphatic and aromatic isocyanates can form isocyanurates at high temperatures. Strong alkalis and lead compounds cause this reaction to occur rapidly at room temperature; tertiary amines can also catalyse the reaction.\(^{(2.10)}\) Isocyanurate formation gives very stable branch points and the reaction is not easily reversed. Isocyanurate ring structure increases thermal stability and stiffness in polyurethane networks.

(i) Carbodiimide and uretoneimine formation

\[
2 \text{R-NCO} \rightarrow \text{R-N=C=N-R} + \text{CO}_2
\]

Carbodiimide

\[
\text{R-N=C=N-R} + \text{R'-NCO} \rightarrow \text{R-N-C=N-R'}
\]

Uretoneimine

Without the aid of catalyst, this reaction normally occurs only at high temperatures, i.e. over 170 °C. However, catalysts such as strong alkalis, phospholine oxides, phospholines, phospholidines, aluminum isopropoxide, or manganese naphthenate promote the formation of carbodiimides at much lower temperatures.\(^{(2.11-2.13)}\) The resulting carbodiimides can then react with additional isocyanate to give uretoneimines.\(^{(2.14)}\)
All of the foregoing reactions are exothermic and will strongly influence the kinetics of the isocyanate reactions. Therefore, this should be considered in the design of any preparation process for polyurethane and for polyurethane structures.

All the isocyanate reactions described above provide important components for the chemist to design and build polyurethane macromolecules. They can provide the required molecular flexibility or rigidity and the chain order, branching or crosslinking precisely tailored for the final performance and properties.

2.1.2 Formation of polyurethanes

As described in the isocyanate reactions, it is obvious that stoichiometrically balanced di- or multifunctional hydroxyl compounds and isocyanates, will give rise to linear or crosslinked polyurethanes respectively.

Linear polyurethanes are the reaction products of diisocyanates and dihydroxyl compounds, as shown below:

\[ n \text{OCN-R-NCO} + n \text{HO-R'-OH} \rightarrow -(R-NH-COO-R'-OCO-NH)_n^- \]

Diisocyanate Dialcohol Linear Polyurethane

Although the polyurethanes are usually prepared by a step polyaddition reaction (or step rearrangement), they may be considered as condensation polymers because they could theoretically be made by either of two condensation reactions:

\[ n \text{HO-OC-NH-R-NH-CO-OH} + n \text{HO-R'-OH} \rightarrow -(R-NH-COOR'OOC-NH)_n^- + 2n \text{H}_2\text{O} \]

Unstable carbamic acid Dialcohol Linear Polyurethane

\[ n \text{H}_2\text{N-R-NH}_2 + n \text{Cl- COOR'OOC-Cl} \rightarrow -(R-NH-COOR'-OOC-NH)_n^- + 2n \text{HCl} \]

Diamine Bischloroformate Linear Polyurethane

The reaction of multifunctional isocyanates (or polyisocyanates) with dialcohols leads to a multitude of polymer structures, ranging from linear flexible materials capable of melting, to hard, brittle, highly crosslinked solids. There is a broad spectrum of material types between these extremes. The isocyanates used include aromatic, aliphatic, or cycloaliphatic types or their mixtures to add variety of
precursor materials. The versatility of compounds is even more extensive on the polyol side which are dominated by the polyether and the polyester polyol types. A large number of polyol compounds are available with respect to their molecular structure, functionality, chain length and reactivity. Frequently, polyhydroxyl and polyamino compounds are used simultaneously to form urethane-urea copolymers. The large versatility of the raw materials results from being able to synthesise polymers which contain not only the urethane link but also other groups, as integral units within or pendant on the polymer chains. Hence, the final polyurethane can be tailor-made for a large range of specific purposes.

2.2 The general materials and preparation of conventional polyurethanes

2.2.1 Important building blocks for polyurethanes

a). Isocyanates

There are a number of commercial diisocyanates employed in the polyurethane industry. They are either aromatic or aliphatic in nature. The aliphatic class (including the cycloaliphatics), are less reactive than the aromatic isocyanates, but they have the advantage of giving light stable products when exposed to ultraviolet radiation or thermoxidative conditions. (2.15, 2.16)

The commonly used aromatic diisocyanates include 2,4- or 2,6-toluene diisocyanate (2,4- or 2,6-TDI), 4,4'-diphenylmethane diisocyanate (MDI), 1,5-naphthalene diisocyanate (NDI), 4,6'-xylylene diisocyanate (XDI), para-phenylene diisocyanate (PPDI). The structures of aromatic diisocyanates are shown in Figure 2.1

Both TDI and MDI are still very popular precursors, mainly due to economic reasons and the physical properties of their products being unsurpassed. (2.17) TDI is normally used as a mixture of the 2,6- and 2,4-isomer in the ratio of 80:20 or 65:35 and is commonly used in the production of flexible foams. However, for rigid foam production MDI is usually chosen. Currently, there is a trend to use MDI instead of TDI for because safety considerations, as MDI is less volatile and therefore less health hazardous in use. (2.18) PPDI is valued for producing thermally stable polyurethanes (i.e. with thermal resistance up to 260 °C). (2.19)
A number of aliphatic and cycloaliphatic isocyanates are now becoming available in commercial quantities. 1,6-hexamethylene diisocyanate (HDI) was the first aliphatic diisocyanate to be used in polyurethane synthesis especially in the production of adhesives and flexible surface coatings. 4,4'-dicyclohexylmethanediisocyanate (H_{12}MDI or Hydrogenated MDI), is a cycloaliphatic diisocyanate which has been used in the production of transparent articles. Isophorone diisocyanate (IPDI) and 1,4 cyclohexyl diisocyanate (CHDI) give products with superior light stability to MDI and also provide excellent high temperature properties.\footnote{2.20-2.22} Other new developments including hydrogenated xylylene diisocyanate\footnote{2.23}; meta- and para- tetramethylxylene diisocyanate (m- and p-TMXDI) have been recently introduced.\footnote{2.24} Even though TMXDI contains aromatic rings, it has characteristics of aliphatic diisocyanates because the isocyanate groups are shielded from the ring by protective methyl groups. The structures of all these aliphatic isocyanates are shown in Figure 2.2.

It is worth noting that the major requirement in preparing water dispersible polyurethanes synthesised in this research, is that the isocyanate must have sufficiently low reactivity with water compared to its reactivity with polyol or amine. Therefore, the isocyanate must be carefully selected. Cycloaliphatic diisocyanates are preferred because of their low reactivity with water and also have a bonus of a naturally neutral colour and contributing better colour stability to the final polymer, compared to aromatic diisocyanates.

All isocyanates are health hazardous and must be handled with great care. They are also lachrymators and respiratory irritants, so prolonged inhalation may lead to symptoms resembling asthma. Therefore good ventilation and hygiene are required when working with isocyanates. The use of isocyanates in industry is controlled by the Health and Safety Executive in the UK. The acceptable working limits (i.e. threshold limit value, TLV) for these materials are maximum allowable concentration of total isocyanate groups in air is 0.02 mg per cubic metre for an 8 hours time weighted average and 0.07 mg per cubic metre for a 10 minute weighted average.\footnote{2.25}
Figure 2.1 Commercially available aromatic diisocyanates for polyurethane synthesis.
Figure 2.2 Commercial available aliphatic diisocyanates for polyurethane synthesis.
b). Polyols

The polyols traditionally used in the polyurethane industry are either polyether or polyester oligomers that are chain-tipped with hydroxyl groups. They have in general an average molecular weight between 200 and 10,000 depending on their application. Commercially the most important polyols are the polyethers with both linear or branch structures and a wide range of molecular weights. The polyethers are cheaper, easier to handle and their resulting urethanes have better hydrolysis resistance than those based on polyesters. However, in general polyester based polyurethanes, yield better mechanical properties. Some common commercially available polyols are shown in Table 2.1.

b.1) Polyester polyols

The polyester polyols are usually prepared by reaction of dibasic acids (e.g. adipic acid) with excess diol. The commonly used diols are ethylene glycol, 1,2-propylene glycol or diethylene glycol but higher functional alcohols such as, glycerol, trimethylolpropane, pentaerythritol, sorbitol, etc. are also employed, if chain branching or ultimately crosslinking are required.

In the preparation of polyesters, conventional methods of polyesterification are used. (2.26), the water of the condensation being removed by distillation. Their molecular weight can be controlled by adjusting the molar ratio of the reactants and the reaction conditions. This type of esterification does not require catalyst, although organic-metallics such as those of titanium or zirconium (e.g. tetrabutyl titanate) are often used to reduce reaction time.

\[(n+1) \text{HO-R-OH + n HOOC-R'-COOH} \rightarrow \text{HO-[RO-CO-R'-CO-O]}_n\text{R-OH + 2n H}_2\text{O}\]

This esterification reaction results in a mixture of low molecular weight polymers. The further reaction at higher temperatures and reduced pressure leads to the elimination of some glycol with the formation of higher molecular weight polyester polyols.

Another commonly used of polyester is based on polycaprolactone obtained by the step polymerisation of e-caprolactone in the presence of an initiator. (2.27) This type of polyester exhibits improved hydrolytic stability and low temperature properties as compared to adipate-polyester based urethane elastomers.
Polymerisation is carried out by a ring opening mechanism which allows control of molecular weight and functionality. Polycaprolactones are saturated aliphatic polyesters containing a single repeat unit and as no water is produced during the polymerisation, the polyol produced is exceptionally pure. The high polarity in these polyols increases the intermolecular attraction in polyurethanes and hence improves mechanical properties.

\[ 2n \text{CH}_2(\text{CH}_2)_4\text{CO} + \text{HOROH} \rightarrow \text{HO-[-(CH}_2)_5\text{COO-}_m\text{-R-[-OOC(\text{CH}_2)_5\text{-}_n\text{--OH}}} \]

**Polycaprolactone polyol**

b.2) Polyether polyols

The polyethers of commercial interest in polyurethane manufacturing are generally the polypropylene glycols and polytetramethylene glycol types. In both cases their manufacture involves the polyaddition of the monomeric epoxide.\(^{(2.28)}\)

\[ \text{CH}_2 - \text{CHCH}_3 \xrightarrow{\text{base catalysts}} \text{H-[-OCH}_2\text{CH}_2\text{-}_m\text{--OH}} \]

**Polypropylene glycol**

\[ \text{CH}_2 - \text{CH}_2 \xrightarrow{\text{Catalysts}} \text{H-[-O(CH}_2)\text{4-}_n\text{--OH}} \]

**Polytetramethylene glycol**

Propylene oxide is manufactured from propylene via a chlorohydrin intermediate and is a liquid with a boiling point of 35 °C. It can be polymerised by use of basic catalysts. Other epoxides are polymerised in a similar manner although temperature and catalysts used vary with the particular epoxide. In the polymerisation of
tetrahydrofuran to polytetramethylene glycol, either boron trifluoride, antimony pentachloride, or a mixture of ferric chloride and thionyl chloride fluorosulphonic acid may be used, and as these catalysts may lead to degradation at elevated temperature, polymerisation is carried out below 10 °C.

Table 2.1 Some common polyols commercially available

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Repeating unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a) Polyester glycol</strong></td>
<td></td>
</tr>
<tr>
<td>Polyethylene adipate</td>
<td>--O(CH₂)₂OOCO(CH₂)₄CO--</td>
</tr>
<tr>
<td>polytetramethylene adipate</td>
<td>--O(CH₂)₄OOCO(CH₂)₄CO--</td>
</tr>
<tr>
<td>polyoxydiethyl adipate</td>
<td>--O(CH₂)₂O(CH₂)₂OOCO(CH₂)₄CO--</td>
</tr>
<tr>
<td>polycaprolactone</td>
<td>--O(CH₃)₂CO--</td>
</tr>
<tr>
<td><strong>b) Polyester glycol</strong></td>
<td></td>
</tr>
<tr>
<td>Polytetramethylene glycol</td>
<td>--O(CH₂)₄--</td>
</tr>
<tr>
<td>poly-1,2-oxypropylene</td>
<td>--OCH₃CH(CH₃)--</td>
</tr>
</tbody>
</table>

All the polyols commercially available for the polyurethane manufacturing are available with a variety of structure, molecular weight and functionality, to satisfy the special purpose of the final performance and properties.

c). Chain extenders

Chain extenders are usually low molecular weight glycols or diamines. The difunctional glycol or diamine extender react with free isocyanate normally in a prepolymer to yield a rigid segment, which is joined together with the flexible polyol segment. Diamine extended materials will result in urea segments, which possess high hydrogen bonding interaction and the elastomers produced using these diamines generally have better mechanical properties.

There are many commercially significant glycols used in the manufacture of polyurethanes such as ethylene glycol, 1,4-butanediol and bis-(hydroxyethyl) hydroquinone, the most widely used is 1,4-butanediol (1,4-BD). In many systematic studies, the influence of short and medium chain diols, such as the number of methylene groups (from 2 to 12) in the glycol chain structure, on the properties of polyurethanes elastomers have been investigated. Glycerol,
trimethylol propane etc. are occasionally used to introduce crosslinking to a polyurethane structure.

Primary and secondary di- or tri-amines can be used as chain extenders or crosslinking agents for polyurethanes. Aromatic amines derived from diaminodiphenylmethane or m-phenylene diamine structures are more significant than other amines. The best known reactants are 3,3′-dichloro 4,4′-diaminodiphenylmethane (MOCA)(2.30) and the 2,4 & 2,6 diamine isomers (35:65) of diethyl toluene diamine (DEIDA).(2.14)

d) Catalysts

Catalysts are used in polyurethane synthesis to control and balance the polymer formation and other side reactions. Catalysts for promoting isocyanate reactions may be of either nucleophilic or electrophilic types. Nucleophilic catalysts are typified by many bases, such as the tertiary amines, while electrophilic types are represented by organometallic compounds. Catalysts are often used in combination to control a number of simultaneously occurring reactions.

d.1) Base catalysts

Catalytic activity of tertiary amine catalysts for promoting isocyanate reactions increases with base strength related to the degree of exposure of electron pair on amine nitrogen atom; the most widely used being triethylene diamine such as diaminobicyclooctone, (DABCO). The efficiency of tertiary amine catalysts also depends upon their chemical structure, their reactivity generally increases as the steric shielding of the amino nitrogen decreases.(2.31) One disadvantage of tertiary amines is their strong irritating effect on the skin. Base catalysts are most effective in promoting the isocyanate-water reaction, therefore they are widely used in polyurethane foam production.

d.2) Organometallic catalysts

Organometallic catalysts are generally based upon mercury, lead or tin carboxylates, with tin complexes being extremely effective.(2.32) Organometallic catalysts promote isocyanate-hydroxyl reactions better than base catalysts but are less effective in catalysing isocyanate-water reactions. The most commonly used catalysts are stannous octoate, stannous oleate and dibutyltin dilaurate.
2.2.2 Preparation methods for conventional polyurethanes

In the preparation of polyurethanes, the molar ratios of isocyanate (NCO), hydroxyl compound (OH) and chain extender (CE), the block ratio is normally used to relate the stoichiometric proportions of these materials to form the polyurethane products. The chemical reaction, reaction temperature, reaction time, reaction medium, mixing rate, curing type, etc. are important variables in the control of the polyurethane properties. The preparation method will have an influence according to the sequence in which the reactants were added, such as in the two shot processes (i.e. prepolymer process or quasi-prepolymer process) and the one-shot process.

a) Two shot process: Prepolymer process (2.33)

This process is the most widely used technique in the manufacture of polyurethane elastomers in large scale. The prepolymer process provide better handling, control synthesis and consequently better resulting polyurethane properties than the other two processes. The prepolymer is first obtained by reacting a long chain polyol with an excess of diisocyanate under dry nitrogen to give an isocyanate terminal group at both ends of the prepolymer chain. Prepolymers are relatively stable high viscosity liquids or low melting solids at room temperature and should be stored in a dark, dry, inert atmosphere to prevent photodegradation, dimerization or moisture attack.

Their second step is the conversion of the prepolymer to a high molecular weight polyurethane by reacting with low molecular weight diol, diamine chain extender or other suitable multifunctional reactant. Diol chain extenders are comparatively less reactive than diamines and need a catalyst system to promote the reaction. As the pot life of bulk polymerised urethane is short, the reacting mixture has to be quickly cast into a mould. It is then cured in a hot air oven for several hours.

A prepolymer can be prepared either by bulk polymerisation or solution polymerisation: the solution technique has to be carried out in a non-reactive solvent. Although the properties of polyurethanes made by a solution technique are not as good as those from the bulk technique, it has the following advantages: the possibility of using higher melting point and more highly reactive isocyanate and chain extension agents, more rapid and efficient dispersion of reactants, longer pot
life and easier casting to form thin films by solvent evaporation. This process is schematically shown in Figure 2.3.

b) Two shot process: Quasi-prepolymer process (2.34)

In this process only some part of the polyol is reacted with all of the diisocyanate to form partial (quasi) prepolymer (i.e. a mixture of prepolymer and free original isocyanate). This resulting isocyanate tipped prepolymer is then reacted with the remainder of the polyol, premixed with a chain extender, to give the final polyurethane. This process is schematically shown in Figure 2.3.

c) One-shot process (2.35)

This technique is the common basis of most foam and reaction injection moulding (RIM) production methods. It involves the simultaneous mixing of polyol, diisocyanate and chain extender in the presence of appropriate catalysts. In practice, the polyol, chain extender and other additives such as blowing agent, foam stabiliser or flame retardant, etc. are first mixed, dried and then the isocyanates were added to the mixture. The mixing rate applied to the reaction is an important factor for the efficiency of mixing. These is no control over the reaction priority, hence random polyurethane structures are likely to be produced. These processes are generally very fast and exothermic. The solidification reaction is practically complete within a few minutes, but the final properties are often achieved after conditioning for 24 to 48 hours. This conditioning time can be reduced to a few hours by post curing at about 100 °C. However, one-shot systems are occasionally used for solid polyurethane elastomers for economic reasons where the components are mixed and extruded in a continuous process. This process is schematically shown in Figure 2.3.
Figure 2.3 Schematic diagrams for general polyurethane synthesis by:
(a) Prepolymer process, (b) Quasi-prepolymer process and
(c) One shot process
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Chapter 3 Background and Preparation of Water Dispersed Polyurethanes

Polyurethanes are a very extensive class of materials. Their structure and final products can be designed and varied to give a very wide spectrum of properties. The solvent based polyurethanes were first introduced in the 1960s for the coating industries but now with the environment related legislation, movement has been to the development of water based polyurethanes. These types of polyurethanes are now not simply scientific curiosities but have become rather valuable commercial industrial products. They have begun to penetrate into most application areas previously serviced only by organic solvent based polymers.

Water based polyurethanes are particularly suited for many applications because of their many advantages over the conventional solvent based materials.

- There are less or no volatile organic solvents involved in the process, therefore there are no residual solvent based odour and a reduction in fire hazards, leading to a safer and more friendly working environment.
- They can be free of surfactants which will improve the adhesion properties and subsequent intercoat adhesion.
- They are completely reacted, therefore no hazardous monomers remain in the product, (cf. reactive polyurethane coating).
- They are easier to use since no further reactants or catalyst are needed.
- They can be thermoplastic or thermoset.
- They can formulated easily to be soft, flexible or very hard rigid products.
- They are suitable for many medical applications since they have a high moisture vapour transmission rate which makes them suitable for wound dressing and medical drapes (3.1)

The special characteristic of water based polyurethanes is their ability to be designed to match to various application requirements.

Unlike many other water dispersed polymers (e.g. made via conventional emulsion polymerisation techniques), isocyanates, polyols and diamines (i.e. the basic building blocks of polyurethanes) must be handled under strictly anhydrous conditions since most types of isocyanates show a similar reactivity with water as the primary hydroxyl group in polyols. Therefore, the preparation of a conventional
polyurethane in the presence of a continuous water phase is not practical. Nevertheless, since the 1960's several compositions and processing techniques have been devised to permit preparation of water dispersed polyurethanes. Most of this work has been done in secrecy in industrial laboratories and therefore little has been reported in literature.

3.1 Raw materials for water dispersed polyurethanes

3.1.1 Basic materials

In practice water dispersed polyurethanes are actually based upon urethane-urea copolymers, which are characterised by the occurrence of both urethane and urea groups in the macromolecule chain. These groups are formed by the well-known step rearrangement reaction between isocyanate with polyol leading to urethane segments and also between isocyanate with amine chain extender leading to urea segments. The schematic structure of urethane-urea copolymers is shown in Figure 3.1.

![Figure 3.1 A typical schematic urethane-urea copolymers structure](image)

Polyurethane dispersions are formed in an aqueous medium but a reaction can occur between isocyanate and water, whereby the water hydrolyses the isocyanate group yielding amine and carbon dioxide via an unstable carbamic acid. The amine group thus formed can react with the isocyanate group to form a urea linkage and contributes to the macromolecule chain. High proportion of urea groups have a major effect on the mechanical properties of the resulting polyurethane products. However, the isocyanate-water reaction must be minimised during the production of high performance polyurethane dispersions because of the undesirable carbon dioxide evolution, which results in foaming. Further more, chains extended by water are inferior in performance to those chains extended by amines. In chain extension by water, two isocyanate groups yield only one urea linkage, (i.e. one reacts with water and the other reacts with isocyanate, resulting amine), whereas each single isocyanate group in amine chain extension will yield a urea linkage.
There are a variety of reaction routes of an isocyanate prepolymer with water, giving rise to a variety of product forms (3.2); as shown in Table 3.1.

Table 3.1 Various results of the reaction of NCO-prepolymer with water

<table>
<thead>
<tr>
<th>NCO prepolymer</th>
<th>Water</th>
<th>Types of mixing</th>
<th>Result</th>
<th>Product group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic</td>
<td>Equivalent</td>
<td>Shearing force mixer</td>
<td>Expansion with CO₂</td>
<td>Foam (hydrophobic)</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>Atmospheric</td>
<td>Diffusion into a thin layer</td>
<td>Slow curing</td>
<td>One-component coating</td>
</tr>
<tr>
<td>Slightly</td>
<td>Atmospheric</td>
<td>Rapid diffusion into foam</td>
<td>Slow curing</td>
<td>One-component coating</td>
</tr>
<tr>
<td>hydrophilic</td>
<td>moisture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>Excess</td>
<td>Shearing force</td>
<td>Inverse emulsion</td>
<td>Microporous coating</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>Excess</td>
<td>Emulsifying agent/shearing force</td>
<td>Emulsion</td>
<td>Coarse particle polyurethane dispersion</td>
</tr>
<tr>
<td>I onically or</td>
<td>Excess</td>
<td>Spontaneous dispersion (possibly with acetone)</td>
<td>Colloidal solution or emulsion</td>
<td>Fine particle polyurethane dispersion or colloidal solution</td>
</tr>
<tr>
<td>non-ionically</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydrophilic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trace ionic</td>
<td>Excess</td>
<td>Shearing force or acetone process</td>
<td>Coarse suspension</td>
<td>Powder</td>
</tr>
<tr>
<td>Very</td>
<td>Excess</td>
<td>Spontaneous solution</td>
<td>Solution</td>
<td>Solution or gel</td>
</tr>
</tbody>
</table>

Whether the resulting end product is a foam, a dispersion or a colloidal solution, a coarse suspension or a microporous coating, will be strongly dependent upon the state of aggregation and the quantity of water, the hydrophilicity of the prepolymer and the type of mixing equipment.

a) Diisocyanates

The selection of a diisocyanate is critical in determining the type of resulting polyurethane. The major requirement in preparing water dispersed polyurethanes is that the isocyanate must be of sufficiently low reactivity with water, during the chain extension step. The choice of diisocyanates is either the aromatic isocyanates (e.g. 2,4- or 2,6-toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI)) or aliphatic isocyanates (e.g. 1,6-hexamethylene diisocyanate (HDI),
tetramethyl xylene diisocyanate (TMXDI), isophorone diisocyanate (IPDI) or 4,4-cyclohexylmethane diisocyanate (H12MDI). The aliphatic polyurethanes are more costly but provide superior light stability, more flexible and have lower glass transition temperatures. Generally aromatic isocyanates have greater rates of reactivity with water than aliphatic isocyanates. However, aliphatic diisocyanates or their prepolymers are preferred in the preparation of water based systems because of their low reactivity with water and better light stability compared to aromatic diisocyanates.

b) Polyols

There are a large number of polyols that can be used, such as linear or slightly branched polyether, polyester or polycarbonate polyols. Choice of the chemical type and molecular weight, determine many of the resulting polymer properties, for example the lower the molecular weight, the shorter the polymer chain length and higher modulus of polymer obtained.

The polyether polyols such as polypropylene glycols or polytetramethylene glycols have the advantages of better hydrolytic stability, lower cost and better solvent resistance than polyester polyols. Polyester polyols such as polyester adipates or polycaprolactones because of their higher polarity, give rise to advantages of excellent adhesion to low energy surfaces, excellent toughness, abrasion resistance and better physical properties than polyether based polyurethanes. Polycarbonate polyols give the advantages of good hydrolytic stability and good abrasion resistance but are costly and there is a limited number of molecular weight types available.

From the information above, it is obvious that the selection of polyol controls the final properties required and the cost of the polymer.

c) Chain extenders

The key factor in selecting a chain extender for water dispersed polyurethane systems is that its reactivity with an isocyanate must be higher than for water, since the chain extension step is normally performed in the water medium. In theory, any low molecular weight diol, triol, diamine or triamine can be used as the chain extenders or crosslinkers. However, in practice the higher reactivity of the chain
extenders with isocyanate is preferred. Amines are chosen over alcohols due to their higher reactivity. The aliphatic or cycloaliphatic di- or tri-amines are used in preference to the aromatic amines because of their relative greater reactivity.  

3.1.2 Special additives for water dispersed polyurethanes

Like most polymeric materials, conventional polyurethanes are not compatible with water. Therefore, they require modification before they can be dispersed in an aqueous medium. This is normally done by incorporating some protective colloids or suitable emulsifier into the polymer chain or system. (3.2)

a) Emulsifiers

Aqueous polyurethane dispersions are generally prepared by emulsifying hydrophobic polyurethanes in water during their polymerisation using the high speed stirring and with the aid of some suitable external emulsifiers. (3.3) However, a better way of dispersing polyurethanes is by building a hydrophilic group into the polyurethane backbone. The main advantages of building in hydrophilic groups onto the polyurethane molecule chain over the conventional external emulsifier technique, are that the dispersion process will not require strong shear forces in mixing, the dispersion is likely to have a finer particle size, the dispersion has a better dispersion stability and it reduces water sensitivity of the resulting polymer film.

Building hydrophilic groups into the macromolecule polyurethane chains requires replacing a small portion of the polyol, polyamine or polyisocyanate by materials which contain ionic groups or other water soluble segments in their molecular structure. Monomers with such building blocks are known as hydrophilic ionomers or internal emulsifiers. (3.3)

a.1). Internal ionic emulsifiers

For a stable aqueous polyurethane dispersion, usually 1% by weight of an ionic group in the polyurethane is adequate. (3.4) This indicates that only a small amount of an hydrophilic ionic group is distributed within the long hydrophobic molecule chain. Figure 3.2 shows the schematic formula as a section of a typical urethane-urea copolymers with internal ionic emulsifier (pendent carboxylic group).
A number of potential ionic compounds suitable for the preparation of polyurethane hydrophilic ionomers are available commercially. Figure 3.3 shows some typical examples of internal anionic and cationic emulsifiers. The sulphonate diamines, sulphonate diols, or dihydroxy carboxylic acids are commonly used. However, dihydroxy carboxylic acids e.g. alpha-alpha dimethylol propionic acid (DMPA), has the best potential as ionic building blocks. The advantage of DMPA is the sterically hindered carboxylic group, which prevents it from reacting with the isocyanate group at low temperatures. Such a reaction is undesirable because it consumes the potential ionic groups and leads to a high viscosity due to branching of the polyurethanes.\(^{(3,46)}\)

A number of techniques have been developed to introduce a carboxylic ionic emulsifier onto a polyurethane main chain such as introducing their functionality with polyester polyol\(^{(3,5)}\), polyether polyol\(^{(3,6)}\) or, by an addition of mercaptocarboxylic acid salts into unsaturated polyurethanes\(^{(3,7)}\) or by grafting maleic acid onto polyether segments.\(^{(3,8)}\)

Many techniques are based on the introduction of sulphonate ionic groups onto a polyurethane main chain. For instance, a segmented polyurethane with olefinic double bonds built into the main chain is epoxidized and then the ring is opened with a nucleophile, such as sodium sulphamate.\(^{(3,7)}\) However, sulphonate groups are usually built in via a diamino alkane sulphonate, as these compounds are soluble in water and their reaction with an isocyanate-tipped prepolymer is not affected by water.\(^{(3,9)}\)

The hydrophilic prepolymers usually have the potential anionic groups neutralised in the main chain with counterions to improve the hydrolytic stability. For example, carboxylic groups contained in a polyurethane hydrophilic prepolymer are neutralised with a mixture of volatile and non-volatile counterions e.g. ammonium
and alkali metal ions.\(^{(3.10)}\) In some cases, thermal labile counterions (i.e. which decompose during cure) are used, result in a non-hydrophilic polyurethane film. This technique is mostly used with cationic emulsifying polyurethane dispersions, in which cyanoacetic acids are used as neutralising agents.\(^{(3.11)}\)

Besides the anionic and cationic emulsifiers used separately, techniques based on amphoteric compounds have also been used. Here water dispersed polyurethanes can be made at nearly neutral pH by placing both anionic and cationic centres in the same polyurethane matrix.\(^{(3.12)}\)

\(\text{a.2). Internal non-ionic emulsifiers} \)

Another way to produce water dispersed polyurethanes without external emulsifiers or protective colloids is to insert non-ionic hydrophilic polymer segments into the polyurethane chain. These are usually based on water soluble polyether chains synthesised predominantly from ethylene oxide. The most common technique is to replace part of the hydrophobic diols with polyoxylene diols. Unfortunately this technique is not very effective because it is necessary to build a large number of hydrophilic polyether segments into the polyurethane backbone resulting in a water sensitive polymers. High water insensitivity is desirable for most of the coating applications.\(^{(3.21)}\)

However, a good compromise between the dispersibility of a polyurethane dispersion and the water resistance of its film can be accomplished by building polyoxylethylene segments onto the terminal positions of the polyurethane molecule. This can be achieved by using either modified diols or diisocyanates as building blocks.\(^{(3.22, 3.23)}\) Figure 3.4 shows some typical examples of modified diols and diisocyanates used as internal non-ionic emulsifiers.
Carboxylate types

\[
\begin{align*}
\text{HO} & \quad \text{CH}_2 \quad \text{C} \quad \text{CH}_2 \quad \text{OH} + \text{Base} \quad 3.13 \\
\text{H}_2\text{N} & \quad \text{(CH}_2\text{)}_4 \quad \text{CH} \quad \text{NH}_2 + \text{Base} \quad 3.14 \\
\text{H}_2\text{N} & \quad \text{CH}_2\text{CH}_2 \quad \text{NH} \quad \text{CH}_2\text{CH}_2 \quad \text{CO}_2\text{Na} \quad 3.15
\end{align*}
\]

Sulphonate types

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{NH} \quad \text{(CH}_2\text{)}_x \quad \text{SO}_3\text{Na} \quad 3.16 \\
\text{R} & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{OH} \quad \text{SO}_3\text{Na} \quad 3.17 \\
\text{OCN} & \quad \text{(Dimer)} \quad \text{NCO} \quad + \quad \text{Base} \quad 3.18
\end{align*}
\]

Cationic types

\[
\begin{align*}
\text{HO} & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{N} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{OH} \quad 3.19 \\
\text{HO} & \quad \text{CH}_2 \quad \text{N} \quad \text{CH}_2 \quad \text{OH} \quad + \quad \text{Acid/Alkylating agent} \quad 3.20
\end{align*}
\]

Figure 3.3 Typical examples of anionic and cationic internal emulsifiers.
3.2 Preparation of water dispersed polyurethanes

For the past twenty years, several production processes for high molecular weight polyurethane dispersions and powders have been developed. Some of the processes are still operated and technically important. These processes are summarised below.

3.2.1 Preparation of water dispersed polyurethanes

A large number of processes for producing water dispersed polyurethane have been developed since the 1940s. However, the first step in all these processes is the formation of a low molecular weight prepolymer which is chain-tipped by isocyanate groups. This is known as an "isocyanate tipped urethane prepolymer". This prepolymer is normally formed by reaction of suitable polyols with a molar excess of a diisocyanate, and also provides hydrophilicity to the prepolymer by incorporating a small portion of suitable emulsifier. It is important that the prepolymer contains a sufficient hydrophilic groups for a stable dispersion, before going through to the water dispersing step.

The most critical step is that the high molecular weight build-up during the chain extension which is normally performed with amine chain extender. Two problems arise, those of the control of the extremely fast isocyanate-amine reaction and the
viscosity build-up resulting from increasing molecular weight. The conditions and techniques are very important because they affect the polymer structure and the properties of the dispersion and the resulting cast film.

Many techniques have been developed to prepare a water dispersed polyurethanes but only the main technical and commercial processes are described below.

a) The solution process

This well-established process uses an organic solvent as an intermediate aid to control the viscosity during the critical chain extension step. A detailed description of this process has been given by Dieterich et al.\(^{(3.24)}\) An example of high molecular weight of urethane-urea ionomers built up in an organic solvent is shown in Figure 3.5

A fully reacted high molecular weight polyurethane, modified with hydrophilic groups, is prepared from an isocyanate tipped prepolymer in an inert polar solvent which is water miscible and has a relatively low boiling point e.g. acetone, methyl ethyl ketone or tetrahydrofuran. This solution is diluted with water. As more water is added, a phase inversion occurs, with water becoming the continuous phase and a dispersion being formed.\(^{(3.25)}\) The solvent is then removed by distillation to form a solvent free high molecular weight aqueous polyurethane dispersion. The transformation of an organic solution into an aqueous dispersion has been discussed by Dieterich, D.\(^{(3.26)}\)

The properties of these dispersions depend on a variety of parameters such as the chemical composition, type and amount of ionic group, molecular weight and method of preparation. The diameter of the emulsified particles can be between about 10 nm to 10 \(\mu m\) and the appearance can vary from an opaque/translucent sol to a milky white dispersion.

Acetone is a preferred solvent for this process because it is inert to isocyanates, miscible with water and has a low boiling point, which makes it easy to remove from the dispersion during the solvent distillation step.

This process is easily performed, very reproducible since the polymer formation is accomplished in a homogeneous solution, has a wide scope for variation in particle
size and low space-time yield. However the acetone process is limited to the production of linear polyurethanes which are modified with hydrophilic groups and are soluble prior to the dispersion step. However, the resulting coating products are still not very solvent resistant. The disadvantages of the acetone process are that a large amount of acetone is used during the dispersing step, a high energy consumption required for the distillation step and there is a low reactor volume yield, which is obviously economically unfavourable.

\[
n \text{HO} \quad \text{OH} + 2n \text{OCN-R-NCO} \\
\downarrow \\
\text{OCN-R-NH-CO} \quad \text{OCN-NH-R-NCO} \\
\downarrow \\
\text{Solvent} \\
\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{SO}_3^-\text{Na}^+ \\
\downarrow \\
\text{CH}_2\text{CH}_2\text{SO}_3^-\text{Na}^+ \\
\downarrow \\
\text{Water} \\
\text{Dispersion of urethane-urea copolymers in water/solvent} \\
\downarrow \\
\text{Solvent removal} \\
\text{Aqueous urethane-urea copolymer dispersion}
\]

Figure 3.5 Formation of urethane-urea copolymers dispersion by the acetone solution process
b) Prepolymer mixing process

In order to avoid use of large amount of solvent, the prepolymer mixing process was developed. This process is designed to use water instead of solvent as an mediate during the chain extension step. This is possible because of the difference in reactivity of active hydrogen species, i.e. the reactivity of the isocyanate-amine reaction must be higher than that of the isocyanate-water reaction.

The prepolymer mixing process (3.26) is usually carried out by first preparing an isocyanate terminated prepolymer which is modified with hydrophilic groups. This isocyanate tipped prepolymer is then dispersed in water and with the aid of high speed agitation forms a dispersion. Chain extension is accomplished by the addition of diamine to the aqueous prepolymer dispersion. Cycloaliphatic diisocyanates are of particular interest because of their low reactivity with water. A typical example of the prepolymer mixing process is illustrated in Figure 3.6

In this process, it must be noted that the hydrophilic modified isocyanate tipped prepolymer begins to react with water during the dispersion step. Therefore, the dispersing step has to be carried out in a short period of time and at a temperature below a critical point (i.e. where the isocyanate starts to react rapidly with water). To control this process, it requires careful selection of the functionality and viscosity of the isocyanate tipped prepolymer. (3.27) However, in practice, it is often necessary to use some organic solvent to ensure that the viscosity is reduced to a workable range.

This process is relatively simple to operate but it is restricted to specific types of isocyanates. Products made by this process do not reach the high quality of dispersion obtainable via the acetone process. (3.26) However, this prepolymer mixing process does have an advantage over the solvent process in that the prepolymer can either react with difunctional amines to yield linear, flexible urethane-urea copolymers or with polyfunctional amines to yield crosslinked urethane-urea copolymers. (3.28, 3.29)
Figure 3.6 Formation of urethane-urea copolymers dispersion by prepolymer mixing process
c) The hot melt process

The hot melt process is also a solvent-free process for preparing water dispersed polyurethanes. The problems associated with amine chain extension such as the strong odour of amines and the exothermic heat generated from amine dissolved in water are avoided. The final molecular weight build up of the polyurethane is achieved by an aminoplast polycondensation.\(^{(3.24, 3.30)}\) A typical example of the hot melt process is shown on Figure 3.7

The first step is the synthesis of an isocyanate terminated prepolymer containing hydrophilic groups, and then followed by capping of the prepolymer at elevated temperature, (i.e. greater than or equal to 130 °C) with an excess of urea to form a biuret. The product is then dispersed directly from the melt into water without the aid of any organic solvent. After the dispersing step, the chain extension is carried out by methylolation of the biuret groups with formaldehyde and subsequent lowering of pH or heating from methylol groups to initiate the polycondensation. This process also can be modified by using other prepolymer capping agents rather than urea, such as ammonia or primary amines, to yield urea end groups which can be methylolated or crosslinked.\(^{(3.31)}\)

This process is simple and easy to control. Solvent is not needed, nor any isocyanate-containing product has to be brought into contact with water. The chain extension step is an easily controllable polycondensation in an aqueous phase. The system is not sensitive to minor stoichiometric variations and gives excellent yields, with no problems in production on a large scale. In addition, a wide selection of polyester, polyethers and isocyanates and a variety of ionic modifying components can be used. From a technical viewpoint, this process is more favourable due to a no problem preparation, with a high yield per unit time. This process allows the preparation of emulsifier free dispersions within a few hours without the use of complicated equipment or organic solvents.
Figure 3.7 Formation of polyurethane-biuret by the hot melt process.
d) Ketimine/ketazine process

This process is developed from solvent process in which ketone is used. The ketone is able to react reversibly either with amines to form ketimines or with hydrazine to form ketazine. The details of this reaction are shown on Figure 3.8.

\[
\begin{align*}
\text{Ketazine} & \quad \text{Hydrazine} \\
\text{Hydrazine} & \quad \text{Ketone}
\end{align*}
\]

Figure 3.8 The formation of block amines (ketimine and ketazine)

In this process, the amine chain extension occurs homogeneously within the dispersed isocyanate tipped prepolymer particles. This can be done by mixing the prepolymer with a blocked amine or a blocked hydrazine before the water dispersing step. Ketimines or ketazine, in normal processing time and temperature ranges are practically inert towards isocyanates. Upon addition of water, free amines or free hydrazines are formed and the systems become reactive.

The ketimine process is similar to the prepolymer mixing method with one important difference. A blocked diamine is used as a latent chain extender. The blocked diamine, a ketimine, can be added to a hydrophilic isocyanate terminated prepolymer without a reaction taking place. As water is added to disperse the mixture, the ketimine is hydrolysed at a rate which is appreciably faster than that of the isocyanate with water. The released diamine then reacts with the dispersed particles of polymer to give chain extended urethane-urea copolymers. The chain extension and dispersing step occur simultaneously and the viscosity increases steadily until a phase inversion takes place. For this reason powerful agitation or
some solvent is often required.\textsuperscript{(3.33)}

A variation of the ketimine process uses ketazine as the latent chain extender. In this case the ketazine hydrolyses to hydrazine. The hydrolysis is slower than that of a ketimine. This is advantageous when an aromatic isocyanate based prepolymer is used. Dispersions prepared from this process can yield high performance coatings. A typical example of the ketimine/ketazine process is shown in Figure 3.9.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.9.png}
\caption{Formation of urethane-urea copolymers dispersion by ketimine/ketazine process}
\end{figure}

A summary of characteristic features of all the poly(urethane-urea) dispersion processes is shown in Table 3.2.
<table>
<thead>
<tr>
<th></th>
<th>Acetone process</th>
<th>Prepolymer mixing process</th>
<th>Hot melt process</th>
<th>Ketimine/ketazine process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyhydroxy compound</td>
<td>linear, variable</td>
<td>variable</td>
<td>variable</td>
<td>variable</td>
</tr>
<tr>
<td>Diisocyanate</td>
<td>variable</td>
<td>TDI, IPDI, H₁₇MDI</td>
<td>TDI, HDI, IPDI</td>
<td>variable</td>
</tr>
<tr>
<td>Emulsifiers</td>
<td>variable</td>
<td>dimethylol propionic acid</td>
<td>mainly ionic</td>
<td>variable</td>
</tr>
<tr>
<td>Product before dispersion</td>
<td>polyurethane ionomers</td>
<td>NCO prepolymer ionomer</td>
<td>ionic-biuret prepolymer</td>
<td>NCO prepolymer + ketimine/ketazine</td>
</tr>
<tr>
<td>Solvent</td>
<td>40 - 70 % acetone</td>
<td>often 10 - 30 % of methyl pyrrolidone</td>
<td>none</td>
<td>possibly 5 - 30 % acetone</td>
</tr>
<tr>
<td>Temperature of dispersion</td>
<td>~ 50 °C</td>
<td>20 - 80 °C</td>
<td>50 - 130 °C</td>
<td>50 - 80 °C</td>
</tr>
<tr>
<td>Procedure after dispersion</td>
<td>acetone distillation</td>
<td>amine extension</td>
<td>polycondensation</td>
<td>possibly acetone distillation</td>
</tr>
<tr>
<td>End product</td>
<td>polyurethane, urethane-urea copolymers</td>
<td>urethane-urea copolymers</td>
<td>polyurethane-biuret</td>
<td>urethane-urea copolymers</td>
</tr>
<tr>
<td>Solvent contents in the final product</td>
<td>&lt; 0.5 %</td>
<td>often 5 - 10 %</td>
<td>none</td>
<td>Possibly &lt; 2 %</td>
</tr>
<tr>
<td>Particle size (nm)</td>
<td>30 - 100,000</td>
<td>100 - 500</td>
<td>30 - 10,000</td>
<td>30 - 1,000</td>
</tr>
<tr>
<td>Post curing temperature</td>
<td>none</td>
<td>none</td>
<td>50 - 100 °C</td>
<td>none</td>
</tr>
</tbody>
</table>

Table 3.2 A summary of the characteristic features of the urethane-urea copolymers dispersion processes
3.2.2 Preparation of polyurethane powders

Polyurethanes have been known for more than half a century. In the 50s & 60s, their main uses centred around crosslinked polyurethane foams and elastomers. Later the potential of thermoplastic polyurethanes was recognised. (3.34) Thermoplastic elastomers are readily processed by conventional thermoplastic processing techniques such as extrusion or injection moulding. However, the techniques to produce the moulding grades of polyurethane powders or granules are still quite costly and requires sophisticated methods.

The techniques of preparation of moulding or extrusion grades of thermoplastic polyurethanes can be generally divided into three principal different methods, as discussed below.

a) Grinding method

Most of the polyurethane powders currently available in the market are prepared by this method. Thermoplastic polyurethane elastomers are first synthesised by conventional bulk polymerisation. The resulting solid polyurethanes are then ground in an inert atmosphere (i.e. free of oxygen) and often cryogenically to the suitable powder size. Normally, the softer the ground product required, the lower the temperature that must be used during the grinding step. Low grinding temperatures can be achieved in brine, dry ice or liquid nitrogen, which lead to very high costs and time consumption to produce the polyurethane powders. Further more, since polyurethanes are shear and heat sensitive, the grinding process can severely degrade the polymer leading to loss of mechanical properties in the final product. This method can also be very dangerous because there is a high potential for dust explosion.

b) In-situ method

The polyurethane powders can be prepared by a conventional solution polymerisation but using selected solvents such as hydrocarbons which permit dissolution of the monomers but not the polymers. The resulting solid polyurethanes are then filtered off from the solvent, washed and dried to obtain the powder form. (3.35) This method is not economical due to the cost of solvent used and recovery and also the cost of safety systems in the working environment. This
method is also restricted to those raw materials which do not have side reactions with the solvents and to a very narrow range of suitable solvents.

c) Aqueous dispersion method

The most attractive preparation procedure for polyurethane powders would be an aqueous dispersion polymerisation process and great efforts have been made in recent years to achieve this objective. Only recently, the development of suitable isocyanates, emulsifiers and fast reaction amine chain extenders has made this possible. It is now possible to prepare polyurethane dispersions with very small amounts of internal emulsifier content at sufficiently high molecular weight (i.e. such as higher than 5,000). The polyurethane dispersions are precipitated but can be redispersed back to a dispersion with the aid of a solvent/water mixture. The resulting sedimented polyurethanes can be dried to yield polyurethane powders.

Information about techniques for preparation of polyurethane powder directly from dispersions are very sparse in the open literature. However, the currently available techniques are described here.

The preparation of an isocyanate prepolymer containing an ionic emulsifier group is carried out by first reacting an excess molar amount of diisocyanate with a hydroxyl compound and chain lengthening agent which contains an ionic emulsifier group. The isocyanate tipped prepolymer is then dissolved in acetone to form a solution before dispersing in water. This ionic modified isocyanate tipped prepolymer dispersion is then mixed with an aliphatic diamine chain extender in aqueous medium. The quantity of water required for the dispersion step, which often dissolves the diamine, amounts to between 1 to 2 times by weight of ionic modified isocyanate tipped prepolymer. One particular advantage of this technique is that there is no need to use high speed stirrers. The acetone is then distilled off and urethane-urea copolymers are obtained in the form of an aqueous sedimenting dispersion. The polyurethane end product can be obtained in pure form by straight forward filtration and can also be redispersed back to dispersion in water at any time by the aid of solvent/water mixture. (3.36)

Coarse, aqueous sedimenting, aqueous polyurethane dispersions can also be prepared from a mixture of part A, a polyurethane, polyurea or urethane-urea copolymer having a molecular weight greater than 5,000 which is free of ionic
emulsifier, and part B, a polyurethane, polyurea or urethane-urea copolymer containing ionic emulsifier forming groups. The required ionic emulsifier content is from 0.0007 up to 0.011 equivalent per 100 grams of solid materials. A mixture of both parts in a suitable solvent is then dispersed in water. The sedimenting polyurethanes can be obtained by filtration. (3.37)

3.3 Water dispersed polyurethane latex properties

Water dispersed polyurethanes are typically dispersions of polyurethane particles which have a diameter from 10 to 1,000 nm in a continuous water phase, with the aid of either internal or external emulsifiers. Emulsifier types are the main influencing factors on the stability and physical properties of a dispersion.

Water compatible polyurethanes can be made by creating quaternary ammonium salts by the reaction of pendent carboxylic groups on the polyurethane macromolecule with a water soluble cation (mainly amine) under aqueous conditions. These quaternary salts supply a multiplicity of hydrophilic sites on the polymer itself to make the urethane water compatible. The desired urethane polymer would therefore need to have pendent hydrophilic quaternary groups as in the structure below.

![Figure 3.10 Schematic diagram of surface structure of water dispersed polyurethanes](image)

Carboxylic group

Creating the quaternary ammonium salts which render the PU-water compatible
Studies by Lorenz (3.38) showed that in water dispersed polyurethanes, the ionic centres are located predominantly on the surface of the dispersed particles, while the hydrophobic chain segments form the interior of the particle.

The explanation of polymer particle stabilisation is based on the well-known theory of the diffuse electrical double layer. (3.39) At the interface between an ionomer particle and water, a double layer is formed by dissociation of salt groups. The ionic constituents of the salt group, which are chemically bound to the polyurethanes, remain fixed to the particle surface, while their counterions migrate into the water phase as far as they are allowed by the attractive forces of the opposite charged particle surface. This forms a layer of decreasing electrical charge. 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.

Evidence for this stabilisation mechanism is that polyurethane dispersions coagulate upon the 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.

Non-ionic emulsified polyurethane dispersions do not behave in quite the same manner. This can be explained by the theory of "Entropic repulsion" (3.40). Entropic repulsion results from the fact that as particles approach each other, the freedom of motion of the non-ionic emulsifier (i.e. polyoxyethylene) chain in the water phase is restricted due to a reduction of entropy. Additionally, the hydration of the polyoxyethylene chains plays an important role. A particle approaching close enough for coagulation would require the desorption of water molecules resulting in considerable short range repulsion. Because of their fundamentally different stabilisation mechanisms, non-ionic and ionic water dispersible polyurethanes show differences in their macroscopic behaviour, as shown on Table 3.3

Non-ionic water dispersible polyurethanes have many advantages over the ionic types, in terms of stability to electrolytes, freezing and strong shearing forces. However, they are heat sensitive due to the decrease of polyether solubility in water with increasing temperature.
Table 3.3 Factors affecting stability of ionic and non-ionic polyurethane dispersions

<table>
<thead>
<tr>
<th>Response to</th>
<th>Ionic</th>
<th>Non-ionic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of electrolytes (acids, bases, salts)</td>
<td>unstable</td>
<td>stable</td>
</tr>
<tr>
<td>Freezing</td>
<td>unstable</td>
<td>stable</td>
</tr>
<tr>
<td>Strong shear (stirring, pumping)</td>
<td>partly stable</td>
<td>stable</td>
</tr>
<tr>
<td>High temperature</td>
<td>stable</td>
<td>unstable</td>
</tr>
</tbody>
</table>

The non-ionic polyurethane dispersions have excellent mechanical stability in the 15 to 45 °C temperature range. The mechanical stability of a dispersion, (i.e. to shear) will decrease at lower or higher temperatures, as the non-ionic emulsifier loses its solubility. The anionic polyurethane dispersions have excellent mechanical stability in the 5 to 45 °C range and are freeze-thaw stable. Both types of the dispersions have long shelf life stability characteristics. Some settling or creaming might be found with storage, but only moderate mixing is required to re-homogenise. (3.41)

Further research has been done to overcome all the problems by combining ionic and non-ionic hydrophilic groups into the same polyurethane backbone. This improves the stability and properties of the dispersion e.g. good heat stability, insensitivity to the addition of electrolytic additives and higher dispersion stability. It also increases water resistance and minimises overall hydrophilicity approaching properties comparable to solvent based polyurethanes. (3.42-3.45)

One of the biggest advantages of water dispersible polyurethanes is that the viscosity of a dispersion is independent of the molecular weight of the polymer. For this reason, polyurethane dispersions can be prepared at a high solid contents with a molecular weight high enough to form strong coherent films only by evaporation of water even at room temperature.

Typically, in both ionic and non-ionic polyurethane dispersions, the particle size decreases as the amount of hydrophilicity of the polyurethane increases. This leads to more stable dispersions. However, it also increases the number of dispersed particles and causes higher dispersion viscosity. (3.46)
Kirn, C.K. et al. (3.47) studied polyurethane dispersions based on isophorone diisocyanate (IPDI)/polytetramethylene adipate/triethylene tetramine. They found that the particle size decreased linearly with the concentration of carboxylic ionic emulsifier (i.e. here, α,α'-dimethylol propionic acid, DMPA) content, whereas the polydispersity of the polyurethane dispersion decreases rapidly at low DMPA content but more slowly at high DMPA content. DMPA provided an anionic centre to the polyurethane chain which gave rise to hydrophilicity in the polyurethane structure. This reduced particle size, with improved stability in the proportion to the amount incorporated into the urethane chain. However, with reduced particle size, the average number of urethane particles increased. This cause an increase in viscosity of the polyurethane dispersion for constant concentration of polyurethanes. (3.26)

Kirn, B.K. et al. (3.48) studied a polyurethane dispersion based on hydrogenated diphenylmethylene diisocyanate (H₁₂MDI)/polytetramethylene adipate glycol and polypropylene glycol/triethylene tetramine with both anionic emulsifiers (α,α'-dimethylol propionic acid) and non-ionic emulsifier (monofunctional ethylene-propylene oxide ether) in the polyurethane dispersion. They found that PPG content directly affected the particle size. Particle size of the dispersion increased slowly at low PPG content but rapidly at high PPG contents. Increasing particle size at high PPG content was most likely due to the temperature sensitivity of polyether polyol. PPG lost its hydrophilicity as the temperature increased above 65 °C.(3.49) Excess amounts of PPG over the solubility limit reduced the total hydrophilicity of the polyurethanes, leading to an increase in particle size. The particle size was found to decrease as the molecular weight of PPG increased.

Dieterich, D. et al. (3.49) found that the particle size distributions of polyurethane dispersions were generally narrow with a high content of ionic groups, (i.e. more than 70 milliequivalent/100 grams of polymer) and much broader in polyurethane dispersions obtained using a lower content of ionic groups, (i.e. even as low as 5 milliequivalent/100 grams of polymer). Polyurethane dispersions containing 2 to 5 milliequivalent of ionic groups/100 grams of polymer exhibited only slight swelling and give particle sizes around 1 μm. Dispersions of this nature can thus be prepared with a solid content of 45 to 60% which have low viscosity even when their molecular weights are very high.
3.4 Water dispersed polyurethane film properties

Properties of water dispersed polyurethanes are often determined using the film formation characteristics of the dispersed particles. These particles must fuse on the substrate surface at ambient or slightly elevated drying temperatures.

The overall film properties are related to the choice of starting materials. Increasing crosslink density will increase solvent resistance. Increasing urethane or urea content, thus increasing hard segment content, will increase hardness, abrasion resistance, polar solvent resistance. Adhesion and elasticity are obtained at higher content or higher molecular weight of polyol, although hydrolytic stability may be relatively poor with high polyester polyol content (cf. polyether).

The disadvantages of water dispersible polyurethanes include poor water swelling resistance and poor hydrolytic stability, because of the presence of emulsifiers. Better solvent resistance could be obtained by higher crosslink density, but two factors limit many improvements in this area. Firstly, highly branched prepolymer have too high a viscosity for them to be dispersed in water at normal processing temperatures. Secondly, highly crosslinked polymers have high glass transition temperatures and, therefore, will not coalesce to form continuous films at normal drying temperatures. Poor water resistance can be greatly improved by eliminating the emulsifier but the polyurethanes will then not form aqueous dispersions. However, it is possible to minimise these disadvantages by carefully balancing the amount and types of hydrophilic groups and the degree of crosslinking.

A large number of studies into water dispersed polyurethanes have been made enabling improved solvent and water resistance properties of polyurethane films, for instance by grafting a portion of the typical polyurethane with other polymers, or by making external crosslinking in the polyurethane structure. These techniques will be discussed below.

Grafting a hydrophobic unsaturated monomer on to the polyurethane backbone is one way to improve the water resistance properties. It is usually accomplished in the aqueous phase using emulsion polymerisation techniques. Monomer and free radical initiators are added to the urethane-urea copolymers which contain unsaturated polyester polyols or polyether polyol. Often, a higher amount of free
radical initiator will be used than in a normal emulsion polymerisation. (3.50) A
typical example of grafting of ester-urethane copolymers is shown in Figure 3.11

![Figure 3.11 Typical example of grafting of ester-urethane copolymers](image)

Anionic and cationic urethane isocyanate tipped prepolymers have been capped
with an unsaturated alcohol and then crosslinked through the use of free radical
initiators and addition copolymerised with unsaturated monomers. (3.50) This
grafting of polymer on to polyurethane dispersion is usually done by the resin
manufacturers.

Another technique to improve the water resistance is the external crosslinking
method. It is usually done by the formulator prior to the application of the water
dispersible polyurethane. Most reactions centre on the carboxylic acids contained
in anionic polyurethanes. Trifunctional aziridines, (as shown on Figure 3.12) have
been used quite extensively for the external crosslinking proposes. (3.51) An
aziridine must be added immediately before the application because it can lose
reactivity after two days storage in water at room temperature and crosslinking
also takes place at room temperature. The schematic crosslinking of polyurethane
dispersion with aziridines is shown in Figure 3.13
Room temperature crosslinking can also be accomplished by using water based polycarbodiimide crosslinkers. This can be done by the reaction of carboxylic acid which is attached to the polyurethane main chain with carbodiimides, as shown in Figure 3.14.

Polyurethanes can also be crosslinked upon heating. Methoxymethylolated melamine/formaldehyde (MMMF) or urea/formaldehyde resin are useful crosslinking agents for cationic polyurethanes. Anionic polyurethanes have been crosslinked by heating with water dispersible blocked polyisocyanates or with mixtures of blocked isocyanates and MMMF. A typical example of melamine/formaldehyde crosslinking of a coating formed from a water dispersed polyurethane is shown in Figure 3.15.
Figure 3.14 Schematic reaction of carbodiimide crosslinking of water dispersed polyurethanes

```
2
\( \text{PU} \)  \( \text{COOH} \)  +  \( R(\text{N} = \text{O} = \text{N} - \text{R})_2 \)  \( \text{PU} \)  \( \text{PU} \)  \( \text{PU} \)
```

Figure 3.15 Schematic reaction of melamine/formaldehyde crosslinking of water dispersed polyurethanes

```
2 \( \text{NH-C-NH} \) + \( R-N \) \( \text{CH}_2\text{-OR'} \) \( \text{CH}_2\text{-OR'} \) \( - \text{R'}-\text{OH} \)  \( R-N \)  \( R-N \)  \( R-N \)  \( \text{CH}_2\text{-OR'} \)
```

```
2 \( \text{O-C-NH} \) + \( R-N \) \( \text{CH}_2\text{-OR'} \) \( \text{CH}_2\text{-OR'} \) \( - \text{R'}-\text{OH} \)  \( R-N \)  \( R-N \)  \( R-N \)  \( \text{CH}_2\text{-N-C-O} \)
```

\( \text{R-N} \)  \( \text{CH}_2\text{-OR'} \)
\( \text{N(\text{CH}_2\text{-OR'})}_2 \)
```
\( \text{N(\text{CH}_2\text{-OR'})}_2 \)
```
\( \text{Melamine/Formaldehyde resin} \)

52
3.5 Water dispersed polyurethane applications

The areas of use of aqueous polyurethane dispersions, in principle, are the same as for other types of polymer dispersions. They can designed to suit specific purposes.

The earliest application of water dispersed polyurethanes were in the coatings area and this is still one of the largest market areas for them. Coating can be made either by a direct coating process or by a transfer coating process. (3.57, 3.58)

In the transfer coating process, a topcoat can be applied onto grained or smooth siliconized paper, dried, coated with an adhesive layer and laminated onto the textile and release paper removed. A newer version of the transfer coating process uses thermoactive crosslinkable polyurethane dispersions. These materials can either be applied as adhesive coats (3.59) or as heat reactive topcoats. (3.60)

Textile, leather and cellulosic fibres were all originally sized with solvent based polyurethanes. The water dispersed polyurethanes can now be used to prevent explosive vapour build up at the high processing temperatures and to lower costs. Textile fibres can be sized with water dispersed polyurethanes to improve their properties. The treatment can provide fabrics with increased tensile strength and resistance to dry cleaning solvents (3.61, 3.62) and detergent solutions. (3.63)

Paper fibres are sized with water dispersed polyurethane to increase the strength of the paper and also to reduce the tendency of ink to run on the surface. (3.64, 3.65) High strength cardboard with resistance to fats and oils is produced by coating cardboard with emulsified blocked polyurethane prepolymer or with unsaturated ester containing polyurethane dispersion which will crosslink later to form a network structure to improve the oil resistance. (3.66)

Water dispersed polyurethanes have long been used as adhesives (3.67), especially for polymeric substrates. (3.68) They are often mixed with other polymers to lower their cost, such as polyvinyl acetate (3.69), phenolic resins (3.70), epoxies (3.71) and acrylics (3.72). Ionically modified polyurethane dispersions have good adhesion to natural and synthetic rubber surfaces (3.73) and can be used in the manufacture of footwear. (3.74) Dispersions of thermoplastic polyurethanes are successfully used to bond metal to many other polymers. (3.75) Typically, non-ionically stabilised
polyurethanes with excellent electrolyte stability or cationically modified polyurethanes are used. They provide excellent adhesion to glass surfaces as well as to the surface of most polymers which contain glass fibres leading to higher modulus and tensile strength. (3.76 - 3.79)

The extremely good film formation properties, good adhesion properties, compatibility with acrylic resins or wetting agents and high gloss, enable their use in paint applications. Pigment paste (3.80), pigments thickeners (3.81), textile dyes (3.82) have been made from anionic polyurethane dispersions. However, because water is present, special consideration should be given to the drying conditions, such as the use of forced hot air flow, or the combinations with infra-red lamps to increase operating speeds.

Another interesting area is in medical application. Water based polyurethane films have found use as clear wound dressings and medical drapes. These polyurethanes are non-toxic and pass subcutaneous cell testing showing no primary ocular irritation in rabbits. Water based polyurethanes also have excellent moisture vapour transmission properties and are soft and very flexible which are ideal for wound dressings. (3.1)
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3.65 German Patent 2,400,490., 1974

3.66 German Patent 3,063,047., 1983

3.67 German Patent 3,313,238., 1983

3.68 German Patent 2,960,711., 1981

3.73  German Patent 2,804,609., 1978
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3.77  German Patent 2,456,655., 1974
3.78  German Patent 2,456,656., 1974
3.79  German Patent 2,456,657., 1974
3.80  German Patent 2,730,514., 1978
3.81  U.S. Patent 4,514,552., 1985
3.82  U.S. Patent 4,373,043., 1983
3.83  German Patent 3,433,029., 1985
The study of structure-property relationships in polyurethanes has been the subject of many investigations. In general, thermoplastic polyurethanes are formed by joining dissimilar segments along the main polymer backbone, both soft segments (rubbery) and hard segments (glassy). The physical properties of these materials are determined not only by the chemical structure within the hard and soft segments but also by their two phase microstructure. The flexible soft segments influence the elastic nature of the polymer and its low temperature performance, while providing an important contribution towards modulus, hardness and tear strength. The rigid hard segment particularly, directly affects modulus, hardness, tear strength and the ability of the phase to remain associated at elevated temperatures. A number of additional structural features also influence the polymer properties. These are stiffness of chain units, side group and their length, ease of rotation of chain segments, crystallisation and interaction force between the polar entities like urethane, urea or ester.

4.1 Polyurethane morphology

Polyurethanes have the general structure \((-A-B-)_n\), where A (hard segment) is usually formed by extending a diisocyanate with a low molecular weight diol or diamine and B (soft segment) is formed from a polyester or polyether polyl. In the thermoplastic polyurethanes, phase separation of the hard segments into the microdomains has been observed even when the segment length is relatively short. The primary force for domain formation is the strong intermolecular interactions between the urethane units, which are capable of forming inter-urethane hydrogen bonds. Factors that control the degree of microphase separation include not only copolymer compositions, block lengths, crystallisibility of either segment, size of chain extender but also synthesis condition (e.g. rate of the reaction, reaction temperature, reaction type i.e. bulk or solution polymerisation). In general, interconnected or isolated hard segment domains may be present within a phase of soft segment materials due to incomplete phase separation.
The micro-heterogeneous nature of polyurethanes has been the subject of many investigations (4.10-4.17) and many models of phase aggregated polyurethane systems have been proposed (4.18-4.22).

From X-ray diffraction studies, Bonart et al. (4.18) proposed a model for the structure of segmented polyurethane elastomers under varying degrees of extension. Polyether and mixed polyester based urethane-urea copolymers were studied. The hard segments were found to form discrete highly ordered regions, (i.e. about 25 Å in width) separated by soft domains, (i.e. about 100-200 Å width). Polyether soft segments were found to stress crystallise at about 150 % elongation, whereas polyester soft segment showed only paracrystalline behaviour, (i.e. distortion of the crystalline lattice over a longer range in which each lattice point varies its position with respect to its neighbour rather than with respect to the ideal lattice). This may be due to the more irregular chemical structure of polyester soft segments used in that work. At all elongations the soft segments tended to orient in the direction of stretch. Hard segment behaviour was more complex and the orientation was followed as a function of strain. The hard segments became oriented perpendicular to the stretch direction at elongation values below 200%. Further stretching indicated that the hard segments were then orienting in the stretch direction, (see Figure 4.1) and caused hard segments to slip past each other, breaking up the original structure. As elongation continued, hard segments become progressively more oriented into the stretch direction, (see Figure 4.2). This model provides a possible explanation of the stress softening phenomenon and high hysteresis observed in polyurethane elastomers.

Estes et al. (4.12) proposed the domain structure in an unstrained segmented polyurethane, (see Figure 4.3, in which the shaded areas are the hard domains). Both phases are represented as being continuous and interpenetrating, showing a polymer molecule which crosses several domains. The model also presumes that phase separation is not complete and some urethane blocks are also dispersed in the rubbery matrix. In an unstrained state, the soft segments are randomly arranged so that the rubbery domains are isotropic. Urethane segments are aligned perpendicular to the long direction of the hard domains, thereby making the hard domains locally anisotropic. Overall the hard domains are randomly arranged so that the bulk sample appears mechanically and optically isotropic.
Figure 4.1 Schematic diagram of the structure of a polyether polyurethane elastomer stretched to 200% (4.19)

Figure 4.2 Schematic diagram of the structure of polyether polyurethanes stretched at 500% and placed in warm water at 80 °C (4.23)
Figure 4.3 Schematic representation of domain structure in a polyurethane

Chen et al. (4.24) used optical microscopy to follow the copolymerisation of a model polyurethane system (hydroxy-terminated polybutadiene/2,4 or 2,6 TDI/1,4 butanediol), and found that initial reactants incompatibility was the key factor in determining the final morphology of bulk sample. Based on these and previous findings (4.25), models have been proposed to describe the morphology during polymerisation of this particular polyurethane system for several hard segment compositions where both macro-phase separation of reactants and micro-phase separation of the copolymers can occur during polymerisation.

During phase separation in a segmented polyurethane, the Tg value of the soft segment phases has been shown to decrease logarithmically with time. (4.26) The kinetics of phase separation for the soft segment has been described by first order kinetics. (4.27) From the studies, it was suggested that the phase segregation mechanisms involved two elementary steps which can be characterised by two discrete relaxation times. The work also showed quantitatively that a polyether based polyurethane recovers its original domain structure faster than a polyester.

The role of hydrogen bonding in promoting the degree of crystallinity and domain formation in segmented polyurethane elastomers has received much attention. The use of IR spectroscopy has been very useful in detecting variations of hydrogen bonding with composition, temperature and deformation history. (4.11, 4.12) It is
generally recognised that extensive hydrogen bonding is present in most segmented polyurethanes, but to a higher extent in polyester based than in polyether based systems. Hydrogen bonding interactions between urethane or urea groups and polyol derived components also contributed to hard segment domain formation. Hydrogen bonding interactions between hard segment NH groups and soft segment oxygen (O) atom have been suggested.\(^{(4.28)}\) This was suggested as a reason for incomplete domain separation of hard segment dispersed in a soft segment matrix. It has also been postulated that some of these interactions may occur at the domain matrix interface. The polymer chain mobility and ability to organise extensively on to crystalline lattices are restricted due to hydrogen bonding, resulting in sub-ordered regions.

There is indirect evidence that NH bonding to the ester oxygen of the polyester soft segment is greater that hydrogen bonding to polyether.\(^{(4.10)}\) Extensive research on hydrogen bonding in TDI based polyurethanes, by use of quantitative IR analysis, has been reported by Paik Sung and Schnedier\(^{(4.29, 4.30)}\) Two series of polyurethanes, one of which is based on 2,4-TDI and the other on 2,6-TDI have been investigated. Due to the asymmetric structure of 2,4-TDI, only amorphous hard domain structures were formed from these systems. In the 2,6-TDI series the hard domain was found to be crystalline. The Tg of the polyether soft segment was found to exhibit a strong dependence on urethane concentration in the 2,4-TDI polymers, while it was independent of urethane concentration in the 2,6-TDI polymers. This was suggested to be due to extensive hard segment mixing with the soft segment phase in the 2,4-TDI polymers. Much less hard and soft segment mixing takes place in the 2,6-TDI polymers due to their more highly ordered domains. At room temperature, almost all the urethane NH groups in both series were reported to form hydrogen bonds. About 80% and 50% of urethane carbonyl groups were found to form hydrogen bonds in the 2,6-TDI and in the comparable 2,4-TDI polyurethanes respectively.

Crystallisation of either hard or soft segments in a polyurethane elastomer can lead to a development of macro-scale superstructure beyond the domain level. The morphology depends upon several factors, such as the nature and concentration of the crystallisable components, solvent and thermal history. Wilkes et al.\(^{(4.31 - 4.33)}\) reported that in materials incapable of hydrogen bonding as well as hydrogen bonded elastomers, it appears that the superstructure entities, (i.e. spherulites) contain preferentially oriented domains, (see Figure 4.4). The spherulitic structure of the soft segment is readily apparent at high soft segment content, whereas at
lower soft segment content spherulites are formed by aggregation of hard segment domains. Spherulites have also been observed in urethane-urea copolymers\(^{(4.34)}\), segmented caprolactone based polyurethanes\(^{(4.35)}\) and segmented ether/ester based thermoplastic elastomers\(^{(4.36-4.38)}\). The effect of different spherulitic structures on the mechanical properties of segmented ether and ester based polyurethanes has also been reported\(^{(4.39)}\).

**Figure 4.4** Possible models of spherulitic structure \(^{(4.40)}\)

### 4.2 Influence of polyol structure

Generally, phase mixing is greater in ester than in ether based polyurethanes because NH-ester carbonyl hydrogen bonds are stronger than the urethane NH-ether oxygen bonds\(^{(4.41)}\). Because of weaker interchain force ether based polyurethanes have inferior mechanical properties. However, they do give superior hydrolytic stability. Caprolactone polyesters are considered to be a good compromise as polyols, since they produce polymers with both excellent physical properties and good hydrolytic stability\(^{(4.42)}\). Table 4.1 shows the energies of interaction between groups commonly present in polymeric materials.

**Table 4.1** Cohesion energies of groups common in urethane elastomers

<table>
<thead>
<tr>
<th>Group</th>
<th>Structure</th>
<th>Energy of cohesion (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylene</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;-</td>
<td>2.85</td>
</tr>
<tr>
<td>ether</td>
<td>-O-</td>
<td>4.18</td>
</tr>
<tr>
<td>carbonyl</td>
<td>-CO-</td>
<td>11.10</td>
</tr>
<tr>
<td>ester</td>
<td>-CO-O-</td>
<td>12.10</td>
</tr>
<tr>
<td>phenylene</td>
<td>-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;-</td>
<td>16.30</td>
</tr>
<tr>
<td>amide</td>
<td>-CO-NH-</td>
<td>35.30</td>
</tr>
<tr>
<td>urethane</td>
<td>-O-CO-NH-</td>
<td>36.60</td>
</tr>
</tbody>
</table>
Low temperature behaviour of polyurethane elastomers is primarily determined by the Tg of the soft segment blocks. This is related not only by the nature of the soft segment block but also by the degree of phase separation between hard and soft segment blocks.\(^{(4.7)}\)

Seefried et al.\(^{(4.1)}\) studied the caprolactone based polyurethane elastomers, and they found that the Tg of the soft block shifted to a higher temperature as the molecular weight of polycaprolactone decreased. This indicated the restriction of mobility of the soft segment block as the phases become more compatible at the lower molecular weights. At higher molecular weights (i.e. more than 2000), the Tg shows little change, reflecting that the two phases have separated. The physical properties of these elastomers are also considerably influenced by the molecular weight of the soft segment. With increasing molecular weight of polyol (i.e. from 500 to 2000), elongation at break increases whilst hardness, tear strength and modulus decrease. Ultimate tensile strength is at a maximum between a molecular weight of 830 and 1250.

The undesirable tendency of some polyesters to crystallise and produce cold hardening in polyurethanes can be avoided by use of a co-diol such as 1,2-propylene glycol which possesses structural irregularity. However, the resultant properties are usually inferior. A compromise is therefore necessary between the level of physical properties required and the acceptability of cold hardening.\(^{(4.43)}\) Table 4.2 illustrates the effect of some polyester polyol blends upon urethane elastomer properties (here 1,5-naphthalene diisocyanate and 1,4-butane diol based elastomers).

Table 4.2 Effect of polyester blends on urethane elastomer properties.

<table>
<thead>
<tr>
<th>Polyester polyol</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Hardness (IRHD)</th>
<th>Cold hardening</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene adipate)</td>
<td>34</td>
<td>640</td>
<td>60</td>
<td>hardens</td>
</tr>
<tr>
<td>Poly(ethylene propylene adipate) 70:30</td>
<td>28</td>
<td>725</td>
<td>65</td>
<td>only when stretched</td>
</tr>
<tr>
<td>Poly(ethylene propylene adipate) 50:50</td>
<td>26.</td>
<td>750</td>
<td>69</td>
<td>does not harden</td>
</tr>
<tr>
<td>Poly(propylene adipate)</td>
<td>21</td>
<td>780</td>
<td>71</td>
<td>does not harden</td>
</tr>
</tbody>
</table>
The influence that different polyester backbones have upon the properties of polyurethane cast elastomer can be seen in Table 4.3. The data was obtained from MDI/1,4 butanediol based polyurethanes. Tensile strength and 300% modulus depend greatly on the presence of a side chain in the polyester polyol. Those which have methyl side groups gave elastomers with significantly lower tensile strength than the linear polyesters. This is thought to be due to the effect of the side chains, preventing crystallisation of the polyester segments upon extension.\(^{(4.44)}\)

Table 4.3 Effect of polyester side chains on the physical properties.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Permanent set (%)</th>
<th>300% modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene adipate)</td>
<td>47</td>
<td>590</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Poly(1,4 tetramethylene adipate)</td>
<td>41</td>
<td>510</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>Poly(1,5 tetramethylene adipate)</td>
<td>43</td>
<td>450</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Poly(1,3 butylene adipate)</td>
<td>22</td>
<td>520</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>Poly(ethylene succinate)</td>
<td>47</td>
<td>420</td>
<td>40</td>
<td>22</td>
</tr>
<tr>
<td>Poly(2,3 butylene succinate)</td>
<td>24</td>
<td>380</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>Poly(2,2 dimethyl 1,3 trimethylene succinate)</td>
<td>18</td>
<td>400</td>
<td>10</td>
<td>14</td>
</tr>
</tbody>
</table>

Kim et al.\(^{(4.45)}\) studied an aqueous polyurethane dispersion preparing by the solvent process based on hydrogenated diphenylmethane diisocyanate (H\(_{12}\)MDI)/polytetramethylene adipate polyol/polypropylene glycol/dimethylol propionic acid on the effect of polypropylene glycol (PPG, molecular weight 400) content on the tensile properties. He found that the initial modulus and tensile strength increased slowly at low, but rapidly at high PPG content. This should come from the competitive effects of increasing the number of urethane linkages and decreased interchain interactions. He also studied further on the effect of molecular weight of PPG and found as the molecular weight of polyol increases, polyurethane chains lose their rigidity and strength, not only by their fractional increase in weight but also from the reduced number of urethane linkages, which with isocyanate segments form hard segment domains.\(^{(4.46)}\) Therefore, decreases in modulus, tensile strength and increases in ductility are to be expected.

Schneider et al.\(^{(4.47)}\) working on transition behaviour and phase segregation in toluene diisocyanate based polyurethanes found that in the 2,4-TDI polyurethanes extensive phase mixing occurs, (also indicated directly by infra-red spectroscopy), whereas in the 2,6-TDI samples hard segment crystallisation provided a strong driving force for phase segregation. The net effect of the phase mixing is to raise
the Tg of the soft segment. Thus where the low temperature properties of polyurethanes are important, the choice of polyether rather than polyester polyol and the use of 2000 rather than 1000 molecular weight soft segment is preferred, since the hydrogen bonding of an ester is stronger than that of an ether.

Seymour and Cooper\(^{(4.11, 4.28)}\) using DSC studied the effect of annealing temperatures (up to 200 °C) and time on the thermal response of polyester and polyether polyol based polyurethanes. Transition behaviour is strongly dependent upon thermal history as shown in Figure 4.5. Three characteristic endothermic transitions were observed. First, an endotherm (I) centred at approximately 70 °C which was attributed to the disruption of domains with limited short range order. Second, a transition (II) of 120 to 190 °C which represented the dissociation of domains containing long range order; and third, a transition (III) above 200 °C which was attributed to the melting of crystallites of the hard segments. It was also demonstrated that short range ordering could be continuously improved by annealing as evidenced by consistent upward temperature shift of endotherm I until its merger with endotherm II. Greater shifts were found with higher annealing temperature. Endotherm II could be shifted onto the region of endotherm III by prolonged annealing if the hard block was of a sufficient length to produce microcrystalline domains.

![Figure 4.5 Thermal treatment affects on DSC curve. (a) Control, (b) 80 °C, (c) 130 °C, (d) 150 °C, (e) 150 °C, prolonged treatment.](image-url)
Paik Sung et al.\textsuperscript{(4.49)} studied polyether and polyester based urethane-urea copolymers systems based on TDI/ethylene diamine/polytetramethylene oxide or polybutylene adipate, to determine the effect of having urea linkages in the hard segment on the phase segregation and domain structure. The most pronounced effect is reflected in the high Tg of the hard segment domain (i.e. 170 to 190°C), in both types of urethane-urea copolymers. The presence of the amorphous domains is observed not only in high urea content compositions but also in low urea content compositions. The extent of phase segregation, as judged by the extent of solubilised hard segment in the soft segment phase, is also improved greatly in urethane-urea copolymer systems as compared with polyurethanes. Thus, in general, lower Tg of rubbery soft segment phases is observed in urethane-urea copolymer systems. Increasing the molecular weight of the soft segment improves phase segregation. They also found that the thermal transition behaviour is rather insensitive to the total urea content, both in the Tg of the soft segment phase and in the Tg of the hard segment domain, while a strong dependence was usually observed in polyurethanes.

Van Bogart et al.\textsuperscript{(4.50)} reported that the Tg increases for a low molecular weight soft segment as the hard segment content increases. This is believed to be due to more mixing between the hard segment domains and the soft segment matrix, which results in a less flexible soft segment matrix. Furthermore, they concluded that the Tg of higher molecular weight soft segment material is rather insensitive to change in hard segment content. They also studied further on the structure-property relationships of polycaprolactone based polyurethanes.\textsuperscript{(4.51)} The starting materials were varied in hard segment types i.e. MDI/1,4-butanediol or H\textsubscript{12}MDI /1,4- butanediol, soft segment molecular weight, (here 830 or 2000 ), hard segment content (i.e. 23 to 77 % ), and thermal history. They found that low molecular weight, soft segments (i.e. Mw. 830 ), exhibited thermal and mechanical behaviour which indicated a considerable degree of hard segment and soft segment compatibility, (see Figure 4.6). Only a single relaxation was observed, which shifted to a higher temperature as the total hard segment content of the materials increased. For a polycaprolactone Mw. 830 based series, the materials exhibited aspects of both compatible and incompatible systems, as can be seen in figure 4.7. At a low hard segment content, the samples all showed a single relaxation, i.e. samples C and D was shifted to a higher temperature as the hard segment content increased. However, at higher hard segment content, (e.g. sample A and B the polycaprolactone Mw. 830 based materials) both a $\beta_5$ and $\beta_H$ relaxation were exhibited, which are characteristic of an incompatible system. Materials containing
2000 molecular weight soft segment showed a better defined microphase separation, with only a minor degree of hard and soft segment mixing at the interface between phases; see Figure 4.8 and 4.9. This indicated that the properties of one phase are generally independent of the morphology and volume fraction of the other phase.

Figure 4.6 DMTA curve for polycaprolactone/MDI/1,4-butanediol, Mw. 830 series (4.51)

Figure 4.7 DMTA curve for polycaprolactone/H12MDI/1,4-butanediol, Mw. 830 series (4.51)
Figure 4.8 DMTA curve for polycaprolactone/MDI/1,4-butanediol, Mw. 2000 series (4.51)

Figure 4.9 DMTA curve for polycaprolactone/H₁₂MDI/1,4-butanediol, Mw. 2000 series (4.51)
4.3 Influence of the isocyanate structure

The structure of an isocyanate also has a critical influence on the properties of polyurethanes. Bulky aromatic diisocyanates with a symmetrical molecular structure have been shown to give elastomers of higher modulus and hardness than aliphatic isocyanate based polyurethanes. These general relationships are illustrated in Table 4.4.(4.52)

The bulky 1,5-NDI gives a polymer of higher modulus and hardness than the single aromatic ring PPDI, or the more flexible MDI. Asymmetrical molecular structure as represented by the 2,4-and 2,6-TDI, give elastomers of low modulus and hardness. Tensile strength and tear strength are also shown to be higher in the case of a symmetrical molecular structure, particularly those based on the 1,4 substituted benzene ring system (PPDI and MDI).

Paik Sung et al.(4.53) showed that when TDI terminated polytetramethylene glycol prepolymer are extended with 1,4-butanediol, the asymmetrical 2,4-TDI based polymers display amorphous hard segment domains, while the symmetrical 2,6-TDI based hard segments contain crystalline regions. Furthermore the 2,4-TDI based polyurethane exhibit phase mixing between hard and soft segments, whereas this was not observed in the analogous system containing the symmetrical 2,6-TDI.

Aitken & Jeffs(4.54) showed that aliphatic isocyanates give rise to phase separation behaviour in comparison to the aromatic isocyanate. They also found that Tg's of systems based upon HDI, H12MDI and IPDI were lower than those for comparative TDI or MDI based systems. This was attributed to stronger hydrogen bonding obtained in the hard segment domains.
Table 4.4 Effect of diisocyanate structure on physical properties of polyurethane elastomers

<table>
<thead>
<tr>
<th>Diisocyanate</th>
<th>Structure</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tear strength (kN/m)</th>
<th>300 % modulus (MPa)</th>
<th>Hardness (Shore A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-phenylene diisocyanate (PPDI)</td>
<td><img src="image" alt="Structure" /></td>
<td>44.1</td>
<td>600</td>
<td>32.5</td>
<td>15.8</td>
<td>72</td>
</tr>
<tr>
<td>1,5-Naphthalene diisocyanate (NDI)</td>
<td><img src="image" alt="Structure" /></td>
<td>29.4</td>
<td>500</td>
<td>35.3</td>
<td>20.6</td>
<td>80</td>
</tr>
<tr>
<td>Mixed isomer of toluene diisocyanate (2,4- and 2,6-TDI)</td>
<td><img src="image" alt="Structure" /></td>
<td>31.4</td>
<td>600</td>
<td>26.5</td>
<td>2.5</td>
<td>40</td>
</tr>
<tr>
<td>4,4-diphenyl methane diisocyanate (MDI)</td>
<td><img src="image" alt="Structure" /></td>
<td>54.4</td>
<td>600</td>
<td>47.1</td>
<td>11.0</td>
<td>61</td>
</tr>
</tbody>
</table>
Beumel et al. found that the use of isomers of tetramethylene xylene diisocyanate (TMXDI) has a significant effect on the dynamic mechanical properties of polyurethanes. Polyurethanes containing para-TMXDI have a higher Young's modulus and a lower tan δ than corresponding polyurethanes based on meta-TMXDI. The symmetrical para isomer is expected to form urethanes with a more ordered hard segment than meta based urethanes. These more ordered hard segment phases provide improved mechanical reinforcement and resulting in higher modulus. In addition, the para based urethanes are also expected to undergo a more complete phase separation between the hard and soft segment. As a result, the meta based urethanes will have a large number of hard segments which remain mixed in the soft segment phases of the urethane. These mixed-in hard segments increase the Tg of the soft segment and broaden the temperature and frequency range over which it occurs. This broadening of the Tg would explain the higher tan δ values in the meta based urethanes. The differences in phase separation can therefore explain the lower tan δ values which are found in the para based urethanes.

In comparison with TDI based polyurethanes, MDI based polyurethanes possess a more perfect domain organisation, including crystallinity, due to short range order, and consequently show a higher extent of segregation between hard segments and soft segments. On the other hand the TDI based polyurethanes showed a shift in the Tg to the higher temperatures, suggesting that the structure, concentration and organisation of the hard segment are a dominant factor with regard to the extent of domain segregation.

In subsequent temperature dependent IR work, Sung and Schneider used simple curve resolution procedures to determine the amounts of hydrogen bonded and non-bonded NH and carbonyl in the same series of polyurethanes. In the 2,4-TDI polyurethanes free and bonded carbonyl absorption showed little change from 0 to 150 °C while 50 % of the NH groups had dissociated by 150 °C. It was concluded that NH to ether hydrogen bonding was responsible for most of the hydrogen bond dissociation in the NH spectra. In the 2,6-TDI polymers, this hard and soft segment hydrogen bonding was also found to dissociate below 150 °C as indicated by changes in the NH absorption. However, above 60 °C the bonded carbonyl absorption is reduced while the free carbonyl increases, indicating dissociation of hydrogen bonding in the hard segments. Apparently, NH bonding to the ether oxygen is weaker than that of the urethane carbonyl, because the hard segment and soft segment bonding dissociates at lower temperatures.
disruption of hard-soft segment hydrogen bonding in 2,6-TDI polyurethanes, which occurred prior to hard segment and soft segment dissociation, suggested that hydrogen bond disruption in the soft segment phase does not require a hard segment transition process. The higher stability of inter-urethane hydrogen bonds in the 2,4-TDI than in the 2,6-TDI polyurethanes was suggested as being due to the high steric hindrance caused by the methyl group in the 2,6-TDI polymers.

Tanaka et al.(4.57) estimated that 85% of the NH groups were hydrogen bonded in a solid polyurethane based on TDI (i.e. 80/20 mixture of 2,4 and 2,6 isomers). It can be assumed that almost all NH groups in different polyurethanes are hydrogen bonded. However, it appears that only a portion of the urethane carbonyls is involved in bonding as the proton acceptors.

4.4 Influence of chain extender

The choice of chain extender has a considerable effect on the polyurethane elastomeric properties. A symmetrical, rigid and bulky chain extender is desirable for improved mechanical properties while an asymmetric, flexible and less bulky chain extender would lower the mechanical properties due to the weakening of the interchain forces between the hard segments.

The use of an amine chain extender is known to give much better mechanical properties than a diol chain extender, because of their better phase separation behaviours.(4.41) Wright(4.58) and Robert(4.59) showed that urethane-urea copolymers with excellent physical properties could be prepared using an amine chain extender but giving the disadvantage of being distinctly coloured, typically having strong yellow to orange tints.

Paik Sung et al.(4.49, 4.53, 4.60) examining the properties of urethane-urea copolymer based on polytetramethylene glycol/2,4-TDI/ethylene diamine, found that a considerable improvement in the extent of microphase separation resulted from chains extended with ethylene diamine, compared to all polyurethane systems chain extended with 1,4-butanediol. This was indicated by the much lower glass transition of the soft segment phase and much higher glass transition of the hard segment domains in urethane-urea copolymer. The incorporation of urea linkages in the urethane hard segment has a profound effect on the phase separation and domain structure of urethane-urea copolymers. This is due to the high polarity...
difference between the hard and soft segments and the likely development of a three dimensional hydrogen bonding network.

Wilkes et al.\textsuperscript{(4.61)} examined the morphology of urethane-urea copolymers using small angle X-ray scattering and found a consistent interpretation of their data was possible by using mechanical and thermal tests. They suggested that the diamine chain extenders promoted better phase separation since the thickness of interface between the diamine in the urethane-urea copolymer was less than that of conventional butanediol chain extended polyurethanes.

Chen et al.\textsuperscript{(4.62)} found that the thermal cycling of polyureas from room temperature up to 200 °C did not alter either the position or shape of the soft segment Tg. This is in contrast to equivalent polyurethanes, whose behaviour is very sensitive to their thermal history. They also found that the thermal history has little effect on the tensile properties of these polyureas, (e.g. by annealing the samples at 170 °C for 3 hours, followed by quenching to room temperature), and thus could not detect any significant changes in their stress-strain behaviour. Diamine chain extenders are often used with non-symmetrical diisocyanates since the strong interaction force between the urea groups will compensate for the structure irregularities in the diisocyanate. Diols are often used successfully with 4,4'-MDI, NDI and other symmetrical diisocyanates to produce strong elastomers.

4.5 Influence of hard segment content

The quantity of the hard segment present in a polymer can also influence the mechanical properties of a polyurethane. Basically, increasing hard segment content can be effected by increasing the reaction ratio but the decreasing of molecular weight of the soft segment at the particular fixed reaction ratio will also have the same effect.

Zdrahala et al.\textsuperscript{(4.4)} found that by increasing the hard segment content from 20 to 80 % of a polyether based MDI elastomer, brought about an increase in hardness, modulus, tensile strength and tear strength while elongation at break decreased. With evidence from dynamic mechanical and specific heat (DSC) data, it was concluded at about 60 to 65 % hard segment, that phase inversion occurred. This change altered the nature of polyurethane from a tough elastic material to a brittle, high modulus plastic.
Seefried et al.\(^{(4.2)}\) have shown that decreasing the soft segment molecular weight has similar effects as increasing hard segment content. Working with a polycaprolactone/MDI/1,4-butanediol system, the series of polymers were synthesised for each of two polycaprolactone diols of molecular weight 830 and 2100. They found that increasing in hard segment content, (i.e. by increasing the reaction ratio), brought about increases in hardness, modulus and tear strength. Polyurethanes based on molecular weight 830 exhibited a progressive increase in T\(_g\) at higher levels of hard segments. While the polyurethane based on molecular weight 2100 polyol, maintained a relatively constant T\(_g\). These differences were attributed to the relative degree of phase separation between the constituent block of the polymer. At a soft segment molecular weight of 830, increasing the hard segment content leads to a large amount of phased mixed materials. Whereas for 2100 molecular weight soft segment materials, the degree of interaction between the phases appears to be less pronounced. Van Bogart et al.\(^{(4.51)}\) investigated on the similar polyurethanes system based on polycaprolactone/H\(_{12}\)MDI/1,4-butanediol. They found that increasing hard segment content at a constant soft segment molecular weight increased crystallinity, and resulted in increases in the following; hard segment crystalline melting point, tendency of materials to form a morphology with a hard segment matrix, isolated soft segment domains, and interfacial area.

Wright\(^{(4.58)}\) and Roberts\(^{(4.59)}\) have also investigated the effect of increasing hard segment content on a polycaprolactone/H\(_{12}\)MDI/1,4-butanediol system. Increasing the block molar ratio from 1/2/1 to 1/13/12 brought about an increase in hardness and tensile strength and a decrease in elongation at break. Those materials with low block ratio were flexible elastomers while those of high block ratio were tough, rigid plastics. The polymer based on a block ratio of 1/13/12 was very brittle and opaque, as a result of the hard segment crystallisation.

Chen and coworkers\(^{(4.62)}\) studied the influence of hard segment content on the mechanical, dynamic mechanical and thermal properties of polypropylene glycol/MDI/diethyl toluene diamine based polyureas. They found that the modulus of the rubbery plateau measured from dynamic mechanical spectra increased with hard segment concentration due to the reinforcing effect of the hard segment domain. However, continuous improvement in the dynamic mechanical modulus is not significant when the hard segment is above 50% because of the higher degree of phase mixing in high hard segment concentration systems.
Beumel et al. (4.55) found that the Young's modulus increased as the isocyanate content in the prepolymer was increased. In addition, the magnitude and frequency of the tan δ peak was reduced for samples containing higher isocyanate content in the prepolymer. Increasing the isocyanate content will increase the size and relative amount of hard segment block in the polyurethanes. Since the hard segment acts as a reinforcing region, the increasing in modulus can be explained to be analogous to the modulus increase which is observed when adding a filler to a rubber. (4.72) The decrease in the tan δ value with increasing isocyanate content is due to less soft segment in the polyurethane and the loss tangent directly reflects the glass transition of the soft segment. As the isocyanate content increases, there is less soft segment in the resultant urethane, causing a decrease in the tan δ.

The dynamic properties of polyurethane elastomers have revealed the effects of the composition and structure of the raw materials. Seefried et al. (4.1-4.3, 4.56) made observations concerning the effects of variation of segment length, diisocyanate structure and the effect of cycloaliphatic chain extender on the dynamic mechanical properties. They found that at a fixed molar concentration of hard segment, the Tg of a soft segment in a block copolymer decreased as the molecular weight of the soft segment increased. This variation was interpreted in terms of the relative increase in the flexibility of the amorphous soft segment structures. In contrast, increasing hard segment concentration affected the Tg of the urethane polymers in a manner which was dependent on the molecular weight of the respective caprolactone polyol soft segment. The polyurethanes based on an 830 molecular weight caprolactone polyol (f = 2) exhibited a progressive increase in glass transition temperature, at increased levels of hard segments. However, for a caprolactone polyol soft segment of 2100 molecular weight, the degree of interaction between the phases appears to be less pronounced and the Tg of polymer is relatively insensitive to hard segment concentration. This suggests that the extent of microphase separation between the hard and soft segments of these thermoplastic urethane elastomers is significantly influenced by the sequence length of the soft segments, and the domain organisation within the block copolymer structures.

Spathis, G. et al. (4.63) studied the dynamic mechanical properties of polyurethanes based on MDI/polyethylene adipate polyol/1,4-butanediol. They found two tan δ peaks. The first one appeared at temperatures around -20 °C to -5 °C. The intensity and location of this peak was strongly dependent on the chemical composition of the polyurethane. As the MDI content increased this transition
shifts to a higher temperature while the peak intensity became lower and broader. They suggested that the first tan δ peak, (i.e. α relaxation) was mainly determined by the mobility of the soft segment. By increasing the aromatic urethane content, (i.e. hard segment content), the motions are restricted, shifting the α relaxation to a higher temperature. In other words, the hard segment exerts pressure on the expanding soft segment at the Tg region, resulting in higher Tg at higher hard segment concentration. The second tan δ peak appears at -60 °C for all types of MDI content. The intensity and location of this peak are independent of the MDI content and of the hard segment concentration. This secondary tan δ peak, (i.e. β relaxation) may be attributed to the motion of NH or C=O groups to which water molecules are attached by hydrogen bonding.

Paik Sung and co-workers(4.64) investigated hydrogen bonding in two series of polyether polyol based urethane-urea copolymers based on 2,4-TDI/ethylene diamine/tetramethylene oxide. They concluded that three dimensional hydrogen bonding(4.20) may exist within their hard segment domains, where one urea carbonyl is hydrogen bonded to two NH groups. As suggested by these studies, this type of three dimensional hydrogen bond formation may provide the driving force for improving the phase segregation, even at low urea content. It is noted that this type of three dimensional hydrogen bonding has not been detected in polyurethanes extended with diol. The IR studies also indicated that the interface between the hard segment domain and the soft polyether matrix is quite sharp, since most of the urethane carbonyl is free from bonding.

In MDI based urethane-urea copolymers extended with ethylene diamine, studied by Ishihara et al.(4.65), a band at 1645 cm⁻¹ was assigned for a hydrogen bonded urea carbonyl and a band at 1695 cm⁻¹ for the free urea carbonyl. Infra-red studies on urethane-urea copolymers have been repeated subsequently by Paik Sung et al.(4.29) on toluene diisocyanate based urethane-urea copolymer. They also assigned both 1640 cm⁻¹ and a 1660 cm⁻¹ peaks for the hydrogen bonded urea carbonyl and a peak at 1695 cm⁻¹ for the free urea carbonyl.

4.6 Influence of hard segment sizes

The effect of varying hard segment size generally indicates an increase in physical and mechanical properties. This is associated with an increase in urethane concentration in an elastomer. The effects of hard segment size and molecular weight distribution were investigated(4.8, 4.66) using polytetramethylene glycol as
the soft segment and a piperazine/1,4-butanediol mixture as the hard segment. These systems provide no possible sites for hydrogen bonded interactions. Polymers having a narrow hard segment molecular weight distribution were found to have a higher modulus than polymers with a wide molecular weight distribution. Tensile strength and elongation at break were found to be highest for polymers having a narrow soft segment molecular distribution. Permanent set was found to increase as the molecular weight distributions of hard and soft segments were narrowed. By preparing blends of polymers with different sizes of hard segments, it was found that compatibility depended on the relative size of the hard segment combination. An explanation for the increase in modulus found for materials of higher hard segment content and narrower hard segments molecular weight distribution was given in terms of phase separation and domain formation.

Paik Sung et al.\(^{(4.53)}\) studied the IR spectra of two series of urethane urea copolymers based on 2,4-TDI, ethylene diamine with polytetramethylene glycol either with molecular weight 1000 or 2000. They found that better phase separation accompanied by better mechanical properties obtained by using the polytetramethylene glycol 2000 molecular weight polyol rather than 1000. They also found that the amount of hydrogen bonded urethane carbonyl decreased with increasing urea content.

The effect of hard segment length distribution on properties has been investigated by Fu and MacKnight.\(^{(4.67)}\) They found that the hard segment played an important role in phase segregation as the hard segment chain length increased, the phase segregation was nearly complete at six hard segment units and then this polymer exhibited significantly improvements in mechanical properties.

Miller and co-workers\(^{(4.68)}\) carried out a study of polyether polyol based polyurethanes with different hard segment length distribution. They reported that polyurethanes with fewer single hard segments units, (i.e. from MDI) exhibited a higher degree of phase separation. However, these fewer single hard segment length polyurethanes, possessed lower ultimate tensile strength, and it was believed to be due to the higher phase separated morphology, restricting the ability of soft segments to crystallise under strain because of increased hard segment crystallinity and domain interconnectivity.
4.7 Influence of carboxylic ionic emulsifiers

Dynamic mechanical response of polyurethane dispersion cast films based on \( H_{12}MDI/polytetramethylene adipate/polypropylene glycol/triethyl tetraamine \) with the incorporating of non-ionic emulsifier (monofunctional ethylene-propylene oxide ether) and carboxylic anionic emulsifier (dimethylol propionic acid, DMPA) was studied by Kim, B.K. et al.\(^{4.45}\) They found that storage modulus (\( E' \)) is directly related to load bearing capabilities\(^{4.69}\) and this increases with carboxylic ionic emulsifier content, a result consistent with the mechanical properties dependence on carboxylic ionic emulsifier content. It was found that the loss modulus (\( E'' \)) peak moves towards higher temperatures as the carboxylic ionic emulsifier content increases, indicative of an increased stiffness of the chain.

Further studies\(^{4.70, 4.71}\) confirmed that carboxylic ionic emulsifiers (DMPA) directly affect the mechanical properties of polyurethanes. A carboxylic ionic emulsifier (dimethylol propionic acid) has been used to provide anionic centres in polyurethane ionomers. With increased number of ionic centres, more coulombic force is obtained. Generally, carboxylic emulsifiers can be considered also as low molecular weight chain extenders. With increasing proportion of low molecular weight chain extender, less long chain polyol is incorporated into the polymer and more urethane linkages result. As the chain extender content increases, modulus and tensile strength increased, while elongation at break decreased linearly. The increase of tensile strength properties comes directly from the increased number of urethane linkage and interchain interactions of polyurethanes ionomers and from the reduced polyol soft segment content in the polyurethane structure. The resulting polyurethane becomes rigid and hard leading to a high tensile strength. With increased stiffness and strength, polyurethanes lose their ductility.
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Chapter 5 Preparation & Characterisation of Water Dispersed Polyurethanes

This chapter is mainly focused on the selection of suitable materials, a programme for synthesis, techniques for preparation without organic solvents and a selection of characterisation methods for studying the morphology and structure-property relationships of water dispersed urethane-urea copolymers, their dispersion cast films and injection moulding sheet from urethane-urea copolymers powders.

5.1 Selection of raw materials

The general criterion for the selection of materials for water dispersed urethane-urea copolymers was the reactivity of raw materials. The most important factor was that an isocyanate must have low reactivity with water but reasonable reactivity with polyol or amine chain extender. The polyols should provide good hydrolytic stability and good mechanical properties in the resulting solid urethane-urea copolymers. An anionic emulsifier was incorporated at the early stage of reaction, which was stable throughout the oligomerisation and polymerisation stages. The amine chain extender had to be miscible with water since the chain extension stage took place in water. The properties of each precursor material is discussed below.

5.1.1 The diisocyanate

The major requirement for preparing water dispersed urethane-urea copolymers is that the isocyanate must have sufficiently low reactivity with water during synthesis. Cycloaliphatic diisocyanates seemed to be the best choice because of their low reactivity with water and a bonus of good colour stability. An aliphatic diisocyanate tetramethyl xylene diisocyanate (TMXDI, equivalent weight 122), developed by American Cyanamid Company, was used in this programme. This isocyanate contains a benzene ring in its structure which has the potential to give mechanically stronger urethane-urea copolymers, than those based on aliphatic isocyanates. However, TMXDI has the typical properties of many aliphatic diisocyanates, although it consists of aromatic rings but with the isocyanate groups shielded from the ring by protective methyl groups. American Cyanamid offer two
isomeric forms of this, i.e. meta- and para- tetramethyl xylene diisocyanates (m- and p- TMXDI) as shown in Figure 5.1.

Figure 5.1 Structure of m- and p- tetramethyl xylene diisocyanate(5.1)

A summary of the principal properties of these two isomeric isocyanates is given in Appendix I. Many of the physical properties of the two isomeric TMXDI are similar, but an important difference is that the m-TMXDI is liquid at room temperature while the p-TMXDI melts at 72 °C. The p-TMXDI has been reported to give higher modulus polyurethane products(5.1). Meta-TMXDI was used, as received, throughout this research programme.

The reactivity of TMXDI is similar to that of other aliphatic diisocyanates in most respects. It reacts more slowly with hydroxyl and amino compounds than the aromatic isocyanates. This is illustrated in Figure 5.2 where the reactivity profiles of a number of aliphatic and aromatic diisocyanates with 2-ethylhexanol are given, (i.e. excess 2-ethylhexanol in toluene solution was employed at 25 °C with 0.15% dibutyltin dilaurate as catalyst).(5.1) Unfortunately, directly literature data for the reaction of TMXDI with water is currently unavailable, although the manufacturers(5.2) have stated that TMXDI has very low reactivity towards water. The indirect comparative data of TMXDI with active hydrogen compounds are shown below in Table 5.1a and 5.1b.
Figure 5.2 Reaction of some diisocyanates with 2-ethylhexanol (5.1)

Table 5.1a The comparison of isocyanates reacting with various active hydrogen materials (uncatalysed at 23 °C) (5.3).

<table>
<thead>
<tr>
<th>Diisocyanate</th>
<th>Reaction Rate Constant (x 10^{-4} \text{ 1/mole Sec.})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydroxyl</td>
</tr>
<tr>
<td>2,4-TDI</td>
<td>21.0</td>
</tr>
<tr>
<td>2,6-TDI</td>
<td>7.4</td>
</tr>
<tr>
<td>1,5-NDI</td>
<td>4.0</td>
</tr>
<tr>
<td>1,6-HMDI</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Table 5.1b The comparison of reactivity of some diisocyanates with excess of 2-ethylhexanol in toluene at 25 °C with 0.15 % dibutyltin dilaurate (5.1)

<table>
<thead>
<tr>
<th>Diisocyanate</th>
<th>Time for 50% NCO consumption (minutes)</th>
<th>Relative reaction rate to m-TMXDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDI</td>
<td>4.8</td>
<td>13.6</td>
</tr>
<tr>
<td>80/20 TDI</td>
<td>12.7</td>
<td>5.1</td>
</tr>
<tr>
<td>HIDI</td>
<td>25.4</td>
<td>2.6</td>
</tr>
<tr>
<td>HMDI</td>
<td>50.8</td>
<td>1.3</td>
</tr>
<tr>
<td>m-TMXDI</td>
<td>65.1</td>
<td>1</td>
</tr>
<tr>
<td>IPDI</td>
<td>95.2</td>
<td>0.7</td>
</tr>
<tr>
<td>p-TMXDI</td>
<td>123.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Comparison of isocyanate reactivities from Table 5.1a and 5.1b shows that aliphatic diisocyanates have slower reactivity rates than aromatic isocyanates. Therefore, TMXDI is a better choice of isocyanate for water dispersed urethane-urea copolymers system. Table 5.1b showed that m-TMXDI is around 5 times less reactive than 80/20 TDI and 2,4- and 2,6-TDI (which have around $6 \times 10^{-4}$ to $4 \times 10^{-4}$ l./mole-second reaction rate constant to water). Therefore, it is assumed that m-TMXDI have a very slow reaction rate to water. However, more definitive reaction rate data need to be obtained before firm conclusions can be drawn on the relative reaction rates.

A large number of isocyanate-hydroxyl reaction specific catalysts have been examined in order to increase the reactivity of the TMXDI isomers. Amine catalysts, such as triethylene diamine, have been found to be relatively ineffective, in comparison to metal salt compounds. Dimethyltin dilaurate, lead octoate and tetrabutyl diacetyl distannoxane have been found to be the most effective. (5.4)

5.1.2 Polyols

Many of the polyurethane text books (5.5 - 5.8) review the types and synthesis of polyols commercially available. Therefore, only the polyols used in this research programme will be described here briefly.

a) Polyester polyols

There are a wide variety of polyester polyols, (e.g. the cheapest being based on adipic acid/ethylene glycol). However, the polyester polyols used in this research programme were based on polycaprolactone polyol, trade name "Capa" supplied by Solvay-Interox Chemicals Ltd. Capa 210, Capa 220 and Capa 240 were used with equivalent weights (its molecular weight divided by the number of reactive groups available) of 500, 1000 and 2000 respectively, each with a functionality of 2. These polyols were selected at the start of the programme on the advice of the manufacturers, as ones offering the best hydrolytic stability and also providing good mechanical properties in the resulting polyurethanes.

Capas are normally white pasty solids at molecular weight 1000 and white waxy solids at molecular weight of 2000 and 4000. They are odourless and have a melting range between 30 and 60 °C with increasing molecular weight, melting to colourless, low viscosity liquids. They are miscible with many aromatic and
chlorinated hydrocarbons but not with water. The details of the Capa used are listed in Table 5.2.

b) Polyether polyols

There are a wide variety of polyether polyols, the polypropylene glycols (PPGs) being of the most commercial importance. However, the polyether polyols used in this research were based on polyoxytetramethylene glycol with the trade name "Terathane". Terathane 1000, Terathane 2000 and Terathane 2900 were used, having equivalent weights of 500, 1000 and 1450 respectively and each with a functionality of 2. These were supplied by Du Pont (UK). The Chemical Abstracts Service (CAS) covers them under two names, furan, tetrahydro, polymer or poly(oxy-1,4-butanediol)-α-hydro-α-hydroxy. The main reason for selecting the Terathanes as the representative polyether polyols was to produce better mechanical properties in the resulting polyurethanes, compared to other commercial polyether polyols.

Terathanes are waxy, white solids that melt to clear, low viscosity colourless liquids. They are readily soluble in alcohols, esters and ketones but insoluble in aliphatic hydrocarbons. They also dissolve in aromatic and chlorinated hydrocarbons but are only partially soluble in water. The solubility of Terathanes in a series of solvents, decreases with increasing length of the solvent's aliphatic chain, for example they are completely miscible with methanol but insoluble in dodecanol. All these glycols are hygroscopic. At room temperature Terathane can absorb up to 2% water. The details of the Terathanes polyether polyols used are listed in Table 5.2

5.1.3 Chain Extenders

The selection of chain extenders for water dispersed urethane-urea copolymers is very important, with respect to the structure of the urethane-urea copolymers. The comparative reaction rate of aromatic diisocyanates with active hydrogen compounds has the general trend as shown below:

Aliphatic NH₂ > aromatic NH₂ > primary OH > water > secondary OH > tertiary OH > carboxylic acid = urea > amide > urethane
As can be seen aliphatic amines react faster with isocyanate than water. In this research work, the chain extension stage is carried out in water medium, therefore the reactivity of the selected chain extender with isocyanate to form urethane-urea copolymers must be as fast as possible. This will eliminate or minimise the water-with-isocyanate side reaction, which will generate undesired products. Many low molecular weight aliphatic and cycloaliphatic diamines are used as chain extenders in commercial water dispersed urethane-urea copolymers. However, the chain extenders used in this research programme were linear aliphatic diamines selected for their faster reactivity compare to diols. \(^{(5,11)}\) They vary by the number of the methylene groups in the main chain and also had a methyl side group. Details of the chain extenders used are listed in the Table 5.3. They were used as received from their manufacturers.

5.1.4 Other additives

A number of other special additives were used, these included:

a) Carboxylic acid ionic emulsifier agent

Ionic emulsifying agents are critical components in the preparation of stable water dispersed urethane-urea copolymers systems. The choice of emulsifier is limited to a few commercial materials and typically a dihydroxy alkanoic acid is used. It provides water dispersing pendent carboxylic acid salt groups, incorporated onto the polyurethane chain backbone. In this research, 2,2 dimethylol propionic acid or (2,2 bis(hydroxymethyl)propionic acid), (DMPA) was used, since it is available on a commercial scale. It has the equivalent weight of 67. The structure is \(\text{CH}_3\text{C(CH}_3\text{OH)}_2\text{COOH}\) and supplied by Aldrich Chemical.

DMPA is an off-white crystalline solid with a melting range from 192 to 194°C. It is soluble in water and methanol, slightly soluble in acetone but insoluble in benzene. The DMPA was dried in a silica gel desiccator for at least 24 hours before use.

b) Emulsion stabilising agent

For successful stabilisation of latex particles during polymerisation, an anionic emulsifier centre must be produced on the surface of the particle to give stabilisation. Amine neutralised carboxylic ions on a particle surface give
satisfactory latex stabilisation. A low boiling point inert amine was preferred for water dispersed urethane-urea copolymers. Triethyl amine, (TEA) was used in this research programme. It has a structure of \((C_2H_5)_3N\) with molecular weight equal to 101. It was supplied by Fisons Plc.

TEA is colourless liquid with a strong ammonical odour, soluble in water and alcohol. It has a boiling point of 90 °C, flash point -7 °C (open cup). TEA was used as received.

C) Catalyst

Dibutyltin dilaurate, (DBTDL) was used to accelerate the isocyanate-hydroxyl reaction. Its structure formula is \((C_4H_9)_2Sn(OOCOC_{10}H_{20}CH_2)_2\). It is a clear pale yellow liquid, soluble in acetone and benzene but not in water. Its freezing point is 8 °C and flash point is 226 °C (open cup). The DBTDL was supplied by Fisons Plc. and used as received.
<table>
<thead>
<tr>
<th>Polyol type</th>
<th>Polyester</th>
<th>Polyether</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol name</td>
<td>Polycaprolactone polyol</td>
<td>Polyether glycol</td>
</tr>
<tr>
<td>Trade name</td>
<td>Capa 210</td>
<td>Capa 220</td>
</tr>
<tr>
<td>Reference</td>
<td>C1</td>
<td>C2</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td>Hydroxy number, mgKOH/g</td>
<td>112</td>
<td>56</td>
</tr>
<tr>
<td>Structure</td>
<td>Linear</td>
<td>Linear</td>
</tr>
<tr>
<td>Physical form</td>
<td>White paste</td>
<td>White waxy solid</td>
</tr>
<tr>
<td>Functionality</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Viscosity @ 60 °C (mPa.s)</td>
<td>170</td>
<td>525</td>
</tr>
<tr>
<td>@ 40 °C (mPa.s)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Density @20 °C (g/ml)</td>
<td>1.05</td>
<td>1.07</td>
</tr>
<tr>
<td>@40 °C (g/ml)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Melting range ( °C)</td>
<td>30 to 40</td>
<td>40 to 50</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>&lt; 0.02</td>
<td>&lt; 0.02</td>
</tr>
</tbody>
</table>

* The abbreviation for this research work

N/A = not available

Table 5.2 Polyols used in this research programme
<table>
<thead>
<tr>
<th>Chain extender</th>
<th>Ethylene diamine</th>
<th>Tetracethylene diamine</th>
<th>Hexamethylene diamine</th>
<th>2-methylpentamethylene diamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other name</td>
<td>1,2-diaminoethane</td>
<td>1,4-diaminobutane</td>
<td>1,6-diaminohexane</td>
<td>1,5-pentanediame, 2-methyl</td>
</tr>
<tr>
<td>Reference</td>
<td>EDA</td>
<td>TMDA</td>
<td>HMDA</td>
<td>MPMDA</td>
</tr>
<tr>
<td>Functionality</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Equivalent weight</td>
<td>30</td>
<td>44</td>
<td>58</td>
<td>58</td>
</tr>
<tr>
<td>Structure</td>
<td>H₂NCH₂CH₂NH₂</td>
<td>H₂N(CH₂)₄NH₂</td>
<td>H₂N(CH₂)₆NH₂</td>
<td>H₂NCH₂CH(CH₃)(CH₂)₂NH₂</td>
</tr>
<tr>
<td>Supplier</td>
<td>Fisons Plc.</td>
<td>Fluka Chemicals Ltd.</td>
<td>Fluka Chemicals Ltd.</td>
<td>Du Pont (UK) Ltd.</td>
</tr>
<tr>
<td>Characteristic</td>
<td>Colourless, alkaline liquid with ammonia odour, soluble in water and alcohol, slightly soluble in ether, insoluble in benzene.</td>
<td>Colourless crystals with strong odour, soluble in water with strong basic reaction, combustible.</td>
<td>Colourless leaflets, soluble in water, slightly soluble in alcohol and benzene.</td>
<td>Clear, low viscosity liquid, miscible in water, dimethylformamide, toluene and isopropanol.</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>0.8995 (20°C).</td>
<td>N/A</td>
<td>N/A</td>
<td>0.86 (25°C)</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>N/A</td>
<td>27</td>
<td>39-42</td>
<td>N/A</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>116-117</td>
<td>158-159</td>
<td>205</td>
<td>193</td>
</tr>
<tr>
<td>Flash point (°C), (closed cup)</td>
<td>33.9</td>
<td>N/A</td>
<td>N/A</td>
<td>83</td>
</tr>
<tr>
<td>Number of methylene groups</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Side methyl group</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>1</td>
</tr>
</tbody>
</table>

N/A = not available

Table 5.3 Chain extenders used in this research programme
5.2 Synthesis programme for water dispersed urethane-urea copolymers

In the preparation of urethane-urea copolymers, the term "block ratio" has been used to indicate the stoichiometric proportions of precursor materials employed. For example a urethane-urea copolymer based on a 1/0.25/0.25/0.50 block ratio signified that the stoichiometric equivalent weight ratio based on the diisocyanate (1) with respect to the polyol (0.25), the carboxylic ionic emulsifier (0.25) and the chain extender (0.5); as abbreviation, NCO/OH/COOH/CE = 1/0.25/0.25/0.5. A number of formulation variations were examined and are detailed below.

5.2.1 Water dispersed urethane-urea copolymers

While a single isocyanate (i.e. TMXDI) and single carboxylic ionic emulsifier (i.e. DMPA) were used in the formulations, the chain extender and polyol types were varied. A summary of formulations variation is shown in Table 5.4.

Table 5.4 Summary of formulations variation of water dispersed urethane-urea copolymers

<table>
<thead>
<tr>
<th>Sample reference</th>
<th>Equivalent mole ratio</th>
<th>Chemicals used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NCO/OH/DMPA/CE</td>
<td></td>
</tr>
<tr>
<td>Series A: Effect of isocyanate building block ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO 3</td>
<td>1.0/0.333/0.333/0.33 (3/1/1/1)</td>
<td>Polyol: Capa 220, Chain extender: MPMDA</td>
</tr>
<tr>
<td>ISO 4</td>
<td>1.0/0.250/0.250/0.50 (4/1/1/2)</td>
<td></td>
</tr>
<tr>
<td>ISO 5</td>
<td>1.0/0.200/0.200/0.60 (5/1/1/3)</td>
<td></td>
</tr>
<tr>
<td>ISO 6</td>
<td>1.0/0.167/0.167/0.67 (6/1/1/4)</td>
<td></td>
</tr>
<tr>
<td>ISO 7</td>
<td>1.0/0.143/0.143/0.72 (7/1/1/5)</td>
<td></td>
</tr>
<tr>
<td>ISO 8</td>
<td>1.0/0.125/0.125/0.75 (8/1/1/6)</td>
<td></td>
</tr>
<tr>
<td>Series B: Effect of carboxylic ionic emulsifier block ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 010</td>
<td>1.0/0.40/0.10/0.5 (10/4/1/5)</td>
<td>Polyol: Terathane 2000, Chain extender: MPMDA</td>
</tr>
<tr>
<td>CBG 020</td>
<td>1.0/0.30/0.20/0.5 (10/3/2/5)</td>
<td></td>
</tr>
<tr>
<td>CBG 025</td>
<td>1.0/0.25/0.25/0.5 (10/2.5/2.5/5)</td>
<td></td>
</tr>
<tr>
<td>CBG 030</td>
<td>1.0/0.20/0.30/0.5 (10/2/3/5)</td>
<td></td>
</tr>
<tr>
<td>CBG 040</td>
<td>1.0/0.10/0.40/0.5 (10/1/4/5)</td>
<td></td>
</tr>
<tr>
<td>Series C: Effect of chain extender types</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDA</td>
<td>1.0/0.3/0.2/0.5 (10/3/2/5)</td>
<td>Polyol: Capa 220</td>
</tr>
<tr>
<td>TMDA</td>
<td>1.0/0.3/0.2/0.5 (10/3/2/5)</td>
<td></td>
</tr>
<tr>
<td>HMDA</td>
<td>1.0/0.3/0.2/0.5 (10/3/2/5)</td>
<td></td>
</tr>
<tr>
<td>MPMDA</td>
<td>1.0/0.3/0.2/0.5 (10/3/2/5)</td>
<td></td>
</tr>
<tr>
<td>Series D: Effect of polyol types and molecular weight</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>1.0/0.2/0.3/0.5 (10/2/3/5)</td>
<td>Chain extender: MPMDA</td>
</tr>
<tr>
<td>C2</td>
<td>1.0/0.2/0.3/0.5 (10/2/3/5)</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>1.0/0.2/0.3/0.5 (10/2/3/5)</td>
<td></td>
</tr>
<tr>
<td>PT1</td>
<td>1.0/0.2/0.3/0.5 (10/2/3/5)</td>
<td></td>
</tr>
<tr>
<td>PT2</td>
<td>1.0/0.2/0.3/0.5 (10/2/3/5)</td>
<td></td>
</tr>
<tr>
<td>PT29</td>
<td>1.0/0.2/0.3/0.5 (10/2/3/5)</td>
<td></td>
</tr>
</tbody>
</table>
The detailed amounts of each reactant for various formulation used in the research programme are shown in Tables 5.5a to 5.5d. All the reaction batch sizes were kept constant at approximately 180 grams total solid content, and then dispersed in water to form 40% total solids content urethane-urea copolymers dispersion. The triethyl amine used for neutralising the pendent carboxylic groups was used in 5% excess of equivalent molar weight of carboxylic groups.

Table 5.5a The weight of each chemical used for synthesis of water dispersed urethane-urea copolymers in series A

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Equivalent weight (g)</th>
<th>Sample reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ISO 3</td>
<td>ISO 4</td>
</tr>
<tr>
<td>TMXDI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capa 220</td>
<td>122</td>
<td>44.8</td>
</tr>
<tr>
<td>DMPA</td>
<td>.67</td>
<td>7.9</td>
</tr>
<tr>
<td>TEA</td>
<td>101</td>
<td>6.2</td>
</tr>
<tr>
<td>MPMDA</td>
<td>.58</td>
<td>7.5</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>263.8</td>
</tr>
</tbody>
</table>

Total solid weight (g): 180.0 180.0 180.0 180.0 180.0 180.0
Dispersion weight (g): 450.0 450.0 450.0 450.0 450.0 450.0

Series A: polyol was fixed as Capa 220. The molar block ratio of polyol and pendent carboxylic acid groups was kept at 1. With increasing isocyanate building block ratio, the concentration of pendent carboxylic groups and the amount of triethyl amine were decreased. ISO 3 had the highest concentration of pendent carboxylic acid groups. The percentage of hard segment content per total urethane-urea copolymers weight increased, ISO 8 had the highest hard segment content.

Table 5.5b The weight of each chemical used for synthesis of water dispersed urethane-urea copolymers in series B

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Equivalent weight (g)</th>
<th>Sample reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CBG 010</td>
<td>CBG 020</td>
</tr>
<tr>
<td>TMXDI</td>
<td>122</td>
<td>39.4</td>
</tr>
<tr>
<td>Terathane 2000</td>
<td>1000</td>
<td>129.0</td>
</tr>
<tr>
<td>DMPA</td>
<td>.67</td>
<td>2.2</td>
</tr>
<tr>
<td>TEA</td>
<td>101</td>
<td>1.6</td>
</tr>
<tr>
<td>MPMDA</td>
<td>.58</td>
<td>9.4</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>264.4</td>
</tr>
</tbody>
</table>

Total solid weight (g): 180.0 180.0 180.0 180.0 180.0 180.0
Dispersion weight (g): 450.0 450.0 450.0 450.0 450.0 450.0
**Series B:** polyol was fixed as Terathane 2000. The molar block ratio of amine chain extender was kept constant. Increasing carboxylic ionic emulsifier block ratio led to higher concentration of pendent carboxylic groups and also higher amounts of triethyl amine. The amount of hard segment per total urethane-urea copolymers weight also increased. CBG 040 had the highest carboxylic acid content and also highest hard segment content.

Table 5.5c The weight of each chemical used for synthesis of water dispersed urethane-urea copolymers in series C

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Equivalent weight (g)</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDA</td>
<td>TMDA</td>
</tr>
<tr>
<td>TMXDI</td>
<td>122</td>
<td>51.2</td>
</tr>
<tr>
<td>Capa 220</td>
<td>1000</td>
<td>116.2</td>
</tr>
<tr>
<td>DMPA</td>
<td>67</td>
<td>6.3</td>
</tr>
<tr>
<td>TEA</td>
<td>101</td>
<td>5.0</td>
</tr>
<tr>
<td>EDA</td>
<td>30</td>
<td>6.3</td>
</tr>
<tr>
<td>TMDA</td>
<td>44</td>
<td>—</td>
</tr>
<tr>
<td>HMDA</td>
<td>58</td>
<td>—</td>
</tr>
<tr>
<td>MPMDA</td>
<td>58</td>
<td>—</td>
</tr>
<tr>
<td>Water</td>
<td>—</td>
<td>265.0</td>
</tr>
<tr>
<td>Total solid weight (g)</td>
<td>180.0</td>
<td>180.0</td>
</tr>
<tr>
<td>Dispersion weight (g)</td>
<td>450.0</td>
<td>450.0</td>
</tr>
</tbody>
</table>

**Series C:** polyol was fixed as Capa 220. The equivalent molar block ratio was kept constant at NCO/OH/DMPA/CE = 1/0.3/0.2/0.5. Therefore, carboxylic ionic emulsifier and amount of neutralising agent were constant. The percentage of hard segment content per total urethane-urea copolymers weight was slightly increased with longer methylene groups in the amine chain extender. The variation associated with the chain extenders, was change in the numbers of methylene groups in the chain (i.e. 2 to 6), and the introduction of side methyl group in MPMDA.
Table 5.5d The weight of each chemical used for synthesis of water dispersed urethane-urea copolymers in series D

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Equivalent weight (g)</th>
<th>Sample reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1</td>
<td>C2</td>
</tr>
<tr>
<td>TMXDI</td>
<td>122</td>
<td>81.1</td>
</tr>
<tr>
<td>Capa 210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capa 220</td>
<td></td>
<td>66.4</td>
</tr>
<tr>
<td>Capa 240</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>Terathane 1000</td>
<td>500</td>
<td></td>
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<tr>
<td>Terathane 2000</td>
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<td></td>
</tr>
<tr>
<td>Terathane 2900</td>
<td>1450</td>
<td></td>
</tr>
<tr>
<td>DMPA</td>
<td>67</td>
<td>13.3</td>
</tr>
<tr>
<td>TEA</td>
<td>101</td>
<td>10.6</td>
</tr>
<tr>
<td>MPMDA</td>
<td>58</td>
<td>19.2</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>259.4</td>
</tr>
<tr>
<td>Total solid weight (g)</td>
<td>180.0</td>
<td>180.0</td>
</tr>
<tr>
<td>Dispersion weight (g)</td>
<td>450.0</td>
<td>450.0</td>
</tr>
</tbody>
</table>

**Series D:** with increasing molecular weight of polyol, the percentage of hard segment content per total urethane-urea copolymers weight decreased. The equivalent molar block ratio (NCO/OH/DMPA/MPMDA) was kept constant at 1/0.2/0.3/0.5 but the carboxylic ionic emulsifier per unit chain length decreased. The amount of triethyl amine for neutralising the pendent carboxylic acid groups also decreased.

The resulting water dispersed urethane-urea copolymers were characterised, then converted by casting to solid sheets which were further tested.

5.2.2 Thermoplastic urethane-urea copolymer powders

It was realised in the later stages of the research programme that fine urethane-urea copolymers powders could be precipitated from the dispersions. This led to a short study on the feasibility of making powders directly from a dispersion, which could then be shaped by melt processing techniques, (i.e. injection moulding). This was thought to offer a route of producing much thicker section mouldings.

A single formulation of an equivalent mole ratio of TMXDI/Terathane 2000/DMPA/MPMDA of 1/0.25/0.25/0.5 was selected, since it gave reasonable dispersion properties and also good cast film properties. It is well known that
many melt processed thermoplastics need stabiliser packages, (e.g. antioxidant, ultra-violet stabiliser, heat stabiliser). However, to be able to compare a urethane-urea copolymer's properties produced either by casting from a dispersion or by moulding melt process, a stabiliser was not used.

As a relatively large amount of polymer was required for the injection moulding trials, it was necessary to scale up the reaction batch size from 450 grams to 2000 grams; 40% solid content, (see Appendix 2) in both cases and total of 20 batches of dispersion were collected and mixed before precipitating into powder form.

5.3 Synthesis procedure of water dispersed and powdered urethane-urea copolymers

5.3.1 Water dispersed urethane-urea copolymers

A dispersing shear polymerisation technique was used to synthesise water dispersed urethane-urea copolymers. The following procedure was used.

a) The polyol was melted and dried under vacuum at 100 °C for an hour and cooled to about 60 °C before use. Although m-TMXDI is liquid at 20 °C, laboratory temperatures varied between summer and winter and therefore for the consistency, the isocyanate was conditioned at 35 °C before mixing with other reactants.

b) The required amounts of polyol, TMXDI, DMPA and DBTDL totalling approximately 180 grams were weighed and placed in a 500 ml. round bottom reaction flask. These reactants were simply mixed together for a few seconds at room temperature by stirring to produce a mixture ready for the controlled reaction.

c) The reaction flask was fitted with a multi-socket head with a nitrogen inlet and an anchor stirrer was driven by a variable speed constant torque stirrer motor. Nitrogen gas pre-dried by passing it through a silica gel guard tube was fed at a constant rate, (i.e. 25 cc/min.) into the reaction flask.

d) The reaction flask was placed in a temperature controlled hot oil bath set at 90°C. The temperature was monitored using a mercury-in-glass thermometer immersed in the oil, near the side of the reaction flask. The contents of the flask were continuously stirred at low speed, (i.e. 30 rpm) under dry nitrogen until the free isocyanate content had reduced to a
constant value. The free isocyanate content was determined by the dibutylamine back-titration method. (See Appendix 3)
e) The reaction flask and oil bath were cooled to about 60 °C. The resulting isocyanate terminated prepolymer was neutralised with triethylamine in N-methyl pyrrolidone (25 % V./V.), and then dispersed in water to produce 40 % of total solid content. The solution was mixed vigorously by high speed stirring, (i.e. 450 rpm) to produce a urethane oligomer dispersion.
f) The appropriate amount of amine chain extender was quickly added to the dispersion and stirred for another hour at 60 °C at 150 rpm.
g) The resulting urethane-urea copolymer dispersion was then left to cool for 16 hours before the resulting latex was examined or used in preparation of cast sheet.

The flow diagram of urethane-urea copolymers dispersion synthesis steps are shown schematically in Figure 5.3.

```
TMDXI + Polyl + DMPA + DBTDL
  \_________\   \_________\   \_________\  \\
Oligomerisation  Neutralisation  Dispersion  \\
  \   \   \   \  \   \   \   \  \\
Mixed together at 90°C  + TEA in N-methyl pyrrolidone at 60°C  + Water under vigorous stirring at 60°C  \\
  \   \   \   \  \\
Isocyanate terminated urethane prepolymer  Hydrophilic urethane prepolymer  Water dispersed urethane prepolymer  \\
  \   \   \   \  \\
  until the % NCO constant  \\
  \   \   \\
  \   \\
Water dispersed urethane-urea copolymers
```

Figure 5.3 Process flow diagram for the laboratory production of water dispersed urethane-urea copolymers.
5.3.2 Thermoplastic urethane-urea copolymers powder

Each batch of thermoplastic urethane-urea copolymer powder was prepared using the following procedure:

20 batches of water dispersed urethane-urea copolymers were synthesised in the identical condition over a period of a month, after which they were mixed before precipitation. The dispersion was poured into a three-fold excess of a 3% acetic acid aqueous solution with high speed stirring, (i.e. 600 rpm) to coagulate. The powder was precipitated and filtered from the solution using a 180 μm sieve. The powder was then neutralised in 1% aqueous potassium hydroxide solution until pH = 7. The pH change was followed by using litmus paper. The powder was washed in running distilled water for another half an hour and then dried in a circulating air oven at 25 °C. The dry powder was kept in a polyethylene bag and left in a plastic container with silica gel as a desiccant to prevent moisture absorption. The process is summarised in Figure 5.4

Water dispersed urethane-urea copolymers

Coagulation
in 3 % Acetic acid
with high speed stirring

Precipitated urethane-urea copolymers

Separation
using 180 μm sieve

Wet urethane-urea copolymers powder

Washing and drying
in 1 % KOH until pH = 7
washing in water for half hour
dry at room temperature

Urethane-urea copolymers powder

Figure 5.4 Process flow diagrams for the laboratory production of urethane-urea copolymers powder
5.4 Characterisation of the water dispersed urethane-urea copolymers products

5.4.1 pH

The pH of each dispersion was measured using a glass electrode and a saturated calomel electrode cell after standardising the pH meter with borax and potassium hydrogen phthalate solutions. The method of measurement followed the standard method BS 6057 Part 3 Section 3.9, (1990).

5.4.2 Viscosity

The viscosity of the dispersions were determined using a Brookfield viscometer model UBT with spindle number 1 and speed of 50 rpm. The method of measurement followed the standard method BS 6057 Part 3 Section 3.11, (1992).

5.4.3 Surface Tension

A Krüss automatic surface tension balance, model K10T, with a platinum ring of 19 mm circumference, was used to determine the surface tension of the urethane-urea copolymer dispersions. Each dispersion was adjusted to a 40% total solid content before testing. The measurement procedure was followed the standard method BS 6057 Part 3 Section 3.10, (1987).

5.4.4 Particle size and distribution

The particle size and distribution of the dispersions were determined by using a Coulter LS 130 machine which combines laser diffraction and polarisation intensity differential scattering (PIDS) methods of measurement; (see Figure 5.5).

The Coulter LS 130 machine measures a particular type of light scattering known as diffraction, over a particle size distribution range of 0.1 μm to 800 μm. It can be used over a very wide particle size distribution range, a volume distribution method being used. Laser diffraction provides the highest degree of accuracy down to 0.4 μm and the PIDS enables sizes down to 0.1 μm to be measured.

The PIDS method is based on the polarisation of light which is broken into two components, the vertically and horizontally plane polarised components. The
particles are then illuminated with vertically and horizontally polarised light at three different wavelengths. The detectors are positioned at around 90° to the direction of the light path so that the peak particle scatter intensity is seen by the detectors in approximately 1/3rd the wavelength of the light through the PIDS cell. The wavelengths used are 450 nm, 600 nm and 900 nm enabling detection at 0.1 to 0.2 μm, 0.2 to 0.3 μm and 0.3 to 0.4 μm respectively. The PIDS makes a total of 30 measurements; these are made at 5 scattering angles and 3 wavelengths, each at two polarisations. The results of each polarisation are summed for accuracy giving 15 specific measurements of particle size in the 0.1 to 0.4 μm range.

Each dispersion was diluted to approximately 0.1% of total solid content in water before placing into the Coulter LS130.

![Figure 5.5 Schematic diagram of the Polarisation Intensity Differential Scattering (PIDS)](image)

5.5 Characterisation of the cast films

Each dispersion was left overnight after synthesis and then cast onto a highly polished aluminium tray (6" X 6"), treated with a suitable mould releasing agent (i.e. Ambersil Polyurethane/2). Each casting was kept at room temperature (20 ± 2°C).
°C) for four days to allow water loss by evaporation and to obtain a tack-free coherent solid film. Each resulting film was conditioned in a circulating air oven at 80 °C for another eight hours to remove any residual water. Each film was then removed from its tray and kept in a dark room at 20 ± 2°C, 50 % R.H., before testing. The thickness of each film was approximately 2 mm.

5.5.1 Differential scanning calorimetry (DSC)

Since the early 1960s, a number of types of thermal analyser equipment have been put into the market. Differential thermal analysis (DTA), particularly the Differential scanning calorimetry (DSC) has been shown to be a valuable technique for the analysis of polymers.\(^{(5.12-5.15)}\) Thermal analysis of polyurethanes has been reviewed in many papers.\(^{(5.16-5.19)}\)

The thermal properties of all films were measured using a Du Pont Differential Thermal Analyst 2000 with a Du Pont 910 Differential Scanning Calorimeter accessory. The instrument was first calibrated against a temperature reference, i.e. indium (melting point = 156.6 °C). A specimen of urethane-urea copolymer film (approximately 10 mg) was placed into a standard closable aluminium specimen pan. The pan and an empty reference pan were then placed on platforms of the thermocouple cell, (see Figure 5.6). The cell was cooled to -120 °C using liquid nitrogen, before being heated at a constant rate of 20 °C/min. in dry nitrogen gas at a constant flow rate, (i.e. 50 cc/min.). The DSC temperature scanning range was recorded from -100°C to 260°C. Three specimens of each material were tested separately to ensure repeatability.

![Figure 5.6 Schematic diagram of the Du Pont DSC cell](image_url)
Many polyurethanes materials show one or more transitions as their temperature is raised. Typical thermograms include features as shown in Figure 5.7. In this research work, glass transition (Tg), second transition melting temperature, third onset transition temperature and onset of thermal degradation temperature were determined. The Tg was taken as the onset of the change in slope of the base line.

Figure 5.7 Schematic representation of interpreting the transition temperature from DSC thermograms in this research work.

5.5.2 Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) is a technique for studying the effect of molecular structure and phase morphology on the properties of polymeric materials. DMTA gives a quantitative measurement of modulus change with Tg and crystallisation changes. DMTA detects Tg and other transitions, with a sensitivity about 1000 times higher than the DSC method and can be used to measure the transitions quantitatively.
Many modes of vibration of a specimen are available, but the most popular are reversed bending (e.g. the double cantilever, (see Figure 5.8a); axial tension, (see Figure 5.8b); torsion, (see Figure 5.8c); shear, (see Figure 5.9d)).

Figure 5.8 Loading options for dynamic mechanical testing: (a) double cantilever; (b) reversed uniaxial tension; (c) torsion; (d) shear. $S =$ specimen

Measurement by DMTA of all cast films was made using the Polymer Laboratories Dynamic Mechanical Thermal Analyser (PL-DMTA), as shown on Figure 5.9a. The specimens were in the form of rectangular bars which had the dimensions of 15x 10x 2 mm$^3$. A specimen was firmly clamped at one end and held by a central clamp at other end (i.e. in single cantilever mode). The central point of the bar was continuously vibrated sinusoidally by a drive shaft connected to an oscillator, (see Figure 5.9b). Initial experiments using the double cantilever mode, (Figure 5.8a), caused problems due to the softness of the materials at elevated temperatures. The clamped samples were then cooled using liquid nitrogen, which was introduced into the chamber via a glass funnel. All measurements were carried out at 1 Hz frequency with a strain setting of X 4. The heating rate was set at 3 °C/min. and specimens were tested over the temperature range from -100 °C to 100 °C, above which the specimens were found to have become excessively softened and could
not be properly flexed. The sensitivity values for different functions of X-Y recorder were set, and the $E'$ and tan $\delta$ were plotted.

The typical forms of storage modulus ($E'$), tan $\delta$ and onset of Tg from the storage modulus curve for urethane-urea copolymers in this research work are shown on Figure 5.10.

Figure 5.9 (a) A schematic diagram of the mechanical head of PL-DMTA. (b) A typical single cantilever damping device used in the bending mode for this research work.

Figure 5.10 Schematic representation of interpreting the tan $\delta$, storage modulus and onset of Tg from DMTA thermogram.
5.5.3 Fourier transform infra-red spectroscopy (FT-IR)

The instrumentation and mode of operation of a FT-IR have been described frequently in the literature.(5.25-5.27) The FT-IR equipment used in this research programme was a Mattson 3000 Galaxy FT-IR spectrometer. A description of the Mattson 3000 Galaxy is not given here; this is readily available in the manufacture literature.(5.28) The FT-IR equipment offers substantial advantages over the conventional IR for this work, in that it uses abilities to use multiple scanning of a specimens, which greatly increases the intensity that can be reliably extracted signals from the specimens, it is less time consuming to obtain a spectra and in particularly it has the ability to be used in attenuated total reflectance mode, which enables measurements to be made directly from the surface of polymer.

A technique known as attenuated total reflectance (ATR) was used. The infra-red ATR unit consists essentially of a flat crystal of zinc selenide, (ZnSe) arranged in the sample beam of spectrophotometer so that infra-red radiation can pass through it by total internal reflection. A specimen was clamped firmly to the surface of the crystal. When radiation is totally internally reflected at the surface of crystal, a small proportion is absorbed by the sample. With repeated internal reflection along the crystal, the sum intensity of absorption increases. Therefore, the emerging radiation has a lower intensity than the reference beam and a spectrum is obtained in the usual way. The spectra obtained by this method is independent of the thickness of the sample. Spectra of each cast film were recorded using the SPACAC horizontal ATR unit installed in the FT-IR spectrometer. The samples were vacuum dried before analysis to remove any surface moisture, which would lead to misinterpreted OH absorption bands. The spectra was recorded between 4000 cm\(^{-1}\) and 600 cm\(^{-1}\) using the 200 scanning mode. Specimens approximately 1x4x2 mm (width x length x thickness) were cut to cover the surface of the crystal, (see Figure 5.11).

Infra-red spectroscopy is a suitable technique for providing information on the extent and distribution of hydrogen bonding in polyurethane materials as well as molecular changes due to polymerisation or degradation.(5.29,5.30) In polyurethanes, the proton donor is primarily the N-H group of the urethane linkage. The proton acceptor may be in the hard segment, (i.e. the carbonyl of the urethane or urea group), or the soft segment (i.e. an ester carbonyl or ether oxygen). The proportion of N-H bonded to hard segment acceptors compared to soft segment acceptors reflects the degree of microphase separation. The hydrogen
bonding is manifested by shifts in the N-H and C=O stretching frequencies to lower values than those observed when these groups are not hydrogen bonded. The stretching frequencies are the most useful for characterising the groups present in polyurethanes. Table 5.6 lists the molecular groups band and their assignments.

![Figure 5.11 Horizontal attenuated totally internal reflected IR radiation](image)

**Table 5.6 Useful IR bands for polyurethanes with their assignment (5.31)**

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Group</th>
<th>Assignment</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400-3500</td>
<td>-N-H</td>
<td>free -NH stretching</td>
<td>Sh, W</td>
</tr>
<tr>
<td>3300-3400</td>
<td>-N-H</td>
<td>bonded -NH stretching</td>
<td>S</td>
</tr>
<tr>
<td>2930</td>
<td>-CH₃, -CH₂</td>
<td>stretch of -CH₂-</td>
<td>VS</td>
</tr>
<tr>
<td>2850</td>
<td>-CH₂</td>
<td>symmetric stretch of -CH₂</td>
<td>S</td>
</tr>
<tr>
<td>2270</td>
<td>-N=≡C=O</td>
<td>stretching</td>
<td>W, S</td>
</tr>
<tr>
<td>1640</td>
<td>C=O (urea)</td>
<td>stretching</td>
<td>S</td>
</tr>
<tr>
<td>1720</td>
<td>-C=O</td>
<td>C=O stretching (free)</td>
<td>S</td>
</tr>
<tr>
<td>1700</td>
<td>-C=O</td>
<td>C=O stretching (bond)</td>
<td>S</td>
</tr>
<tr>
<td>1412</td>
<td>isocyanurate</td>
<td></td>
<td>M</td>
</tr>
</tbody>
</table>

Sh = shallow, W = weak, S = strong, VS = very strong, M = medium

Significant bands in the polyurethane IR spectra are the NH stretch absorption at 3000 to 3500 cm⁻¹ and the carbonyl vibrations at 1750 to 1700 cm⁻¹. When NH forms hydrogen bonds its frequency decreases while its intensity increases. The carbonyl absorption is of greater relevance for polyether polyol based polyurethanes, as the presence of two types of carbonyl groups in polyester polyol based systems give only a broad unresolved peak.
Analysis of the IR spectra of a polyurethane can be used to measure the degree of phase interaction between the hard and soft segments. This can be determined by measuring the degree of hydrogen bonding between the active hydrogen of the NH group and possible proton acceptors. The estimation of hydrogen bonding is based on the resolution of the urethane NH and carbonyl bond into the bonded and non-bonded components.

IR spectra of samples prepared in various ways will show a strong band, assigned to hydrogen bonded -N-H stretching vibration present at 3280 cm\(^{-1}\). The free -N-H stretch appears as a shoulder on the high frequency side of the band. Determination of the amount of the hydrogen bonded NH has been performed by the base line density method(5.32) as follows:

Determine the absorbance at the absorption maximum according to the Beer-Lambert equation:

\[ A = \log \left( \frac{I_0}{I} \right) = E.C.L \]

Where:
- **A** = absorbance
- **I** = intensity of transmitted radiation
- **I** = intensity of incident radiation
- **E** = extinction coefficient
- **C** = concentration of the NH groups
- **L** = radiation path length (cm)

From the IR spectra, the NH stretching vibration will be apparent at a wavelength around 3300 to 3500 cm\(^{-1}\). The IR spectra of urethane near the NH stretching vibration is shown on Figure 5.12.

Absorbance at bonded NH stretching (\(A_b\)) and absorbance at free NH stretching (\(A_f\)) can be found using the base line method as follows:

\[ A_b = \log (AC/BC) \]
\[ A_f = \log (DF/EF) \]

By the Beer-Lambert equation, the absorbance, \(A_b\) of the hydrogen bonded absorption maximum is given by:

\[ A_b = E_b C_b L_b \]
Similarly, for the free NH absorption maximum:

\[ A_f = E_f C_f L_f \]

Assuming \( E_b = E_f \) as an approximation:

\[ A_b = K C_b \]

and

\[ A_f = K C_f \]

where \( K \) is constant.

The proportion of hydrogen bonded NH groups is then given by:

\[
\text{hydrogen bonded (NH) } \% = 100 \times \frac{A_b}{A_b + A_f}
\]

Figure 5.12 Baseline density method in a typical NH absorption band of polyurethane elastomers.
5.5.4 Tensile properties

The tensile behaviour of a polyurethane depends specifically on the types of precursor components used, its morphology and phase structure. Polyurethanes are also sensitive to degradation, oxidation and hydrolysis effects. Tensile properties are also an important means of determining the useful applications for many types of polyurethanes.

Each of the urethane-urea copolymers cast films (e.g. as made, after heat ageing and after hydrolytic treatment) was tested for tensile properties. The tensile properties were measured on a J.J. Lloyd Instrument model 1000s tensiometer at room temperature (20 ± 2 °C) using a cross head speed of 200 mm/min., load cell 500 N and extension range 600 mm. in conjunction with an X-Y plotter. Test specimens were prepared from cast films by cutting with a dumbbell cutter, BS dumbbell type 1. The test specimens were conditioned in a dark room (20 ± 2 °C, 50 % R.H.) for 24 hours before testing. The test procedure followed the standard method BS 903 Part A2, 1989.

Load/extension measurements were made on each of the cut urethane-urea copolymers dumbbells. Information derived from these curves included the tensile strength at break, elongation at break and secant modulus at 300% extension. The later was used because of the non-linearity of the load/extension curves, especially at low strains. Five specimens were tested for each sample of urethane-urea copolymers, results being averaged from each of the five specimens.

a) Heat ageing test

Cut dumbbell specimens were suspended in a hot air circulating oven at 70 ± 2 °C for 168 hours. When the ageing was completed, the specimens were removed from the oven and immediately cooled and conditioned at room temperature (20 ± 2 °C, 50 % R.H.) for 24 hours before tensile testing.

b) Hydrolytic test

Cut dumbbell specimens were completely immersed in distilled water, maintained at 25 ± 2°C for 168 hours. The specimens were removed from the water and excess surface water removed with filter paper. The test specimens were left to dry at
room temperature \( (20 \pm 2 \, ^\circ C) \) for at least 24 hours, (or until the weight no longer significantly changed), before tensile testing.

5.6 Characterisation of injection moulding sheet from urethane-urea copolymers powders

5.6.1 Melt flow characteristics of urethane-urea copolymer powders

To enable the best conditions (e.g. melt temperature) to be determined for the moulding equipment, it was necessary to examine the urethane-urea copolymer's melt flow characteristics. Rheological properties were examined using a Davenport capillary rheometer. The Davenport capillary rheometer consists of an electrically heated and thermostated barrel into which dies can be fixed at its bottom. Dies of different capillary diameter and length are usually employed. The powder was allowed to melt in the barrel for ten minutes before being forced through the die by a plunger at selected shear rates. Plunger speeds ranging from about 1.25 to 200 mm/min. were used. The pressure drops in the capillary were measured using a Dynisco PT pressure transducer, model 460E-10N-6, (0 to 1000 psi), sited at the end of the barrel and before the entry to the die. Signals from the pressure transducer were amplified and relayed to a chart recorder. Conventional and electric "Comark" thermometers were also used to ensure controllable temperature within \( \pm 0.1 \, ^\circ C \). The typical schematic of a capillary rheometer is shown in Figure 5.13 and the capillary dies and the temperatures used in this programme are listed in Table 5.7.

![Figure 5.13 Typical diagram of capillary rheometer](image-url)
Table 5.7 Capillary dimension and temperature used for flow data
(diameter of the barrel = 9.5 mm)

<table>
<thead>
<tr>
<th>Factors</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of measurement (°C)</td>
<td>130,140, 150,160</td>
</tr>
<tr>
<td>Diameter of capillary (mm)</td>
<td>2</td>
</tr>
<tr>
<td>Length of capillary (mm)</td>
<td>20</td>
</tr>
<tr>
<td>Ram speed (mm/min.)</td>
<td>10, 20, 30</td>
</tr>
</tbody>
</table>

The following parameters were recorded: pressure inside the capillary at different ram speeds, mass output rate, cross section diameter size of extrudate, percentage of die swell and appearance of extrudate, (e.g. colour, presence of bubbles, surface finish etc.).

The percentage die swell was calculated by the following equation:

\[
\text{Percentage die swell} = 100 \times \frac{A-B}{B}
\]

where 

- \(A\) = Cross section diameter of the extrudate (mm)
- \(B\) = Diameter of the capillary (mm)

5.6.2 Sheet preparation

The Negri Bossi NB55 injection moulding equipment, (with DIMI card closed loop control) was used for sheet preparation. The operating parameters of the Negri Bossi NB55 are given in Table 5.8.

Table 5.8 The operating parameters of the Negri Bossi NB55 injection moulding equipment

<table>
<thead>
<tr>
<th>Technical data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Screw diameter (mm)</td>
<td>38</td>
</tr>
<tr>
<td>Screw length to diameter ratio</td>
<td>14.5</td>
</tr>
<tr>
<td>Calculated injection volume (cm³)</td>
<td>141</td>
</tr>
<tr>
<td>Real injection volume (cm³)</td>
<td>120</td>
</tr>
<tr>
<td>Real injection capacity (PS) (cm³)</td>
<td>126</td>
</tr>
<tr>
<td>Injection rate (cm³/second)</td>
<td>84</td>
</tr>
<tr>
<td>Max. pressure on materials (bar)</td>
<td>1170</td>
</tr>
<tr>
<td>Nozzle mould hold on force (kN)</td>
<td>30</td>
</tr>
<tr>
<td>Barrel heating zones (number)</td>
<td>3</td>
</tr>
<tr>
<td>Mould clamping force (kN)</td>
<td>550</td>
</tr>
<tr>
<td>Screw speed (rpm)</td>
<td>10 to 410</td>
</tr>
</tbody>
</table>
Prior to injection, the powder was dried for 48 hours in an air circulating oven at 70 °C. A polished steel mould machined for four tensile bars cavities, (which have a narrow parallel waist portion of 12.5x60x3 mm, width x length x thickness), was fitted into the clamping unit of the injection moulding machine. No mould release agent had to be used. Once the urethane-urea copolymers in the barrel was considered to be stabilised, the effects of the following parameters shown in Table 5.9 were examined.

Table 5.9 The summary of the parameter variations for injection moulding study

<table>
<thead>
<tr>
<th>Study Parameters</th>
<th>Fixed parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Effect of injection speed (%)*</td>
<td>Mould cooling time = 30 second</td>
</tr>
<tr>
<td>@ 20, 40, 60, 80</td>
<td>Injection temperature = 160 °C</td>
</tr>
<tr>
<td>2) Effect of mould cooling time (sec.)</td>
<td>Injection speed = 40 %</td>
</tr>
<tr>
<td>@ 30, 50, 70</td>
<td>Injection temperature = 160 °C</td>
</tr>
<tr>
<td>3) effect of injection temperature (°C)</td>
<td>Injection speed = 40 %</td>
</tr>
<tr>
<td>@ 150, 160, 170, 180</td>
<td>Mould cooling time = 30 second</td>
</tr>
</tbody>
</table>

* The percentage of injection speed is relative to the maximum injection rate that the machine is capable. The Negri Bossi NB55 injection moulding machine has a maximum injection rate is 84 cm³/second (based on polystyrene).

The fixed parameters of the injection moulding experiment were:

a) Mould temperature set at 10 °C.
b) Short size set at 55 mm.
c) Screw position trip set at 65 mm.
d) Hold-on pressure set at 60 bar and hold on time set at 5 second.
e) Injection pressure set at 140 bar maximum.
f) The second and third heating zones were set at 10 °C below the injection temperature.

Once the samples were made, they were stored in a dark room (20 ± 2 °C, 50 % R.H.) for at least 24 hours before testing. Samples were prepared for testing by DSC, DMTA and tensile techniques.
5.6.3 Differential scanning calorimetry (DSC)

The thermal properties of samples from each of the injection moulding parameters were examined. The test conditions were as detailed in Section 5.5.1.

5.6.4 Dynamic mechanical thermal analysis (DMTA)

Measurements by DMTA for samples prepared from each of the injection moulding parameters were made. The test conditions were as detailed in Section 5.5.2.

5.6.5 Tensile properties

For each of the injection moulding machine parameters, nine sample pieces were collected and the middle five pieces were subsequently tested. Specimens were cut to a BS 903 standard dumbbell type 1 shape and conditioned at room temperature, 50% R.H. for a week before proceeding with the tensile test. The test conditions were as detailed in Section 5.5.4. Tensile strength at break, elongation at break and 300% modulus were reported.
References


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5.17 Singh, A., Weissbein, L., Mollica, J.C., Rubb. Age, 98, 77, 1966


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Chapter 6 New Technique for Preparation of Water Dispersed Polyurethanes and Their Structure-Property Relationships in Latex Form

This chapter will describe the technique developed for preparation of water dispersed urethane-urea copolymers, without the aid of solvent and also study of the structure-property relationships of the resulting latices. The selected characterisation methods included: pH, viscosity, particle size and distribution and surface tension.

6.1 The new technique for preparation of water dispersed polyurethanes

The technique used in this research programme was a development of the prepolymer mixing process, (details of the prepolymer mixing process were given in Section 3.2.1). The procedure and flow diagram of this new technique were given in Section 5.3.1. The chemical reactions involved in forming of a dispersion are illustrated in Figure 6.1.

The first step of this new technique was identical to the original prepolymer mixing process. A low molecular weight isocyanate tipped prepolymer was first prepared by the bulk polymerisation technique. Calculated amounts of polyol, (either Capa or Terathane of various molecular weights), carboxylic acid ionic emulsifier agent, (α,α'-dimethylol propionic acid, DMPA) and dibutyltin dilaurate (0.1% per total prepolymer weight), were mixed together with an excess of tetramethyl xylene diisocyanate (TMXDI) for the prepolymerisation. The extent of reaction was followed by sampling the reaction liquid and using a dibutylamine back titration technique to determined the free isocyanate content, (see Appendix 3). The reaction was allowed to proceed until the free isocyanate content was constant, or the value of free isocyanate content was approximately equal to the calculated excess amount of free isocyanate in the particular formulation. The resulting number average molecular weight (Mn) of prepolymer was around 30,000 to 45,000 and the weight average molecular weight (Mw) of prepolymer was around 65,000 to 75,000, depending on the formulation. This molecular weight was determinated from the equivalent molar block ratio of TMXDI/polyol/DMPA (same equivalent molar block ratio with no chain extender).
Figure 6.1 The chemical reaction of water dispersed urethane-urea copolymers formation
Normally, the carboxylic acid emulsifier agent (i.e. DMPA) was used in molar equivalent ratios varying from 0.08 to 0.2, based on the total molar equivalent of isocyanate, polyol, DMPA and chain extender. When lower levels of DMPA were employed the amine-neutralised polyurethane began to lose water-compatibility. Commercial production of polyurethanes based on higher ratios of DMPA was thought likely to become less economic and the polymer becomes too hydrophilic.

The reaction temperature during the prepolymer preparation depended mainly on the type and reactivity of isocyanate, and the presence of catalyst. For example, an aliphatic diisocyanate based system is likely to need a higher temperature than an aromatic diisocyanate system, in the absence of catalyst. Ideally in the isocyanate prepolymer preparation stage, the reaction temperature is preferred to be as low as possible to prevent the undesirable side reaction of isocyanate with pendant carboxylic acid, (i.e. in emulsifier agent) which in most cases will occur at approximately 100 °C (6.1, 6.2) (If this happens, it will lead to the reduction of hydrophilic performance) and also to prevent the reaction of isocyanate with itself, resulting the undesirable products which affect the final polymer properties. In this programme, the reaction temperature of oligomerisation of about 90 °C was found to be satisfactory, to achieve a balance between the desired reaction rate and minimise the undesirable side reactions with TMXDI based systems. Reaction temperatures lower than 60 °C gave a slow reaction (i.e. long reaction time).

The pendent carboxylic acid in the prepolymer was then neutralised by the addition of a tertiary amine, to form quaternary ammonium salts rendering the prepolymer compatible with water, while reducing viscosity of the prepolymer. To obtain maximum water compatibility of the prepolymer, sufficient tertiary amine must be employed to react with all the pendant carboxylic groups in the urethane structure, (i.e. equivalent or slightly higher than the stoichiometric balance). In this research work, a 5 % excess, (by weight based on the weight of the stoichiometric requirement of tertiary amine), was used to further improve the water compatibility of the urethane polymer. Triethylamine, (a tertiary amine) was preferred over any primary or secondary amines since it is non-reactive with isocyanate, and has the bonus of catalysing the isocyanate-amine reaction during the subsequent chain extension stage. The addition of the tertiary amine was simply achieved by adding as an aqueous solution (i.e. 50% solution in water) and stirring into the urethane prepolymer. However, high boiling coalescent agents such as N-methyl pyrrolidone etc. may be mixed into the aqueous amine solution to improve subsequent film forming properties.
A 1.5 to 2-fold excess of water was quickly added into the hydrophilic urethane prepolymer and stirred at high speed to form a dispersion. This can be achieved because of the highly hydrophilic character of the quaternary ammonium salt. This step differed from the conventional prepolymer mixing process in that there was no solvent involved in the synthesis. Time and temperature were important factors in this step. The neutralising and dispersing temperature must not be above a critical temperature at which the isocyanate shows a significant reactivity with water, (i.e. at around 60 °C for TMXDI based system).

The final step of this preparation process was an amine chain extension which was carried out in the aqueous two phase system. Water soluble, low molecular weight, aliphatic diamine, chain extenders such as ethylene diamine or tetramethylene diamine etc. were preferred. It must be kept in mind that a hydrophilic isocyanate- tipped urethane prepolymer will begin to react with water as soon as the water is introduced. Therefore, the amine chain extender had to be added immediately to the dispersion after the phase inversion from water in oligomer (i.e. transparent) to oligomer in water (i.e. milky white), was formed. This stage normally took a few minutes at 450 rpm stirring speed. Not only are difunctional amines used for the synthesis of linear polyurethanes but higher functionality amines can also be used to obtain crosslinked polyurethanes.

A number of formulations were prepared using this technique, with variations in the balance of isocyanate/polyol/DMPA/chain extender ratio and using various types of polyols that were currently available, and to explore as fully as time and materials would permit, a broad variation of polyurethanes. With all these formulations, the experimental technique developed, provided an easy and trouble free preparation of stable latices of high solids content. In subsequent work, it was found that it was possible to scale up the method to make stable latices on a large scale.

The technique established in the present work appears to be eminently suitable to prepare a wide range of materials. It is anticipated that further work along the lines advocated in this thesis can form the basic route for industrial manufacture of a wide range of polyurethane products which are environmentally friendly.
6.2 The structure-property relationships of water based polyurethane dispersions

In general, polyurethanes structures are built up from the three basic components, isocyanate, polyol and chain extender. However, with water dispersed polyurethane systems, an extra component of a hydrophilic emulsifier is used.

A range of polyurethane dispersions were synthesised. The study parameters were divided into four groups which corresponded to the four basic components of water dispersed polyurethane systems, i.e. as follow:

- **Series A**: Effect of isocyanate building block ratio
- **Series B**: Effect of carboxylic ionic emulsifier block ratio
- **Series C**: Effect of aliphatic amine chain extender types
- **Series D**: Effect of polyol types and molecular weight.

The summary of the formulations are shown in Table 5.3 in Section 5.2.1. The pH, viscosity, particle size and surface tension of the resulting dispersions for each of the series of dispersions made are shown in Table 6.1.

6.2.1. Appearance of dispersions and their stability.

**Series A.** With increasing isocyanate building block ratio in TMXDI/Capa 220/DMPA/MPMDA based dispersions from 3/1/1/1 (ISO 3) to 6/1/1/4 (ISO 6), the dispersions were all milky white stable latices. However, the dispersions with an isocyanate building block ratio higher that 6/1/1/4 (ISO 6) were found to be unstable. ISO 7 (with the equivalent block ratio of 7/1/1/5), flocculated and ISO 8 (with the equivalent block ratio of 8/1/1/6), coagulated respectively. Destabilisation occurred during the synthesis and the latices could not be used in the characterisation programme.

**Series B.** Increasing carboxylic ionic emulsifier block ratio in TMXDI/Terathane 2000/DMPA/MPMDA based dispersion from 1/0.4/0.1/0.5 (CBG 010) to 1/0.1/0.4/0.5 (CBG 040), resulted in dispersions which were all milky white stable latices. The exception was the dispersion (CBG 010) with the carboxylic ionic emulsifier block ratio at 1/0.4/0.1/0.5, which coagulated in the reaction vessel and could not be used in the characterisation programme.
Table 6.1 The water dispersed polyurethane latex properties.

<table>
<thead>
<tr>
<th>Code letter</th>
<th>Equivalent mole block ratio NCO/OH/DMPA/CE</th>
<th>DMPA molar block per total molar block of polymers</th>
<th>pH</th>
<th>Viscosity (mPa.s)</th>
<th>Particle size (µm)</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series A: Effect of isocyanate building block ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO 3</td>
<td>1.0/0.333/0.333/0.33 (3/1/1/1)</td>
<td>0.167</td>
<td>10.4</td>
<td>0.122 - 0.148</td>
<td>0.130</td>
<td>45.8</td>
</tr>
<tr>
<td>ISO 4</td>
<td>1.0/0.250/0.25/0.50 (4/1/1/2)</td>
<td>0.125</td>
<td>10.2</td>
<td>0.145 - 0.195</td>
<td>0.168</td>
<td>46.2</td>
</tr>
<tr>
<td>ISO 5</td>
<td>1.0/0.200/0.20/0.60 (5/1/1/3)</td>
<td>0.100</td>
<td>9.9</td>
<td>0.188 - 0.273</td>
<td>0.231</td>
<td>46.4</td>
</tr>
<tr>
<td>ISO 6</td>
<td>1.0/0.167/0.167/0.67 (6/1/1/4)</td>
<td>0.083</td>
<td>9.2</td>
<td>0.240 - 0.358</td>
<td>0.299</td>
<td>47.1</td>
</tr>
<tr>
<td>ISO 7</td>
<td>1.0/0.143/0.143/0.72 (7/1/1/5)</td>
<td>0.071</td>
<td></td>
<td></td>
<td>Flocculation</td>
<td></td>
</tr>
<tr>
<td>ISO 8</td>
<td>1.0/0.125/0.125/0.75 (8/1/1/6)</td>
<td>0.063</td>
<td></td>
<td></td>
<td>Coagulation</td>
<td></td>
</tr>
<tr>
<td>Series B: Effect of carboxylic ionic emulsifier block ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 010</td>
<td>1.0/0.40/0.10/0.5 (10/4/1/5)</td>
<td>0.050</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 020</td>
<td>1.0/0.30/0.20/0.5 (10/3/2/5)</td>
<td>0.100</td>
<td>8.4</td>
<td>0.192 - 0.259</td>
<td>0.231</td>
<td>45.5</td>
</tr>
<tr>
<td>CBG 025</td>
<td>1.0/0.25/0.25/0.5 (10/2.5/2.5/5)</td>
<td>0.125</td>
<td>8.7</td>
<td>0.199 - 0.247</td>
<td>0.223</td>
<td>45.0</td>
</tr>
<tr>
<td>CBG 030</td>
<td>1.0/0.20/0.30/0.5 (10/2/3/5)</td>
<td>0.150</td>
<td>8.9</td>
<td>0.192 - 0.229</td>
<td>0.211</td>
<td>43.9</td>
</tr>
<tr>
<td>CBG 040</td>
<td>1.0/0.10/0.40/0.5 (10/1/4/5)</td>
<td>0.200</td>
<td>9.0</td>
<td>0.188 - 0.220</td>
<td>0.204</td>
<td>43.2</td>
</tr>
<tr>
<td>Series C: Effect of aliphatic amine chain extender types</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDA</td>
<td>1.0/0.30/0.20/0.5 (10/3/2/5)</td>
<td>0.100</td>
<td>9.1</td>
<td>0.186 - 0.217</td>
<td>0.201</td>
<td>47.1</td>
</tr>
<tr>
<td>TMDA</td>
<td>1.0/0.30/0.20/0.5 (10/3/2/5)</td>
<td>0.100</td>
<td>9.1</td>
<td>0.190 - 0.224</td>
<td>0.207</td>
<td>47.4</td>
</tr>
<tr>
<td>HMDA</td>
<td>1.0/0.30/0.20/0.5 (10/3/2/5)</td>
<td>0.100</td>
<td>9.0</td>
<td>0.188 - 0.207</td>
<td>0.198</td>
<td>47.3</td>
</tr>
<tr>
<td>MPMDA</td>
<td>1.0/0.30/0.20/0.5 (10/3/2/5)</td>
<td>0.100</td>
<td>9.1</td>
<td>0.192 - 0.219</td>
<td>0.206</td>
<td>46.3</td>
</tr>
<tr>
<td>Series D: Effect of polyol types and molecular weight</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>1.0/0.20/0.30/0.5 (10/2/3/5)</td>
<td>0.150</td>
<td>9.0</td>
<td>0.256 - 0.315</td>
<td>0.285</td>
<td>46.2</td>
</tr>
<tr>
<td>C2</td>
<td>1.0/0.20/0.30/0.5 (10/2/3/5)</td>
<td>0.150</td>
<td>8.7</td>
<td>0.208 - 0.250</td>
<td>0.229</td>
<td>46.8</td>
</tr>
<tr>
<td>C4</td>
<td>1.0/0.20/0.30/0.5 (10/2/3/5)</td>
<td>0.150</td>
<td>8.2</td>
<td>0.132 - 0.141</td>
<td>0.136</td>
<td>48.1</td>
</tr>
<tr>
<td>PT1</td>
<td>1.0/0.20/0.30/0.5 (10/2/3/5)</td>
<td>0.150</td>
<td>8.9</td>
<td>0.168 - 0.204</td>
<td>0.186</td>
<td>44.3</td>
</tr>
<tr>
<td>PT2</td>
<td>1.0/0.20/0.30/0.5 (10/2/3/5)</td>
<td>0.150</td>
<td>8.5</td>
<td>0.137 - 0.177</td>
<td>0.157</td>
<td>44.8</td>
</tr>
<tr>
<td>PT29</td>
<td>1.0/0.20/0.30/0.5 (10/2/3/5)</td>
<td>0.150</td>
<td>8.1</td>
<td>0.128 - 0.142</td>
<td>0.135</td>
<td>46.6</td>
</tr>
</tbody>
</table>
Series C. Varying the amine chain extender types in the TMXDI/Capa 220/DMPA based dispersion systems, at the same equivalent molar block ratio of 1/0.3/0.2/0.5, gave dispersions which were all milky white stable latices.

Series D. Varying the molecular weight and types of polyol, (here molecular weight from 1000 to 4000 for Capas and from 1000 to 2900 for Terathanes), in TMXDI/DMPA/MPMDA based dispersions at the constant block ratio of 1/0.2/0.3/0.5, gave dispersions which were all milky white stable latices.

For dispersions in both series A and B, instability occurred when the equivalent carboxylic, ionic-emulsifier molar block per total molar block of polyurethanes fell below 0.083. The unstable dispersions seen from Table 6.1 such as ISO 7, ISO 8 and CBG 010 had (equivalent carboxylic emulsifier molar block per total molar block of polyurethane) ratios of 0.071, 0.063 and 0.050, respectively. This showed that reducing the proportion of pendant carboxylic groups in a polymer's structure, decreased the hydrophilicity to a critical point when latex instability occurred during the reaction. In series C and D, the dispersions took place at a constant equivalent molar ratio, with the equivalent carboxylic emulsifier molar block per total molar block of polyurethane ratio, of 0.100 and 0.150, respectively. These values were above the probable critical point of instability of these types of dispersion, hence giving stable dispersions.

Water compatible polymers were created by producing quaternary ammonium salts by the reaction of an anionic carboxylic acid, (i.e. here DMPA) with a water soluble cation, (i.e. here a tertiary amine) in aqueous conditions. Ideally a quaternary salt should have a multiplicity of hydrophilic sites on the surface of a polymer particle to render it water compatible. The dispersion stability may be explained by the amount of carboxylic groups on the surfaces of the polyurethane particles, and in term of the electric charges of the carboxylic groups. The presence on the particle surface of multiple electric charges of similar polarity will cause mutual coulombic repulsion between the particles. Therefore, higher amounts of negatively charged carboxylic groups on the surface of the particle will lead to higher coulombic repulsion between the particles, which gives greater stability to the dispersion.
6.2.2 pH

In series A, with increasing isocyanate building block ratio from 3/1/1/1 (ISO 3) to 6/1/1/4 (ISO 6), the pH of the dispersions become less alkaline, i.e. from 10.4 to 9.2. In series B, increasing the carboxylic ionic emulsifier block ratio from 1/0.3/0.2/0.5 (CBO 020) to 1/0.1/0.4/0.5 (CBO 040), gave dispersions whose pH's increased from 8.4 to 9.0, respectively.

The pH values of both series A and B, increased with higher DMPA molar block content. This was contrary to the conventional expectation, i.e. higher pendent carboxylic groups should provide lower pH. This is explained from the higher concentrations of pendent carboxylic groups needing more triethyl amine to neutralise the carboxylic groups to form quaternary ammonium salts. In this programme, 5% extra weight of triethylamine was added to ensure all the carboxylic groups were neutralised and also to improve the water compatibility of the dispersion. Therefore, it was likely that the residual triethylamine increased the pH value of the resulting dispersions.

Varying the amine chain extender types in series C, resulted in the pH of the dispersions remaining constant at around 9.1. This was not surprising since the reaction block ratio was keep constant.

In series D, varying molecular weight and types of polyol, the pH values of both polyol based dispersions showed the same trend. Both types of polyol showed that pH decreases with higher molecular weight of polyol. The pH values of Capas based dispersions decreased from 9.0 to 8.2, while Terathanes based dispersions decreased from 8.9 to 8.1. This was due to keeping the same batch size in all formulations and the higher molecular weight of polyol based dispersions required lower amounts of DMPA, (see Table 5.4d). The amount of triethylamine used was directly proportional to the amount of the DMPA present in the dispersion. Therefore, lower amounts of triethylamine were added and remained in the higher molecular weight polyol based system, and pH values decreased as expected. Capa based dispersions had slightly higher pH values than Terathane based dispersions for the same equivalent weight of polyol.
6.2.3 Viscosity

For series A, with increasing the isocyanate block ratio from 3/1/1/1 (ISO 3) to 6/1/1/4 (ISO 6), the viscosity of dispersions decreased from 140 to 41 mPa.s. It should be noted that the lowest isocyanate building block ratio (ISO 3) had a much higher value (i.e. 140 mPa.s) than the other dispensations in the series which had values between 40 to 60 mPa.s.

In series B, increasing the carboxylic ionic emulsifier block ratio from 1/0.3/0.2/0.5 (CBG 020) to 1/0.1/0.4/0.5 (CBG 040), viscosity of the dispersion increased from 40 to 153 mPa.s. The dispersion with the highest carboxylic emulsifier block ratio (CBG 040) had a substantially higher viscosity value (i.e. 153 mPa.s) than other formula in the series which had viscosities between 40 to 73 mPa.s.

Both in series A and B, the viscosities increased with higher concentrations of pendent carboxylic groups in the urethane structure. This can be explained by the stability of dispersion systems. Higher contents of carboxylic groups at the surface of the polyurethane particle will cause greater coulombic repulsion forces leading to a reduced tendency to aggregate into larger particles and also there are more particles per unit volume of dispersion. The viscosity of a fluid is a measurement of its resistance to flow and is closely related to the particle size and content. If the particle size become smaller for a given solids content, the number of particles in dispersion systems will be relative high and there will be more particle collisions leading to greater resistance to flow and therefore higher viscosity.

Dispersion viscosities increased dramatically when the pendent carboxylic groups (DMPA) molar block per total polyurethane molar block ratios rise above 0.150; for example ISO 3 and CBG 040 which had DMPA molar block per total polyurethane molar block ratios of 0.167 and 0.200 respectively. This may be explained by the polyurethanes being highly hydrophilic and were solubilised in water. As a result they showed an increasing tendency for their chains to partially uncoil and interact with water molecules and hence promote higher viscosity. Figure 6.2 shows the relationship of dispersion viscosity and DMPA molar block per total polyurethane molar block.
In series C, with a fixed carboxylic molar block per total polyurethane block ratio at 0.1 but varying amine chain extender types, the viscosity of dispersions increased from 70 to 96 mPa.s as the number of the methylene groups increased from 2 to 6 in the linear amine chain extender structure. With longer chain extender lengths, slightly less carboxylic group was required in the formulation to keep the same reaction batch size. The viscosity of MPMDA, (i.e. with the side methyl groups) based dispersion had a lower viscosity of 40 mPa.s, (cf. linear amine chain extender based dispersions). This might be due to the pendent methyl group in MPMDA providing an irregular shape at the particle surface leading to increase in distance between the polyurethane particles, so that there was more water between each particle leading to easier flow of the dispersion.

In series D, using a fixed DMPA molar block ratio per total polyurethane molar block of 0.150, and varying the molecular weight and types of polyol in the dispersion, both of the polyol based dispersions showed the same trends. The viscosities of dispersions increased with the higher molecular weight of polyol. Viscosities of Capas based dispersions increased from 39 to 53 mPa.s and those of Terathanes based dispersions increased from 53 to 98 mPa.s. This indicated that the dispersion viscosity was not only affected by the pendent carboxylic group content but also by the molecular weight of polyol. This could be explained by the
ether or ester linkages in polyol segments interacting with water and increasing the overall compatibility of polyol-water molecules. This would have prevented the particles aggregating into a larger particles, which would otherwise lead to a lower viscosity.

The Capa based dispersions had lower viscosity values than Terathane based dispersions at the same equivalent molecular weight of polyol. This was believed to be due to polycaprolactone polyol components tendency to be more polar, so they will aggregate to form larger particles than polytetramethylene glycol based dispersions. This is also supported by the particle size analysis, (see later).

6.2.4 Particle size and size distribution

The average particle size of all stable dispersions was 0.1 to 0.3 μm.

For series A, with increasing isocyanate building block ratio, (i.e. from 3/1/1/1 to 6/1/1/4), the average particle size of the dispersions increased from 0.130 μm to 0.299 μm. As shown in Figure 6.3, the particle size distribution curve became broader in shape with higher isocyanate building block ratio.

For series B, increasing the carboxylic emulsifier block ratio (i.e. from 1/0.3/0.2/0.5 to 1/0.1/0.4/0.5), gave average particle sizes of dispersion which decreased from 0.231 to 0.204 μm respectively. The particle size distribution curve became slightly narrower with higher carboxylic ionic emulsifier block ratio, indicating a less broad distribution of slightly smaller particles, (see Figure 6.4).

In both series A and B, the particle size was increased with lower pendent carboxylic content, as expected. As the pendent carboxylic group content decreased, less coloumbic repulsion resulted. Aggregation may be increased during polymerisation, leading to larger particles. The particle distribution curve becomes narrower with higher pendent carboxylic group content. As more carboxylic groups become available at the surface of polyurethane particles, a more homogeneous distribution of particle size resulted. This observation is supported by the studies of Dieterich, D.(6.3) and Kim C.K.(6.4)

In series C, by varying the amine chain extender types, the particle size of dispersion remained almost constant at around 0.20 μm, as shown in Figure 6.5. The particle size distribution curve became slightly higher in magnitude and the shape slightly shifted towards the lower particle size, with the higher numbers of
methylenegroups in the amine chain extender structure. This indicated that longer chain extenders might be more beneficial and promote more homogeneous particle sizes. The MPMDA based dispersion, (i.e. with the side methyl group) had the highest magnitude and broadest shape of the particle size distribution curves, as indicated in Figure 6.5. This was believed to be due to the side methyl group promoting an steric irregular urethane particles.

Varying the molecular weight and types of polyol in the dispersions, as in series D, resulted in the particle sizes of both types of polyol based dispersions showing the same trend. The particle size of dispersions decreased with higher molecular weight of polyol. Capas based dispersion sizes decreased from 0.285 to 0.136 μm, while Terathanes based dispersions decreased from 0.186 to 0.135 μm. This is believed to be due to a higher overall compatibility of polyol-water in higher molecular weights of polyol based dispersion leading to smaller particle sizes. The particle size distribution curve from both polyol based dispersions also showed the same trends. With higher molecular weight of the polyol, the magnitude and the shape of the curve became higher and narrower, (see Figure 6.6 and 6.7). The Capas based dispersion had a higher particle size than Terathanes based dispersions for the same equivalent molecular weight of polyol. This was due to polycaprolactone being more polar than polytetramethylene glycol, leading to greater particle aggregation.

6.2.5 Surface tension

The principal results for surface tension measurements of the various dispersion made by the Du Nouy ring technique are given in Table 6.1.

For series A with increasing isocyanate building block ratio, (i.e. from 3/1/1/1 to 6/1/1/4), the surface tension values of the dispersions were slightly increased from 45.8 to 47.1 mN/m.

Increasing the carboxylic emulsifier block ratio, (i.e. from 1/0.3/0.2/0.5 to 1/0.1/0.4/0.5) in series B, showed the surface tension values of the dispersions slightly decreased from 45.5 to 43.2 mN/m.

In series C, with varying amine chain extender types, the surface tension value of the dispersions were almost constant at around 47 mN/m. The MPMDA based
dispersion, (i.e. with the side methyl group) had the slightly lower surface tension value compared to others from linear chain extenders, (i.e. 46.3 mN/m).

In series D in with the molecular weight and types of polyol in the dispersion being varied, both polyol based dispersions showed similar trends. The surface tension of the dispersions increased with the higher molecular weight of polyol. Capa based dispersions with the molecular weight of polyol from 1000 to 4000 had the surface tension values of 46.2 to 48.1 mN/m respectively, while Terathane based dispersions with the molecular weight varying from 1000 to 2900 had the surface tension values of 44.3 to 46.6 mN/m respectively. The Capa based dispersion had a higher surface tension than Terathane based dispersions for the same equivalent molecular weight of polyol.

Pure water has a surface tension of about 72 mN/m. The surface tension values of all the stable dispersions produced were in the range of 43 to 49 mN/m. Generally there were small or insignificant differences between any of the four series of dispersions as listed in Table 6.1.

It would be expected in any coating applications that any one of these stable dispersions could be applied to a clean surface of high surface free energy such as metals or ceramics, and wetting and spreading will result. Coating problems will arise when trying to apply them as coatings or adhesives to many types of polymers, which have lower surface free energy values than the surface tension values of these dispersions, and as a result non-wetting would be expected. Surface treatment of polymers, for example by oxidative methods, or the application of suitable primers, or use of additional surfactant materials in the dispersions may overcome this problem. Evidence from casting dispersions on to cleaned aluminium sheet to make the sheet samples, showed that wetting or spreading readily occurred. Adhesion was excellent unless a release agent was first applied.

It must be remembered that the molecular layer present on the surface of the liquid gives rise to the surface tension property of a liquid. Therefore it is possible any one or any combination of the following factors will contribute to the reduction of water’s surface tension in the polymer dispersions: (6.5-6.7)

i) aqueous solution formed from residual reactants;
ii) phase separated residual reactant present at the surface of the dispersions;
iii) interaction of polymer particles with the surface molecules of dispersions.
However, because trends were consistent, in series A and B the surface tension value were slightly reduced with higher concentrations of carboxylic ionic emulsifiers. This could have been due to the carboxylic group acting as a surfactant at the surface of polyurethane particle which, as concentration increases, will reduce the surface free energy of the particle.

Surface tension was unaffected by the length of the chain extender but with MPMDA based dispersion, the dispersion had a slightly lower surface tension value than those for other chain extenders. This was possibly due to the side methyl group increasing the phase separation of the particles and also lowering the balance of the surface free energy of the polyurethane particle leading to the lower surface tension value.

The surface tension values were slightly increased with higher molecular weights of polyol. This is believe to be due to the lesser number of carboxylic groups available on the surface of the urethane particles. Therefore a higher surface free energy of the particle will be obtained. Polycaprolactone based dispersions had higher surface tension values than polytetramethylene glycol based dispersions for comparable formulations.

![Differential Volume](image)

Figure 6.3 Effect of isocyanate building block ratio on particle size distribution
Figure 6.4 Effect of carboxylic ionic emulsifier block ratio on particle size distribution

Figure 6.5 Effect of chain extender types on particle size distribution
Figure 6.6 Effect of molecular weight of polycaprolactone on particle size distribution

Figure 6.7 Effect of molecular weight of polytetramethylene glycol on particle size distribution
References

6.2 U.S. Patent 4,460,738., 1984
6.5 Shaw, D.J., "Introduction to Colloid and Surface Chemistry ", 3rd edit., p60-86, Butterworth & Co., 1980
Chapter 7 Structure-Property Relationships of Water Dispersed Polyurethanes in Solid Cast Film

This chapter focuses on the properties of cast films formed from water dispersed urethane-urea copolymers. In this study, formulation parameters were the same as those used in the latex production form, (see Section 5.2.1). However, only the formulations giving stable latices were selected for this stage of the programme. A summary of various formulations is shown in Table 7.1.

7.1 Water dispersed polyurethanes film formation

Commercially, polymer dispersions are manufactured and applied as liquids and then converted into solid films for use such as coating, dipping, casting etc. Polyurethane latex is a dispersion of high molecular weight polymer, (either as a thermoplastic or thermoset) in water and stabilised by negative charge repulsion at the surfaces of the particles. When a dry film is prepared, the forces that stabilise the dispersion of latex particles are overcome and the particles will coalesce into a continuous film. The film formation can be generally described in the following steps,(7.1 - 7.3)

In a latex, the particles move around in Brownian motion. However, as the water evaporates, the solids content increases and their movement becomes more restricted, so the particles are forced to come closer and closer together. As they approach each other, uniform shrinkage of the inter-particle distances occurs and the water-air interfacial tension gradually forces the particles into packed arrays with their double electrical layers in contact. On further drying, as more water is lost, the void spaces are gradually filled by particle sliding and deformation. Coalescence results in the formation of a dense packing of the latex particles. When water has almost completely evaporated, the particles have increased surface forces causing more coalescence, overcoming the repulsive forces between the particles, resulting in many polymer-polymer contacts. Further coalescence by inter-diffusion of polymer chains of neighbouring particles gradually takes place. At this stage, a small amount of water remains in the film which has to diffuse through the polymer particles to the air/polymer interface. Time is required for the "dry" film to reach equilibrium. This can be reduced by conditioning the film at higher temperatures to
Table 7.1 A summary of the formulation variations

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>Equivalent molar ratio, respectively: NCO/OH/DMPA/CE</th>
<th>Hard Segment * (% wt)</th>
<th>Urea content* (% wt)</th>
<th>COOH Content* (% wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series A: Effect of isocyanate block ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO 3</td>
<td>1.0/0.333/0.333/0.33 (3/1/1/1)</td>
<td>33.5</td>
<td>4.2</td>
<td>3.0</td>
</tr>
<tr>
<td>ISO 4</td>
<td>1.0/0.250/0.250/0.50 (4/1/1/2)</td>
<td>40.1</td>
<td>6.9</td>
<td>2.6</td>
</tr>
<tr>
<td>ISO 5</td>
<td>1.0/0.200/0.200/0.60 (5/1/1/3)</td>
<td>46.0</td>
<td>9.4</td>
<td>2.4</td>
</tr>
<tr>
<td>ISO 6</td>
<td>1.0/0.167/0.167/0.67 (6/1/1/4)</td>
<td>50.8</td>
<td>11.4</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Note
• Fixed polyol as Capa 220
• Fixed molar block ratio of polyol to pendent carboxylic acid as 1:1
• Increased molar block ratio of NCO/polyol, therefore hard segment content increased, ISO 6 had the highest hard segment content.
• Increased molar block ratio of NCO/carboxylic acid, therefore the molar block ratio of pendent carboxylic acid per total molar block of polyurethanes decreased, ISO 6 had the lowest pendent carboxylic acid content.
• Increased molar block ratio of NCO/amine chain extender, therefore urea content increased, ISO 6 had the highest urea content.

Series B: Effect of carboxylic ionic emulsifier block ratio

| CBG 020 | 1.0/0.30/0.20/0.5 (10/3/2/5) | 35.6 | 6.3 | 1.8 |
| CBG 025 | 1.0/0.25/0.25/0.5 (10/2.5/2.5/5) | 40.4 | 7.1 | 2.6 |
| CBG 030 (PT2) | 1.0/0.20/0.30/0.5 (10/2/3/5) | 46.3 | 7.9 | 3.6 |
| CBG 040 | 1.0/0.10/0.40/0.5 (10/1/4/5) | 64.3 | 10.7 | 6.4 |

Note
• Fixed polyol as Terathane 2000
• Increased molar block ratio of NCO/carboxylic acid, therefore anionic species increased, CBG040 had the highest pendent carboxylic acid content.
• Increased molar block ratio of NCO/polyol, therefore hard segment content increased, CBG040 had the highest hard segment content.

Series C: Effect of chain extender types

| EDA | 1.0/0.3/0.2/0.5 (10/3/2/5) | 35.4 | 3.5 | 2.4 |
| TMDA | 1.0/0.3/0.2/0.5 (10/3/2/5) | 36.4 | 5.0 | 2.4 |
| HMDA | 1.0/0.3/0.2/0.5 (10/3/2/5) | 37.4 | 6.5 | 2.2 |
| MPMDA | 1.0/0.3/0.2/0.5 (10/3/2/5) | 37.5 | 6.7 | 2.2 |

Note
• Fixed polyol as Capa 220
• Fixed molar block ratio, therefore the pendent carboxylic acid content constant
• Hard segment content slightly increased with longer chain extender length

Series D: Effect of polyol types and molecular weight

| C1 | 1.0/0.2/0.3/0.5 (10/2/3/5) | 63.1 | 10.7 | 5.0 |
| C2 | 1.0/0.2/0.3/0.5 (10/2/3/5) | 46.0 | 7.8 | 3.6 |
| C4 | 1.0/0.2/0.3/0.5 (10/2/3/5) | 29.9 | 5.1 | 2.4 |
| PT1 | 1.0/0.2/0.3/0.5 (10/2/3/5) | 63.1 | 10.7 | 5.0 |
| PT2 (PT2) | 1.0/0.2/0.3/0.5 (10/2/3/5) | 46.0 | 7.8 | 3.6 |
| PT29 | 1.0/0.2/0.3/0.5 (10/2/3/5) | 37.2 | 6.3 | 3.0 |

Note
• Fixed molar block ratio of isocyanate/polyol/carboxylic acid/chain extender
• Varied polyol molecular structure (Capa and Terathane)
• Increased the molecular weight, therefore hard segment content and pendent carboxylic acid content decreased, lowest polyol molecular weight had the highest of both per unit chain length.

Note *see appendix 4 for the calculation of hard segment content, urea content and COOH content
accelerate the film to an equilibrium dry point. The physical properties of the film improve considerably during this ageing period, presumably as a result of interdiffusion of molecules.

In practice there is a minimum temperature at which films from any particular latex can be formed. This temperature is known as the minimum film formation temperature (MFFT) and is influenced by the glass transition temperature (Tg) of the polymer. The effect of water content, coalescing solvent or volatile impurities in the polymer can also play an important role on the MFFT. In practice, the MFFT must usually be less than the temperature at which the film is made.

7.2 Visual appearance of cast films

The visual appearance of each cast film was examined with the naked eye. Dry, solid cast films were of approximately 2 mm thickness, they were all transparent and had very low colouration. Films containing visual defects were rejected.

Series A films with increasing isocyanate content changed from a slightly water white to very pale yellow colour and also from soft elastic materials to tougher elastic materials with higher isocyanate block ratio.

In series B, with increasing pendent carboxylic emulsifier block ratio, the films changed from very pale yellow to slight water white colour and also from soft elastic materials to harder elastic materials with higher carboxylic emulsifier block ratio.

Changing the chain extender types as in series C showed no differences in sample colouring, they are all very pale yellow and elastic materials.

For series D, with changing polyol type and molecular weight, the samples based on low molecular weight polyol were very pale yellow and hard elastic materials and changed to slightly water white and softer elastic materials with increasing molecular weight. The Capa based cast films were slightly whiter in colour than Terathane based cast films.

For all the formulations, the colour of the films became whiter with either higher concentration of carboxylic emulsifier or higher molecular weight of polyol.
Therefore, it can be assumed that both of these chemicals features contribute to the colour of polymer. Higher concentration of carboxylic emulsifier leads to higher hydrophilicity suggesting higher moisture absorbance in the solid polymer. The higher molecular weight of polyol will lead to greater tendency for the polyurethanes to crystallise. Both residual water content and crystallisation of the polyol component in the chains may have caused the whiter products. The milky white colour disappeared when any sample was heated, but reappears especially in a damp atmospheres.

7.3 Differential scanning calorimetry (DSC)

7.3.1 Analysis of polyols

DSC analyses of the polycaprolactone and polytetramethylene glycol polyols were carried out to determine their Tg and Tm so that comparisons could be made with the cast polyurethanes. DSC thermograms of the base polyols are shown in Figures 7.1 and 7.2 and a summary of the thermal properties result is given in Table 7.2

<table>
<thead>
<tr>
<th>Polyl</th>
<th>Transition temperature (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capa 210</td>
<td>20, 31, 48*</td>
<td>three exothermic peaks baseline shift at -70 °C and -30 °C</td>
</tr>
<tr>
<td>(Mw. 1000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capa 220</td>
<td>15, 59*</td>
<td>two exothermic peaks, shoulder at second peak baseline shift at -70 °C and -27 °C</td>
</tr>
<tr>
<td>(Mw. 2000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capa 240</td>
<td>70*</td>
<td>one single exothermic peak baseline shift at -70 °C</td>
</tr>
<tr>
<td>(Mw. 4000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Terathane 1000</td>
<td>19, 38*</td>
<td>two exothermic peaks, shoulder at first peak baseline shift at -82 °C and -43 °C</td>
</tr>
<tr>
<td>(Mw. 1000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Terathane 2000</td>
<td>18, 44*</td>
<td>two exothermic peaks baseline shift at -80 °C and -23 °C</td>
</tr>
<tr>
<td>(Mw. 2000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Terathane 2900</td>
<td>45*</td>
<td>one single exothermic peak baseline shift at -80 °C</td>
</tr>
<tr>
<td>(Mw. 2900)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes:
1. The transition temperature marked * was the largest peak transitions.
2. All Capa polyols showed a baseline shift at around -70 °C.
3. The largest melting peak of all polyol, (either Capa or Terathane) was shifted to the higher temperatures with increasing molecular weight of polyol.
4. All Terathane polyols showed a baseline shift at around -80 °C.
The most notable feature found in some of the polyol thermograms, was the presence of more than one endothermic peak. In all cases the largest endothermic peak was relatively narrow which corresponded to the melting temperature of polyol given by the manufacturer (7.7, 7.8); (see Table 7.3). Generally the melting peak was related to the molecular weight of polyol: higher the molecular weight of polyol, higher melting peak temperature was found. The separated peaks in the Capa 210, Capa 220, Terathane 1000 and Terathane 2000 suggested that these polyols were blends, the ratio of blend being designed to obtain a specific average molecular weight or for required performance in the end product.

Table 7.3 The melting temperature of polycaprolactone (Capa) and polytetramethylene glycol (Terathane) polyols

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Melting temperature from the experiment (°C)</th>
<th>Melting temperature range from the manufacturer (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capa 210</td>
<td>48 ± 3</td>
<td>30 to 40</td>
</tr>
<tr>
<td>Capa 220</td>
<td>59 ± 3</td>
<td>40 to 50</td>
</tr>
<tr>
<td>Capa 240</td>
<td>70 ± 3</td>
<td>55 to 60</td>
</tr>
<tr>
<td>Terathane 1000</td>
<td>38 ± 3</td>
<td>25 to 33</td>
</tr>
<tr>
<td>Terathane 2000</td>
<td>44 ± 3</td>
<td>28 to 40</td>
</tr>
<tr>
<td>Terathane 2900</td>
<td>50 ± 3</td>
<td>30 to 43</td>
</tr>
</tbody>
</table>

7.3.2 Analysis of cast films

The summary of results obtained by DSC of cast films of water dispersed systems are shown in Table 7.4, while the DSC thermograms are shown in Figure 7.3 to 7.7.

All the DSC thermograms showed a number of transitions. Details and assignations are as follows:

i) Tg's were between -80 to -45°C.

ii) A second transition occurred between 55 to 95°C. This is thought to be associated with the combination of melting of the soft segments of the polyurethanes and the disruption of the hard segment domains with limited short range orders (7.9-7.10).

iii) A third transition, which was relatively weak, occurred between 165 to 210°C. This is thought to be associated with dissociation of the hard segment domains containing long range ordered urethane-urea hard segment (7.9-1.10).
iv) Probable onset of degradation temperature occurred between approximately 225 and 255°C.

v) There was no evidence of sharp crystalline melting temperatures for any of the polymers except at the low hard segment content, (i.e. below 37.5%) of Capa based cast films.

vi) Polyurethanes based on both types of polyol showed similar trends. Tg increased with lower molecular weight of polyol and the size of the transition became difficult to detect. The second transition and degradation temperatures were shifted to lower temperatures and the shape of the transitions became narrowed and sharper with higher molecular weight of polyol. The Terathane based polyurethanes had lower Tg value than Capa based cast films (at the same molecular weight).

Table 7.4 DSC: Summary of results of urethane-urea copolymers dispersion cast films

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>Tg (°C)</th>
<th>Other transition temperature (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Second</td>
<td>Third</td>
</tr>
<tr>
<td>Series A: Effect of isocyanate building block ratio</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO 3</td>
<td>-57</td>
<td>54</td>
<td>180</td>
</tr>
<tr>
<td>ISO 4</td>
<td>-52</td>
<td>75</td>
<td>184</td>
</tr>
<tr>
<td>ISO 5</td>
<td>-51</td>
<td>88</td>
<td>200</td>
</tr>
<tr>
<td>ISO 6</td>
<td>-47</td>
<td>95</td>
<td>207</td>
</tr>
<tr>
<td>Series B: Effect of carboxylic ionic emulsifier block ratio</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 020</td>
<td>-79</td>
<td>62</td>
<td>207</td>
</tr>
<tr>
<td>CBG 025</td>
<td>-76</td>
<td>65</td>
<td>190</td>
</tr>
<tr>
<td>CBG 030 (=PT2)</td>
<td>-73</td>
<td>73</td>
<td>177</td>
</tr>
<tr>
<td>CBG 040</td>
<td>-70</td>
<td>75</td>
<td>165</td>
</tr>
<tr>
<td>Series C: Effect of chain extender types</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDA</td>
<td>-53</td>
<td>57</td>
<td>199</td>
</tr>
<tr>
<td>TMDA</td>
<td>-53</td>
<td>58</td>
<td>200</td>
</tr>
<tr>
<td>HMDA</td>
<td>-52</td>
<td>57</td>
<td>202</td>
</tr>
<tr>
<td>MPMDA</td>
<td>-53</td>
<td>59</td>
<td>202</td>
</tr>
<tr>
<td>Series D: Effect of polyol types and molecular weight</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>-52</td>
<td>85</td>
<td>205</td>
</tr>
<tr>
<td>C2</td>
<td>-57</td>
<td>82</td>
<td>188</td>
</tr>
<tr>
<td>C4</td>
<td>-62</td>
<td>62</td>
<td>180</td>
</tr>
<tr>
<td>PT1</td>
<td>-60</td>
<td>81</td>
<td>194</td>
</tr>
<tr>
<td>PT2 (=CBG 030)</td>
<td>-72</td>
<td>75</td>
<td>180</td>
</tr>
<tr>
<td>PT29</td>
<td>-75</td>
<td>70</td>
<td>178</td>
</tr>
</tbody>
</table>
Figure 7.1 DSC: The thermal transitions of polycaprolactone polyols
Figure 7.2 DSC: The thermal transitions of polytetramethylene glycol polyols
Figure 7.3 DSC: Effect of isocyanate building block ratio, i.e. from ISO 3 to ISO 6
Figure 7.4 DSC: Effect of carboxylic ionic emulsifier block ratio, i.e. from CBG 020 to CBG 040
Figure 7.5 DSC: Effect of chain extender types, i.e. EDA, TMDA, HMDA, MPMDA
Figure 7.6 DSC: Effect of molecular weight of polycaprolactone polyol segment, i.e. from C1(1000) to C4(4000)
Figure 7.7 DSC: Effect of molecular weight of polytetramethylene glycol segment, i.e. from PT1(1000) to PT29 (2900)
For both the Capa and Terathane based cast films, for series A and B respectively, the intensity of the Tg signal in the thermogram decreased with increasing hard segment content, (see Figure 7.3 and 7.4). The increase of Tg value was almost linear with hard segment content. This effect can be more readily seen in Figure 7.8, with the hard segment content range from 30 to 65%.

For the Capa based cast films, (i.e. series A and D), Tg's for similar hard segment contents were greater than for the corresponding Terathane based cast films, (i.e. series B and D). This reflects the greater capacity for hydrogen bonding of the polyester polyols. The transition results for series D cast films are shown in Figure 7.8 and show the effect of molecular weight on both the polyester and polyether based cast films. C1 to C4, (representing a increase in Capa molecular weight from 1000 to 4000), showed a decrease in Tg, following the consequent decrease in hard segment content and the plasticising action of the longer soft segment. PT1 to PT29 polyether based cast films also showed a similar trend.

In series C, as the amine chain extender length, (i.e. number of methylene groups increased from 2 to 6), the size of the glass transition signal transitions increased but the Tg value for all chain extenders remained constant at around -53 °C, (see Table 7.4 and Figure 7.5). This is believed to be due to the longer amine chains giving more flexible urea hard segments, leading to higher chain mobility but were not sufficient to have a significant increase on the flexibility of the molecule chain. The chain extender with the side methyl group also showed no difference in Tg value.

The second transition occurring at temperatures between 54 to 95 °C in all cast films, is believed to be related to the melting of the soft segments and the disruption of the hard segment domains with limited short range orders.(7.9, 7.10) The results are showed in Figure 7.9, in which the second transition is plotted against the hard segment content. The polyester based cast films in series A, showed a sharper increase in the transition with hard segment content than the polyether based cast films in series B. This is probably due to the increasing hydrogen bonding and to the increasing urea content with hard segment increase.
Figure 7.8 The relationships of Tg and hard segment content of urethane-urea copolymers cast films.

The effect of increasing molecular weight of either the polyester or polyether polyol in series D is also shown in Figure 7.9. Again the second transition temperature was increased with higher hard segment content for both types of polyols. The second transition temperature values for polyester series were slightly greater than those of polyether based cast films; this result was expected because of the greater potential for hydrogen bonding in the polyester based cast films.

No change of a second transition temperature was found in cast film series C. This value was constant at around 58 °C. It was very surprising to see the sharp melting peaks for all the samples obtained in this series, as shown in Figure 7.5. This was also found with sharp melting peak in sample ISO 3 and C4; (see Figure 7.3 and 7.6). It should be noted that all samples showing the sharp melting peak had a hard segment content below 37.5%. This sharp melting peak was due to crystallinity of Capa based polyurethanes with low hard segment content, which was later confirmed by wide angle X-ray diffraction (WAXD). This showed a sharp intensity of scattering angle at around 20° and 24° which is consistent with the studies of Van Borgart(7,11) and Davis, G.P.(7,12). However, it was quite surprising to see no sharp crystallinity in the Terathane based urethane-urea copolymers.
The third transition temperature, (interpreted as the dissociation of the hard segment domains containing long range order(7.9)) and temperature for the onset of degradation, are shown plotted against percentage hard segment in Figures 7.10 and 7.11 respectively. As expected with increasing hard segment content and consequent increase of urea content, enhanced domain interactions resulted in higher transition and degradation temperatures. For series A and D, third transition and degradation temperatures were shifted to higher temperatures, with higher hard segment content or lower molecular weight of soft segment. This is thought to be due to higher hard segment content increasing the hard segment melting point, the interaction between hard phases and also increased phase mixing between hard and soft segments. This will improve the stability of urethane-urea copolymers at high temperatures.

![Graph](image)

Figure 7.9 The relationships of second transition temperature and hard segment content of urethane-urea copolymers cast films.

However, for the polyether based cast film series B, the results are quite different and unexpected. The third transition and degradation temperatures decreased with increasing hard segment content. In cast films series B, increasing hard segment content was also associated with an increase of pendent of carboxylic acid emulsifier (DMPA), unfortunately DMPA was likely to promote polymer decomposition at elevated temperatures, resulting in reduction of both third transition and degradation temperature. (7.13)
It should be noted that the CBG 030 and PT2 cast film (both in the same equivalent molar ratio but PT2 film produced two months later) gave the same range of thermal properties, (see table 7.4). The DSC results were within the experimental error, indicating the reproducibility of this synthesis technique.

In Series C, with hard segment slightly increasing from 35.6 to 37.5 % by weight, and with the longer chain extender length, the resulting third transition and degradation temperatures were almost constant at around 200 °C and 240 °C respectively. This suggests that the variation of the chain extender length is too small (i.e. the number of methylene groups in the amine chain increased from 2 to 6) to produce significant changes. The chain extender with a side methyl group (MPMDA) based polymers also showed no significant difference.

![Figure 7.10 The relationships of third transition temperature and hard segment content of urethane-urea copolymers cast films.](image)
Figure 7.11 The relationships of degradation temperature and hard segment content of urethane-urea copolymers cast films.

7.4 Dynamic mechanical thermal analysis (DMTA)

A summary of results obtained from the thermal analysis by DMTA of the four series of cast films are shown in Table 7.5. The storage modulus (E') and tan δ against temperature of each series are shown in Figures 7.12 to 7.21.

The following general observations for all the cast films formed in the DMTA thermograms are summarised below.

i) Tg increased with increasing the hard segment content or decreasing the molecular weight of polyol. Using the convention of determining Tg from the onset of E' change, there were good matches with those values determined by DSC analysis, (in almost the same range of -85 to -45°C), while individual values were within experimental error of ±5°C. However, using the convention of Tg being at a maximum tan δ peak, comparative resulting temperature values were higher, (i.e. ranging from -70 to -25°C).

ii) Maximum E' below Tg of the four series of cast films are shown in Table 7.5 and Figure 7.22. This generally demonstrates that changing the molecular weight of the soft segment has slightly more effect than changing hard segment content, indicated by the higher slope of maximum E' and hard segment content in series D than series A and B.
iii) $E'$ values at $T_g$ for the four series of films are shown in Table 7.5 and Figure 7.23. These generally demonstrate that changing the molecular weight of soft segment has slightly less effect than changing hard segment content, indicated by the lower slope of $E'$ at $T_g$ against temperature in series D than series A and B.

iv) $E'$ value at 20 °C of four series of cast film are shown in Table 7.5 and Figure 7.24. Here changing hard segment content had more effect than changing the molecular weight of soft segment, indicated by the higher slope of $E'$ at 20 °C against temperature in series A and B than series D.

v) In series C, $E'$ decreased with longer chain extender length. The MPMDA based urethane-urea copolymers cast films, (i.e. with side methyl group) had the highest $E'$ value.

vi) Both polyol types showed similar trends with increasing molecular weight. The maximum $E'$ moved towards the lower temperature and the slope of the $E'$ curve decreased with increasing the molecular weight of polyol, (see Figures 7.18 and 7.20). This reflected a change in morphology, from a phase mixed to phase separated polymer. The $T_g$ value also decreased with increasing polyol molecular weight. This was also supported by DSC analysis.

Table 7.5 DMTA : Summary of results of water dispersed urethane-urea copolymers cast films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>Maximum $E'$ (MPa)</th>
<th>$E'$ at $T_g$ (MPa)</th>
<th>$E'$ at 20°C (MPa)</th>
<th>Maximum tan $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Series A : Effect of isocyanate block ratio

| ISO 3    | -59     | 2885               | 2462              | 35               | -44                 | 0.268 |
| ISO 4    | -57     | 3090               | 2725              | 176              | -41                 | 0.236 |
| ISO 5    | -55     | 3335               | 2950              | 355              | -38                 | 0.165 |
| ISO 6    | -48     | 3595               | 3250              | 650              | -37                 | 0.142 |

Series B : Effect of carboxylic ionic emulsifier block ratio

| CBG 020  | -84     | 2250               | 1925              | 30               | -66                 | 0.216 |
| CBG 025  | -80     | 2515               | 2175              | 55               | -63                 | 0.178 |
| CBG 030 (w/PT2) | -78 | 2850               | 2376              | 165              | -63                 | 0.126 |
| CBG 040  | -74     | 3175               | 2825              | 450              | -60                 | 0.089 |

Series C : Effect of chain extender types

| EDA      | -56     | 3200               | 2906              | 200              | -32                 | 0.142 |
| TMDA     | -55     | 2970               | 2413              | 75               | -35                 | 0.201 |
| HMDA     | -55     | 2750               | 2219              | 45               | -37                 | 0.277 |
| MPMDA    | -53     | 2825               | 2640              | 265              | -30                 | 0.112 |

Series D : Effect of polyol types and molecular weight

| C1       | -49     | 3975               | 3185              | 475              | -26                 | 0.080 |
| C2       | -60     | 2975               | 2789              | 215              | -37                 | 0.169 |
| C4       | -67     | 2000               | 2328              | 95               | -41                 | 0.235 |
| PT1      | -70     | 3460               | 2995              | 450              | -46                 | 0.069 |
| PT2 (w/CG0 20) | -77 | 2775               | 2236              | 145              | -64                 | 0.133 |
| PT29     | -80     | 2410               | 1850              | 75               | -70                 | 0.227 |
Figure 7.12 Series A: Effect of isocyanate building block ratio on E'

Figure 7.13 Series A: Effect of isocyanate building ratio on tan δ
Figure 7.14 Series B: Effect of carboxylic ionic emulsifier block ratio on $E'$

Figure 7.15 Series B: Effect of carboxylic ionic emulsifier block ratio on $\tan \delta$
Figure 7.16 Series C: Effect of chain extender types on $E'$

Figure 7.17 Series C: Effect of chain extender types on $\tan \delta$
Figure 7.18 Series D: Effect of molecular weight of polycaprolactone on $E'$

Figure 7.19 Series D: Effect of molecular weight of polycaprolactone on tan $\delta$
Figure 7.20 Series D: Effect of molecular weight of polytetramethylene glycol on $E'$

Figure 7.21 Series D: Effect of molecular weight of polytetramethylene glycol on $\tan \delta$
Figure 7.22 The relationships of maximum $E'$ and hard segment content of urethane-urea copolymers cast films

Figure 7.23 The relationships of $E'$ at $T_g$ and hard segment content of urethane-urea copolymers cast films
Figure 7.24 The relationships of $E'$ at 20 °C and hard segment content of urethane-urea copolymers cast films.

Figure 7.25 The relationships of $T_g$ and hard segment content of urethane-urea copolymers cast films obtained by DMTA.
For all series of urethane-urea copolymers, Tg increased with higher hard segment content in the structure, as seen from Figure 7.25. This indicated that the polymers were likely to became stronger and more rigid. This was also supported by measurement of tensile properties, (see later). The increase of Tg is believed to be due to higher hard segment content which is likely to create more interface contact between phases. The mobility of the soft segment can be locally affected resulting in a less flexible polymer.

In all cases, except in Series C, increases in E', (both above and below Tg) were related to increasing hard segment content or lower molecular weight of polyol. However, CBG 040, C1 or PT1 which had a hard segment content above 60 % had lower E' values than ISO6 (i.e. 51 % hard segment content). There is no clear explanation why this was observed but possibly it was due to urea in the urethane structure. The ISO 6 had a calculated urea content of 11.4 %, while CBG 040, C1 and PT1 had urea content of 10.7 %. The urea in the polymer structure possibly promotes the interaction between the molecular chains, leading to higher modulus values.

The E' values are slightly more affected by the soft segment content at Tg and below Tg than by the hard segment content. However, above Tg (i.e. at 20 °C), the E' values are more affected by the hard segment than the soft segment, (as stated above in the general trend discussion and seen in Table 7.5). This indicated that at lower temperatures, the soft segments had a more important contribution to the modulus of the polymer while the hard segments were already rigid. On the other hand, the soft segments had a tendency to break down and the hard segments were more stable at higher temperatures. Therefore, hard segments were the main contributors to the modulus at elevated temperatures.

In polymer series C, the effect of chain extender types was demonstrated, the hard segment contents were only slightly increased with the longer chain extender length. However, the value of the E' decreased substantially with increasing chain extender length. The values of E' obtained from this series were not supported by the theory that higher hard segment content should increase the modulus of the polymers. Of greater importance was that the longer chain extender length led to greater flexibility within the hard segment units, which in turn led to higher flexibility of the polyurethane as a whole. This will give the same apparent affect as increasing the molecular weight of the polyol. The MPMDA based chain extender, (i.e. with the methyl side group) had the higher E', especially at 20 °C. This was believed to be
due to the methyl side group increasing the stiffness of the chain extender and thereby the stiffness of the hard segments, resulting in a stiffening of the whole material.

Table 7.5 shows that in series A, B and D, the temperature of maximum tan δ increased to higher values with higher hard segment content or lower molecular weight of the polyol component. The magnitude of tan δ decreased with higher hard segment content or lower molecular weight of polyol; (see Figure 7.13, 7.15, 7.19, 7.21). It is believed that with higher hard segment content or shorter soft segments, the main chain became more rigid and glass-like, leading to lower loss modulus. Tan δ is the ratio of loss modulus to the storage modulus, therefore lower values of tan δ were expected. For series C, the magnitudes of tan δ were lower with shorter chain extender length and chain extender with side methyl group, (see Figure 7.17). These were to be expected since short chain extender lengths or chains with side methyl group lead to a more rigid main chain and increasing restriction of chain movement. Therefore lower loss modulus and lower values of tan δ were obtained.

In general, the breadth of the tan δ curve was influenced by the proportion of pure soft segment involved in the transition stage and therefore decreasing breadth was likely to indicate more phase separation between hard and soft segments. Both in series A and B, the tan δ curve shapes became narrower with higher hard segment content, (see Figure 7.13 and 7.15). This probably indicated that less pure soft segments were involved in the transition stage, with less phase separation between hard and soft segments. In series C, the tan δ curve become sharper and narrower with longer chain extender length, (see Figure 7.17). This means that longer linear chain extender promoted less phase separation. MPMDA based cast films have the broadest shape, (see Figure 7.17), indicating more hard and soft phase separation. This might be anticipated from the branch structure of the chain extender, hindering packing and interaction between phases. In series D, both polyols showed the same trends, the tan δ curve become sharper with higher molecular weight of polyol, as expected; (see Figure 7.19 and 7.21). This was due to more soft segment being involved in the transition stage. The variation in temperature of tan δ were similar to those of Tg (by DSC), already discussed earlier in relation to hard segment content.

However, from these thermograms, it is difficult to argue that any one or group of polymers has significantly different morphology. With Series D polymers, (which compared polyol types and molecular weights), the height of the tan δ curves
increased with molecular weight; (see Figure 7.19 and 7.21). The peak values of the tan δ for Terathane (polyether polyols) were lower than for the equivalent Capa (polyester polyols): the latter were expected to have higher orders of hydrogen bonding.

7.5 Fourier transform infra-red analysis (FT-IR)

Infra-red analysis was mainly used to determine the presence and percentage of hydrogen bonding formation in the polymers. The summaries of the percentage hydrogen bonding of polyurethane cast film results are shown on Table 7.6 and the FT-IR spectra of each series are shown in Figures 7.27 to 7.32.

Generally, IR spectra showed that in diol chain extended polyurethanes, the urethane carbonyl region showed splitting of the absorption band into two peaks around 1700 cm⁻¹ and 1720 cm⁻¹, which were assigned to the bonded and free carbonyl vibrations respectively. In amine chain extended polyurethanes, two weak bands were seen at around 1650 cm⁻¹ for the hydrogen urea carbonyl absorption and a second weak band at around 1680 cm⁻¹ for the free carbonyl absorption. (7.14, 7.15)

All cast films analysed showed the absence of free isocyanate (-NCO) absorption band at 2270 cm⁻¹, indicating the complete reaction of isocyanate. A weak peak at 1458 cm⁻¹ attributed to allophanate was found, indicating some crosslinking in the polyurethanes. This crosslinking resulted normally from the presence of excess isocyanate, possibly from the preparation of prepolymer. Reducing the reaction temperature in the oligomerisation stage might reduce this type of crosslinking, although in practice this does not appear to present a problem.

Both in series A and B, the NH stretch frequency around 3250 to 3400 cm⁻¹ was weak and broad but became slightly larger and narrower in intensity with increasing hard segment content in the structure. The percentage of hydrogen bonding showed a corresponding increase which was almost linear with increasing hard segment content, as seen from Figure 7.26. This was believed to be due to the higher hard segment content giving more interaction between hard segment, (i.e. either urea or urethane) and soft segment, (i.e. ester or ether polyol). In series C, the hydrogen bonding was almost constant at around 85 % and no significant changes in intensity of the NH stretch around 3250 to 3400 cm⁻¹ occurred, although a slightly decrease
in hydrogen bonding was observed. In series D, both polyol based cast films showed the same trends, higher hydrogen bonding was obtained with lower molecular weight of polyol. The hydrogen bonding value of Terathane (polyether) based cast films were lower than Capa (polyester) based cast films for the same equivalent weight of polyol, as expected. The NH stretch frequency at around 3250 to 3400 cm$^{-1}$ became weaker and broader in intensity with higher molecular weight of polyol.

Table 7.6 The summary results of the % hydrogen bonding of water dispersed urethane-urea copolymers cast films, determined from IR spectra.

<table>
<thead>
<tr>
<th>Sample reference</th>
<th>% Hydrogen bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series A</strong>: Effect of isocyanate build block ratio</td>
<td></td>
</tr>
<tr>
<td>ISO 3</td>
<td>82.6</td>
</tr>
<tr>
<td>ISO 4</td>
<td>87.0</td>
</tr>
<tr>
<td>ISO 5</td>
<td>88.5</td>
</tr>
<tr>
<td>ISO 6</td>
<td>92.1</td>
</tr>
<tr>
<td><strong>Series B</strong>: Effect of carboxylic ionic emulsifier block ratio</td>
<td></td>
</tr>
<tr>
<td>CBG 020</td>
<td>80.2</td>
</tr>
<tr>
<td>CBG 025</td>
<td>82.6</td>
</tr>
<tr>
<td>CBG 030 (=PT2)</td>
<td>87.5</td>
</tr>
<tr>
<td>CBG 040</td>
<td>90.4</td>
</tr>
<tr>
<td><strong>Series C</strong>: Effect of chain extender types</td>
<td></td>
</tr>
<tr>
<td>EDA</td>
<td>85.7</td>
</tr>
<tr>
<td>TMDA</td>
<td>85.3</td>
</tr>
<tr>
<td>HMDA</td>
<td>85.4</td>
</tr>
<tr>
<td>MPMDA</td>
<td>85.1</td>
</tr>
<tr>
<td><strong>Series A</strong>: Effect of polyol types and molecular weight</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>92.7</td>
</tr>
<tr>
<td>C2</td>
<td>89.5</td>
</tr>
<tr>
<td>C4</td>
<td>82.6</td>
</tr>
<tr>
<td>PT1</td>
<td>89.2</td>
</tr>
<tr>
<td>PT2 (=CBG 030)</td>
<td>87.0</td>
</tr>
<tr>
<td>PT29</td>
<td>80.8</td>
</tr>
</tbody>
</table>
As seen in Figure 7.27, TMXDI/Capa/DMPA/MPMDA based urethane-urea copolymers in series A had only a single urethane carbonyl peak at around 1700 cm$^{-1}$, which indicated that all the urethane carbonyls were hydrogen bonded. The bonded urethane carbonyl peak was also found to be slightly shifted towards lower wave numbers with increasing isocyanate block ratio. The bonded urea carbonyl peak appeared only at 1650 cm$^{-1}$, whilst no free urea carbonyl absorption was observed at 1680 cm$^{-1}$, indicating all the urea carbonyls were also bonded. The urea amide II absorption at around 1556 cm$^{-1}$ and the intensity of the bonding urea carbonyl peak at 1650 cm$^{-1}$ increased with increasing isocyanate block ratio, implying greater urea content was obtained.(7.16)

In series B, higher pendent carboxylic block ratio showed urethane carbonyl peaks at around 1710 cm$^{-1}$, urea carbonyl peaks at 1645 cm$^{-1}$, urea amide II absorptions at around 1554 cm$^{-1}$ and the peaks at 1250 cm$^{-1}$, (stretch C-N and bend N-H amide III absorption)(7.16), increased in intensity with increasing carboxylic emulsifier contents, as seen in Figure 7.28. This latter result may indicate that some carboxylic groups had reacted with isocyanate during the prepolymer synthesis stage creating the amide absorption peaks. There were no signs of a carboxylic acid salt peak at 1580 cm$^{-1}$, suggesting that all the neutralising amines evaporated from
the cast films during the drying process. There was no clear indication of free carboxylic peak in the polyurethane infra-red spectra, since the major absorption peak that dominated the carboxylic group was also in the same region as the urethane carbonyl group, (i.e. around 1710 cm\(^{-1}\)). It was almost impossible to measure free pendent carboxylic groups concentration in this way. However, the intensity of this peak increased with higher carboxylic block ratio, which may indicate the presence of unreacted pendent carboxylic groups.

Different chain extender length in series C showed little change in the infra-red spectra. This possibly indicated that the variation resulting from the methylene groups in the main chain from 2 to 6, or the one single side methyl group in the amine chain extender were too small to be significant, (see Figure 7.29).

For the cast films in series D, Capa 220 based cast films had a high intensity of carbonyl vibration around 1700 cm\(^{-1}\), indicating a strong carbonyl band, resulting from the ester group. Terathane 2000 based cast films had a high intensity peak at around 2850 cm\(^{-1}\), (CH\(_2\)CH asymmetric stretching) and a small peak at around 2795 cm\(^{-1}\), (CH\(_2\)CH stretching).\(^{7,16}\) It also had a very dominant peak at around 1100 cm\(^{-1}\), strongly indicating the presence of the ether group, (see Figure 7.30).

For low molecular weight Capa polyol based polyurethanes, the carbonyl absorptions were at around 1680 and 1720 cm\(^{-1}\), (i.e. bonded and free carbonyl group respectively) and difficult to resolve. With increasing polyol molecular weight, the vibration peak in this region became easier to resolve, indicating more ester groups in the structure. The peak intensity at around 1360 cm\(^{-1}\), (i.e. CH\(_2\) wagging), increased as expected from the higher amount of CH\(_2\) groups from higher molecular weight polyol, (see Figure 7.31).

As shown in Figure 7.32, with increasing molecular weight of Terathane polyol in the urethane-urea copolymers, the peaks at around 2854 cm\(^{-1}\), (i.e. C-H asymmetric stretching in CH\(_2\)), 2796 cm\(^{-1}\), (i.e. CH\(_2\)CH symmetric stretching) and 1361 cm\(^{-1}\), (CH\(_2\) wagging) increased in intensity.\(^{7,16}\) The peak at 1095 cm\(^{-1}\), (i.e. C-O-C stretching) became broader. This is due to the higher amounts of ether units arising from the higher molecular weights of the polyol.
Figure 7.27 FT-IR spectra: Effect of isocyanate building block ratio on series A
Figure 7.28 FT-IR spectra: Effect of carboxylic ionic emulsifier block ratio on series B
Figure 7.29 FT-IR spectra: Effect of chain extender types on series C
Figure 7.30 FT-IR spectra: Polycaprolactone and polytetramethylene glycol based polyurethanes
Figure 7.31 FT-IR spectra: Effect of molecular weight of polycaprolactone based polyurethanes on series D
Figure 7.32 FT-IR spectra: Effect of molecular weight of polytetramethylene glycol based polyurethanes on series D.
7.6 Tensile properties

The tensile properties of polyurethanes normally depend particularly on the nature of their precursor monomers or oligomers, their morphology and phase structure. They may be susceptible to degradation by heat, oxidation or hydrolysis: these are the principal factors in determining the useful applications for a polyurethane.

The effect of varying isocyanate block ratio on tensile properties of series A urethane-urea copolymers are showed in Table 7.7 and Figures 7.33 to 7.35. A summary of the principal features observed in tensile measurement is as follows:

a) Untreated original cast films, as the isocyanate building block ratio increased
   i) The 300% modulus increased from 4.8 to 25.5 MPa.
   ii) The tensile strength increased to maximum of approximately 50 MPa at an isocyanate block ratio NCO/OH/COOH/CE = 1/0.20/0.20/0.60 (ISO 5), above which the tensile strength values were almost constant.
   iii) The elongation at break decreased from approximately 1420 to 1125 %.

b) After heat ageing of the cast films, in comparison to the untreated films
   i) The value of 300% modulus was higher than the untreated cast film. The higher the isocyanate block ratio, the lower the percentage change found. The change in value decreased from around +65 % to +2 %.
   ii) The value of tensile strength was lower than for an untreated cast film. The higher the isocyanate block ratio, the lower the percentage change found. The change in value decreased from around -27 % to -7 %.
   iii) The elongation at break increased to a maximum value with ISO 4 (NCO/OH/COOH/CE = 1/0.25/0.25/0.50), then decreased. Elongation at break were lower than for the untreated cast film. The higher the isocyanate block ratio, the lower the percentage change found. The change was from around -20 % to -5 %.

c) After hydrolytic treatment of the cast films, in comparison to the untreated films
   i) The value of the 300 % modulus was lower than for the untreated cast film. The percentage change was lower with increasing isocyanate block ratio. The change decreased from around -56 % to -8 %.
   ii) The value of tensile strength was lower than for untreated cast film. The higher the isocyanate block ratio, the smaller the percentage change found. The change was from around -72 % to -25 %.
   iii) The elongation at break increased to a maximum between ISO4 and ISO5 (NCO/OH/COOH/CE between 1/0.25/0.25/0.5 and 1/0.2/0.2/0.6). The elongation at break value was lower than for untreated cast film. The
percentage change decreased with increasing the isocyanate building block ratio. The change was from around -41 % to -11 %.

Table 7.7 The summary of tensile properties of urethane-urea copolymers cast films in series A

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>300% Modulus (MPa) AVG</th>
<th>Tensile strength (MPa) AVG</th>
<th>Elongation at break (%) AVG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>STD</td>
<td></td>
<td>STD</td>
</tr>
<tr>
<td>i) Untreated cast film</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO 3</td>
<td>4.8</td>
<td>0.3</td>
<td>26.9</td>
</tr>
<tr>
<td>ISO 4</td>
<td>12.4</td>
<td>0.4</td>
<td>42.0</td>
</tr>
<tr>
<td>ISO 5</td>
<td>20.8</td>
<td>0.4</td>
<td>50.2</td>
</tr>
<tr>
<td>ISO 6</td>
<td>25.5</td>
<td>0.5</td>
<td>48.8</td>
</tr>
<tr>
<td>ii) After heat ageing at 70 °C for 168 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO 3</td>
<td>7.9</td>
<td>0.7</td>
<td>19.6</td>
</tr>
<tr>
<td>ISO 4</td>
<td>16.8</td>
<td>0.5</td>
<td>34.3</td>
</tr>
<tr>
<td>ISO 5</td>
<td>24.3</td>
<td>0.8</td>
<td>44.5</td>
</tr>
<tr>
<td>ISO 6</td>
<td>25.9</td>
<td>0.4</td>
<td>45.3</td>
</tr>
<tr>
<td>iii) After hydrolytic ageing at 20 °C for 168 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO 3</td>
<td>2.1</td>
<td>0.1</td>
<td>7.5</td>
</tr>
<tr>
<td>ISO 4</td>
<td>9.8</td>
<td>0.4</td>
<td>22.1</td>
</tr>
<tr>
<td>ISO 5</td>
<td>17.5</td>
<td>0.4</td>
<td>35.5</td>
</tr>
<tr>
<td>ISO 6</td>
<td>23.5</td>
<td>0.4</td>
<td>36.5</td>
</tr>
</tbody>
</table>

AVG = average value, STD = standard deviation

Figure 7.33 The relationships of 300% modulus & hard segment content in series A cast films.
Figure 7.34 The relationships of tensile strength & hard segment in series A cast films.

Figure 7.35 The relationships of elongation at break & hard segment in series A cast films.
As shown in Table 7.1, increasing the isocyanate block ratio increased the hard segment content in the urethane structure leading to more interaction between hard/soft segments as supported by the higher hydrogen bonding, (see Table 7.6). Therefore, the higher 300 % modulus and tensile strength values were to be expected. The modulus results were consistent with the DMTA results, and were attributed to an increasing degree of interconnectivity of the hard domains, as the materials change from a predominantly soft segment polymer to a predominantly hard segment and rigid polymer. The elasticity of the cast films was lower as indicated by the lower elongation at break.

Following the heat ageing, the highest positive change in 300 % modulus was found with cast films of lower hard segment content. This was thought to be due to heat ageing increasing the hard and soft phase mixing, leading to a stiffer polymer, (as seen from Figure 7.33). Heat ageing appeared to decrease both tensile strength at break and elongation at break, as seen from Figure 7.34 and 7.35. This is believed to be due to the degradation of the polymer chains, indicated by the cast film yellowing during heat ageing. However, with higher hard segment content, there were lower percentage changes of both tensile strength and elongation at break. This was believed to be due to the higher hard segment content providing greater thermal stability. This was also supported by the DSC analysis which showed that at higher isocyanate block ratio, higher degradation temperatures resulted. Overall, it can be clearly seen that the formulations with higher hard segment content had less change in tensile properties after the heat ageing; this is seen from the smaller difference between the untreated film and heat aged film, in Figure 7.33 to 7.35. Also higher concentrations of DMPA in the polymer structure had an influence in that they introduced increasing heat instability leading to greater loss of tensile properties.

After hydrolytic treatment, the tensile properties were found to be reduced in all formulations. However, at higher isocyanate block ratio, again less change in tensile properties was found. Also the pendent carboxylic acid content decreased with higher isocyanate block ratio, as seen in Table 7.1. However, high content of pendent carboxylic acid in the formulation (here ISO 3) led to more acidic conditions association with the hydrolytic conditions. Therefore, it was possible that a greater degree of hydrolytic degradation of ester linkages in polyol soft segments occurred, leading to polymer chain scission. Chain scission led to loss of tensile properties. It was observed that formulations ISO 5 and ISO 6 had similar percentage changes in tensile properties, supporting the theory that the hydrolytic
degradation occurred more severely with higher pendent carboxylic acid contents. This was also indicated by the larger difference between the untreated cast films and hydrolytic results in Figure 7.33 to 7.35.

For series B polymers, the effects of increasing pendent carboxylic acid block ratio on tensile properties are shown in Table 7.8 and Figure 7.36 to 7.38. A summary of principal features observed in tensile behaviours are as follow:

a) Untreated original cast films, as pendent carboxylic acid content increased:
   i) The 300% modulus increased from 12.1 to 28.4 MPa.
   ii) The tensile strength increased from 27.6 to 51.7 MPa.
   iii) The elongation at break decreased from 1395 to 985 % and this value dropped considerably for CBO 040.

b) After heat ageing cast films, in comparison to untreated film
   i) The value of 300 % modulus was higher. The higher pendent carboxylic block ratio, the higher percentage changes were found. The change value was increased from around +10 % to +18 %.
   ii) Tensile strength was lower. The higher the pendent carboxylic block ratio, the higher the percentages change were found. The change value was increased from around -7 % to -15 %.
   iii) The value of elongation at break was also lower. The higher the carboxylic block ratio, the higher the percentage changes were found. The change was increased from around -5 % to -19 %.

c) After hydrolytic treatment cast film, in comparison to untreated film
   i) The value of 300% modulus was lower. The higher the carboxylic ionic emulsifier block ratio, the higher the percentage changes found. The change of value was increased from around -22 % to -40 %.
   ii) The value of tensile strength was also lower. The higher the carboxylic ionic emulsifier block ratio, the higher the percentage changes found. The change of value was increased from around -23 % to -43 %.
   iii) The value of elongation at break was slightly lower. The higher the carboxylic ionic emulsifier block ratio, the higher the percentage changes found. The change of value was increased from around -1 % to -10 %.
Table 7.8 The summary of tensile properties of urethane-urea copolymer cast films in series B

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>300% Modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AVG</td>
<td>STD</td>
<td>AVG</td>
</tr>
<tr>
<td>i) Untreated cast films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 020</td>
<td>12.1</td>
<td>0.4</td>
<td>27.6</td>
</tr>
<tr>
<td>CBG 025</td>
<td>16.2</td>
<td>0.1</td>
<td>44.4</td>
</tr>
<tr>
<td>CBG 030 (wPT2)</td>
<td>22.8</td>
<td>0.5</td>
<td>47.3</td>
</tr>
<tr>
<td>CBG 040</td>
<td>28.4</td>
<td>0.6</td>
<td>51.7</td>
</tr>
<tr>
<td>ii) After heat ageing at 70 °C for 168 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 020</td>
<td>13.3</td>
<td>0.1</td>
<td>25.7</td>
</tr>
<tr>
<td>CBG 025</td>
<td>18.1</td>
<td>0.3</td>
<td>40.1</td>
</tr>
<tr>
<td>CBG 030 (wPT2)</td>
<td>25.9</td>
<td>0.4</td>
<td>41.7</td>
</tr>
<tr>
<td>CBG 040</td>
<td>33.6</td>
<td>0.3</td>
<td>44.0</td>
</tr>
<tr>
<td>iii) After hydrolytic ageing at 20 °C for 168 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 020</td>
<td>9.5</td>
<td>0.3</td>
<td>21.3</td>
</tr>
<tr>
<td>CBG 025</td>
<td>11.4</td>
<td>0.4</td>
<td>30.7</td>
</tr>
<tr>
<td>CBG 030 (wPT2)</td>
<td>14.9</td>
<td>0.5</td>
<td>30.3</td>
</tr>
<tr>
<td>CBG 040</td>
<td>17.1</td>
<td>0.9</td>
<td>29.6</td>
</tr>
</tbody>
</table>

AVG = average value, STD = standard deviation

Figure 7.36 The relationships of 300% modulus & hard segment content of series B cast films
Figure 7.37 The relationships of tensile strength & hard segment content of series B cast films

Figure 7.38 The relationships of elongation at break & hard segment content of series B cast films
The carboxylic ionic emulsifier is a low molecular weight hydroxyl compound, used as a diol chain extender. With increasing carboxylic ionic emulsifier block ratio, more urethane linkages (or more hard segments) were obtained. Higher hard segment content in the polymer chain lead to more interactions between polyurethane backbone chains. This is supported from the increased hydrogen bonding shown in the infra-red studies, (see Table 7.6). Therefore, it was reasonable to expect higher modulus and higher tensile strengths. The modulus values are also consistent with the DMTA results. The resulting cast films become rigid and hard leading to less elasticity, the elongation at break being decreased under the untreated conditions.

During the heat ageing, phase mixing of hard and soft segments could occur and the cast films became more rigid: increases of 300 % modulus were consequently obtained. A pendent carboxylic group had a greater tendency to decompose at elevated temperatures, releasing water and carbon dioxide. Such degradation will create weaknesses in the polymer leading to decreases in tensile strength and elongation at break. Higher concentrations of pendent carboxylic groups gave greater reductions in tensile strength and elongation, (see Figure 7.36 to 7.38). This was also supported by DSC analysis where higher content of pendent carboxylic groups gave lower third transition and degradation temperatures.

After hydrolytic treatment, the tensile properties in all formulation were reduced. With higher pendent carboxylic groups content, greater reductions were found. This was not surprising since with higher pendent carboxylic content, more acidic conditions were formed. This was likely to lead to higher acceleration of polyether deterioration and greater percentage change in tensile properties. As shown in Figure 7.36 to 7.38, the larger differences between untreated and hydrolytic treated films were obtained with higher DMPA content.

In this research, work concentrated on thermoplastic polyurethanes, (i.e. linear chain). Higher concentration of pendent carboxylic groups seem to give unfavourable tensile properties after heat and hydrolytic treatment. However, it is likely with the crosslinked polyurethane systems that higher levels of pendent carboxylic acid contents will be preferred, in particular to act as crosslinking sites with either trifunctional aziridines(7.17) or carbodiimides(7.18, 7.19). The details of possible crosslinking reactions are described in Figure 3.13 and 3.14.
Formulation Series C showed the effect of chain extender types on the cast films. The summary of results on tensile properties are shown on Table 7.9 and Figure 7.39 to 7.41. The principal features observed in tensile measurement are as follows:

a) Untreated original cast films, with increasing chain extender length
   i) 300% modulus was increased from 6.7 to 11.6 MPa. The MPMDA (i.e. with the side methyl group) based cast films had similar properties as HMDA based cast films, i.e. at around 12 MPa.
   ii) Tensile strength was also increased from 39.9 to 50.6 MPa. The MPMDA based cast films had the similar tensile strengths as HMDA based cast films i.e. at around 51 MPa.
   iii) Elongation at break was almost constant at 1330 to 1350 %. The MPMDA based cast films had the lowest value at around 1295 %.

b) After heat ageing cast films, in comparison to untreated film
   i) The value of 300% modulus was higher. The greater the chain extender length, the lower percentage change found (from around +30 % to +9 %). The MPMDA based cast film has a percentage change at around +12 %.
   ii) The value of tensile strength was lower. The chain extender length and side methyl groups had no effect on the percentage change of tensile strength. The change value was found around -16 %.
   iii) The value of elongation at break was lower. The chain extender length and side methyl groups had no effect on the percentage change of elongation at break. Changes were found to be around -6 %.

c) After hydrolytic test films, in comparison to the untreated film
   i) The value of 300% modulus was lower. Increasing the chain extender length showed only slight effects on the percentage change of 300 % modulus. The change of values were found slightly increased from around -18 % to -20 %. The MPMDA based cast films had the similar percentage change at around -21 %.
   ii) The values of tensile strength were also lower. Varying chain extender length resulted in likely small reductions on percentage change of tensile strength. The change of values were found to have slightly decreased from around -45 % to -43 %. The MPMDA based cast films had the similar percentage change at around -42 %.
   iii) The value of elongation at break was lower. Varying the chain extender length showed only slight difference on the elongation at break. The changes slightly decreased from around -19 % to -17 %. The MPMDA based cast films also had similar percentage change at around -19 %.
Table 7.9 The summary of tensile properties of urethane-urea copolymers cast films in series C

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>300% Modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AVG</td>
<td>STD</td>
<td>AVG</td>
</tr>
<tr>
<td>i) Untreated cast films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDA</td>
<td>6.7</td>
<td>0.2</td>
<td>39.9</td>
</tr>
<tr>
<td>TMDA</td>
<td>8.5</td>
<td>0.2</td>
<td>45.8</td>
</tr>
<tr>
<td>HMDA</td>
<td>11.6</td>
<td>0.3</td>
<td>50.6</td>
</tr>
<tr>
<td>MPMDA</td>
<td>11.9</td>
<td>0.4</td>
<td>51.4</td>
</tr>
<tr>
<td>ii) After heat ageing at 70 °C for 168 hours</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDA</td>
<td>8.7</td>
<td>0.4</td>
<td>33.3</td>
</tr>
<tr>
<td>TMDA</td>
<td>9.8</td>
<td>0.3</td>
<td>38.1</td>
</tr>
<tr>
<td>HMDA</td>
<td>12.6</td>
<td>0.1</td>
<td>42.4</td>
</tr>
<tr>
<td>MPMDA</td>
<td>13.3</td>
<td>0.1</td>
<td>43.3</td>
</tr>
<tr>
<td>iii) After hydrolytic ageing at 20 °C for 168 hours</td>
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<tr>
<td>EDA</td>
<td>5.5</td>
<td>0.4</td>
<td>22.0</td>
</tr>
<tr>
<td>TMDA</td>
<td>6.9</td>
<td>0.4</td>
<td>25.0</td>
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<tr>
<td>HMDA</td>
<td>9.3</td>
<td>0.8</td>
<td>28.9</td>
</tr>
<tr>
<td>MPMDA</td>
<td>9.6</td>
<td>0.3</td>
<td>30.2</td>
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</table>

AVG = average value, STD = standard deviation

Figure 7.39 The relationships of 300% modulus & chain extender types of series C cast film.
Figure 7.40 The relationships of tensile strength & chain extender types of series C cast film.

Figure 7.41 The relationships of elongation at break & chain extender types of series C cast film.
For polymers in series C, increasing the chain extender length gives slightly longer hard segment size, possibly leading to more phase separation of hard and soft segments. Therefore higher modulus and tensile properties were obtained. This was supported by elongation at break being slightly increased with increasing chain extender length, and by the shape of the tan δ curves become narrower with more free soft segments results from the phase separation, (see Figure 7.17). The MPMDA based cast films had higher 300% modulus and tensile strength than HMDA based cast films. The MPMDA has only 5 carbons in the main chain with one carbon at the side while HMDA has 6 carbons in the main chain. It was believed that the side methyl group increased the rigidity of the urethane backbone chain promoting more phase mixing, as evidenced by the breadth of the tan δ curve, (see Figure 7.17).

After the heat ageing treatment, increases in 300% modulus resulted while the change decreased at longer chain extender length. This may be due to heating increasing the phase mixing leading to more rigidity and longer hard segment length providing more flexibility in the hard segment unit. The side methyl groups seemed to have little effect on 300% modulus with heat ageing. It was quite surprising to see that with heat ageing, (i.e. hot air at 70 °C for 168 hours), the percentage change in tensile strength and elongation at break were not significantly changed, with increasing chain extender length. It is thought that the variation of the number of methylene groups in the chain extender structure was too small to be significant.

After hydrolytic treatment, (i.e. immersion in water at 20°C for 168 hours), reductions of 300% modulus were obtained and slight increases in change were observed with longer chain extender length, (i.e. from around -18% to -21%). The tensile strength and elongation at break also had negative differences. The changes were similar although little decreases were observed (from around -45 % to -42 % in tensile strength and around -19% in elongation at break). However, these changes were in the experimental error range. It is not surprising that the change in the tensile properties was little affected by the chain extender length since hydrolytic degradation of these urethane-urea copolymers resulted largely from the degradation of ester linkages in the soft segment, under acidic conditions. In this part of the research, the reaction block ratio was kept constant so the amount of pendent carboxylic group was almost in the same range: in addition only Capa polyester polyol were used in this experiment.
In series D polymer, effects of varying polyol types and molecular weight on the
tensile properties are shown in Table 7.10 and Figure 7.42 to 7.44. The principal
features observed in tensile measurement are as follow:

a) Untreated original cast films, for both polyol types
i) Both showed the same trends. The 300 % modulus decreased with
increasing molecular weight of polyol. Capa based cast films decreased
from 27.7 to 20.6 MPa and Terathane based cast films decreased from 25.2
to 17.6 MPa.
ii) Both showed the same trends in tensile strength and elongation at break.
The 2000 molecular weight polyol based cast films had the highest value.
The tensile strength of Capa based cast films was 46 MPa and Terathane
based cast films was 42 MPa and both types had the same elongation at
break at around 1190 %.

b) After heat ageing cast films, in comparison to the untreated cast film
i) Both polyols showed the same trends in 300% modulus, with higher
values. The higher the molecular weight of polyol, the lower the percentage
change found, (i.e. Capa based cast films, changed from around +9% to
+2% and Terathane based cast films, from around +10 % to +6 %).
ii) Both polyols showed the same trends in tensile strength and elongation
at break, with lower values. The higher the molecular weight of the polyol,
the higher the percentage change found. Capa based cast films had
percentage changes of tensile strength from around -12% to -30% and
Terathane based cast films values are changed from -8% to -24%. With
elongation at break, Capa based cast films changed from -4% to -8% and
Terathane based cast films changed from -5% to -8%.

c) After hydrolytic test films, in comparison to the untreated cast film
i) Both polyols show the same trends in 300% modulus, with lower values.
The higher the molecular weight of the polyol, the higher the percentage
change found. Terathane based cast films had a lower percentage change
than Capa based cast films. Capa based films changed from around -33% to
-60% and Terathane based cast films change from -7% to -24%.
ii) Both polyols show the same trends in both tensile strength and elongation
at break, with lower values. The higher the molecular weight of the polyol,
the higher the percentage change found. Capa based polyurethanes had
percentage changes of tensile strength from -30% to -59% and Terathane
based films changed from -17% to -45%. For elongation at break values,
the Capa based films changed from -6% to -16% and Terathane based films,
from -6% to -9%. Terathane based films had a lower value of percentage change than the Capa based films.

Table 7.10 The summary of tensile properties of urethane-urea copolymers cast films in series D

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>300% Modulus (MPa) AVG</th>
<th>300% Modulus (MPa) STD</th>
<th>Tensile strength (MPa) AVG</th>
<th>Tensile strength (MPa) STD</th>
<th>Elongation at break (%) AVG</th>
<th>Elongation at break (%) STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Untreated cast films</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>C1</td>
<td>27.7</td>
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<td>1.1</td>
<td>790</td>
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<td>23.8</td>
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<td>1195</td>
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<td>C4</td>
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<td>0.5</td>
<td>38.0</td>
<td>1.2</td>
<td>1190</td>
<td>10.5</td>
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<tr>
<td>PT2 (ECBG 030)</td>
<td>22.5</td>
<td>0.5</td>
<td>44.5</td>
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<td>1240</td>
<td>9.6</td>
</tr>
<tr>
<td>PT29</td>
<td>17.6</td>
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<td>34.0</td>
<td>1.4</td>
<td>1150</td>
<td>10.9</td>
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<tr>
<td>ii) After heat ageing at 70 °C for 168 hours</td>
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</tr>
<tr>
<td>C1</td>
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<td>0.9</td>
<td>1165</td>
<td>16.7</td>
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<td>25.8</td>
<td>0.4</td>
<td>1060</td>
<td>12.7</td>
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<tr>
<td>iii) After hydrolytic ageing at 20 °C for 168 hours</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
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<td>735</td>
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<td>1070</td>
<td>17.8</td>
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<td>1.7</td>
<td>1000</td>
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<td>PT2 (ECBG 030)</td>
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<td>0.6</td>
<td>1200</td>
<td>12.7</td>
</tr>
<tr>
<td>PT29</td>
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<td>0.4</td>
<td>18.8</td>
<td>2.2</td>
<td>1043</td>
<td>11.5</td>
</tr>
</tbody>
</table>

AVG = average value, STD = standard deviation
Figure 7.42 The relationships of 300% modulus & hard segment content of series D cast films

Figure 7.43 The relationships of tensile strength & hard segment content of series D cast films
Urethane-urea copolymers based on either types of polyols showed the same trend, i.e. the 300% modulus and tensile strength decreased with increasing molecular weight of the polyol; as seen in Figure 7.42. This was due to an increasing tendency of the soft segment to crystallise as soft segment molecular weight increased and also an increasing tendency for the hard segment domains becoming isolated from the soft segment matrix. The polymer chains lose some of their rigidity and strength with the reduced average numbers of urethane linkages. Again both polyol types gave the maximum value of tensile strength and elongation at break at a molecular weight of 2000, as seen from Figures 7.43 and 7.44. These results were confirmed by repeating the formulation syntheses of the same polymers: therefore, this was assumed to be a real effect. A possible explanation is that the low molecular weight polyol (here 1000) gave a very high hard segment content (i.e. 63.1%). The resulting polymers might be too rigid and brittle. On the other hand, for a high molecular weight of polyol (4000 for Capa and 2900 for Terathane), the hard segment contents (29.9% and 37.2%) were low. The resulting polymers were too flexible. Both extreme characteristics in the resulting polymers can reduce the tensile strength and elongation at break.
After heat ageing, cast films based on either polyols showed the same trends, 300% modulus values were increased, the effect being greater at lower molecular weight of polyol (as indicated by the higher percentage change). The increase on 300% modulus was believed to be due to greater phase mixing, giving rigid polymers. For lower molecular weight polyols, more phase mixing occurred during heat treatment leading to greater rigidity of cast film. The tensile strength and elongation at break decreased after the heat treatment as expected. As previously suggested, more degradation occurred at the ester or ether linkages in the soft segment of the polyurethane main chains. At higher molecular weights of polyol, a greater number of ester or ether weak points will be oxidised: therefore, greater changes of the tensile strength and elongation at break were found. From the study of conventional polyurethanes, it is normal to expect polyesters to display considerably higher thermal stability than polyether based polyurethanes. However, this does not appear quite applicable with the carboxylic acid emulsified polyurethane systems. The Terathane (i.e. polyether) based urethane urea copolymers have the same percentage change range as Capa (i.e. polyester) based urethane-urea copolymers. This is suggested to be due to the pendent carboxylic groups decomposing and releasing water, which could attack the ester group in the Capa polyol. This could reduce the heat resistance of Capa based cast films to the same range as Terathane based cast films.

Films based on both polyols showed the same trends after the hydrolytic treatment, the higher the molecular weight of polyol, the higher percentage changes found in tensile properties, as expected. This was believed to be due to the higher molecular weight of polyol, with a greater number of ester or ether linkages in the soft segments. Therefore, there was a greater tendency to be attacked by water in acidic conditions. However, Terathane based cast films have lower values of percentage change than the Capa based cast films because the ester group in Capa polyols had the poorer hydrolysis resistance.
Reference

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7.3 Vanderhoff, J.W., Polymer News, 3, 4, 194, 1977

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7.9 Seymour, R.W., Cooper, S.L., Macromolecules, 6, 48, 1973


7.14 Paik Sung, C.S., Schneider, N.S., Macromolecules, 10, 452, 1977


7.17 U.S. Patent 4,301,053., 1981

7.18 European Patent Appl. 121.083., 1984

7.19 German Patent 3,441,934., 1985
Chapter 8 Polyurethane Powders Precipitated from Dispersions

The polymer industry has been producing thermoplastics in powder form for over 40 years. Newer gas phase processes for the manufacture of polyethylene and polypropylene now give powdered polymers directly from the reactor. Industry is now adapting to use of these powdered polymers directly form the reactor for extrusion or injection moulding without first pelletising. However, current commercial thermoplastic polyurethane preparations often rely on bulk or solution polymerisation, where the resulting polymers has to be reduced by grinding or chopping to pellet or powder form, ready for extrusion or injection moulding. These may have to be carried out under cryogenic conditions which are energy intensive and costly as well as creating risk hazards due to the potential of dust explosion. Further more, the chopping or grinding operations can give rise to some degradation since these polyurethanes are shear and heat sensitive. The bulk or in particular solution polymerisation techniques also have environmental and cost constraints. With the growing industrial use of polyurethanes, development of thermoplastic polyurethanes from powder processes may be argued as essential to meet environmentally favourable conditions.

This chapter is therefore focused on the conversion of powders directly from the dispersions. It also reviews the melt flow behaviour of the resulting powders to understand their injection moulding behaviour. In particular the effect of injection process conditions such as injection temperature, injection speed and mould cooling time on thermal and mechanical properties were examined.

Unfortunately, because of the limitation of the time and amount of raw materials available, only a single formulation of urethane-urea copolymer dispersion was converted to powder, i.e. at equivalent molar ratio of TMXDI/Terathane 2000/DMPA/MPMDA = 1/0.25/0.25/0.5. The formulation details are given in Chapter 5, Section 5.2.2 and the synthesis procedure for powdered urethane-urea copolymer given in Chapter 5, Section 5.3.2.
8.1 Urethane-urea copolymers powder formation

The dispersions under study are stable by virtue of the carboxylic group present on the surface of the urethane particles through the use of ionic emulsifiers. Theoretically, the stability of a dispersion can be reduced by the addition of some chemical coacervants into the system. These coacervants mainly function by reducing the electrokinetic potential (\( \zeta \)) associated with the electrical double layer surrounding the latex particle. Hence, any substance which generates hydrogen ions will bring about an immediate destabilisation of a polyurethane latex. This effect is due principally to the interaction between the added hydrogen ions and the carboxylic ions which stabilise the latex, i.e.:

\[
\text{CO}_2^- + H^+ \rightarrow \text{COOH}
\]

As a result, there is a formation around the particle of a layer of fatty acid, which is water insoluble. The \( \zeta \) potential falls to virtually zero, and the electrical double layer surrounding the particle collapses. Since there is no repulsive force between the particles, they will attract each other to form larger particles which then precipitate from the water medium. Thus polyurethane powders are obtained.

Using the above hypothesis, polyurethane powder was precipitated from a carboxylic ionic stabilised emulsified latex with an excess of diluted acid, (here 3% acetic acid), under high speed stirring to accelerate the destabilisation of latex. The resulting precipitated solids were simply filtered from the acid medium. The powder was neutralised with a 1% aqueous potassium hydroxide solution until the pH was neutral, to eliminate the remaining acetic acid, which might have effected the properties of resulting solid polyurethanes. The wet neutralised powders were then washed in water to eliminate all the soluble impurities and dried. Powder prepared by this technique did not require a grinding step. Therefore the time and energy consumption, the hazardous working environment and the degradation of polyurethanes were removed. The powder was then to shape by a melt processing technique, i.e. injection moulding to produce much thicker sections than the normal casting technique. This development appeared to offer substantial commercial advantages in the thermoplastic processing of polyurethanes.
8.2 Melt flow properties of polyurethane powders

Before injection moulding was undertaken, it was felt necessary to understand the melt flow behaviour of the polyurethane in order to assess a choice of correct operating parameters for injection processibility. The melt flow properties were studied using a Davenport capillary rheometer, since it was easy to operate and required only a small amount of material. As mentioned earlier in this chapter, the powder study programme was commenced only in the later stages of the research, so time and materials were limited. Therefore, only a limited number of flow behaviour properties were studied.

The experimental details of the melt flow characterisation procedures are given in Chapter 5 Section 5.6.1. The following parameters: pressure inside the capillary, mass output rate, percentage die swell and appearance of the extrudate at different ram speeds (i.e. 10, 20, 30 mm/min.) and barrel melt temperature (i.e. 130, 140, 150, 160 °C), were observed. The results obtained are shown in Tables 8.1, 8.3, 8.5 and 8.6 and Figures 8.1, 8.4 and to 8.5.

8.2.1 Pressure inside the capillary

As anticipated pressure inside the capillary decreased with increasing temperature of the melt and the rate of the decrease of pressure was found to be lowest at higher melt temperatures. The ram speed is consequently related to the shear rate, (see Appendix 5). At higher ram speed, higher shear rates were obtained and with increasing shear rate, higher pressures were obtained, (see Table 8.1 and Figure 8.1). These results were consistent with most thermoplastic materials. (8.3)

### Table 8.1 Pressure inside capillary barrel (MPa) at various conditions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure inside capillary barrel (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ram speed (mm/min.)</td>
</tr>
<tr>
<td>130</td>
<td>140</td>
</tr>
<tr>
<td>140</td>
<td>130</td>
</tr>
<tr>
<td>150</td>
<td>140</td>
</tr>
<tr>
<td>160</td>
<td>150</td>
</tr>
</tbody>
</table>

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The shear stress ($\tau$), shear rate ($\gamma$), apparent viscosity and shear rate relationships were calculated using the equations shown in Appendix 5. The calculated results are shown in Table 8.2. The log shear stress versus log shear rate curves of melt polyurethane was obtained at temperatures between 130 to 160 °C, and are shown in Figure 8.2. The apparent viscosity versus shear rate of melt polyurethanes are shown in Figure 8.3.
Table 8.2 The calculated results by power law equation of the TMXDI/Terathane 2000/DMPA/MPMDA based polyurethane powders.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ram speed (mm/min.)</th>
<th>Shear rate (γ) (s⁻¹)</th>
<th>Pressure (MPa)</th>
<th>Shear stress (τ) (MPa)</th>
<th>K (x 10³)</th>
<th>n</th>
<th>Apparent Viscosity (x 10³ Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>10</td>
<td>66.67</td>
<td>49.33</td>
<td>1.23</td>
<td>389</td>
<td>0.28</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>133.33</td>
<td>61.76</td>
<td>1.54</td>
<td></td>
<td></td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>200.00</td>
<td>66.49</td>
<td>1.66</td>
<td></td>
<td></td>
<td>8.31</td>
</tr>
<tr>
<td>140</td>
<td>10</td>
<td>66.67</td>
<td>27.01</td>
<td>0.68</td>
<td>178</td>
<td>0.32</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>133.33</td>
<td>35.44</td>
<td>0.89</td>
<td></td>
<td></td>
<td>6.65</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>200.00</td>
<td>38.62</td>
<td>0.97</td>
<td></td>
<td></td>
<td>4.83</td>
</tr>
<tr>
<td>150</td>
<td>10</td>
<td>66.67</td>
<td>10.25</td>
<td>0.26</td>
<td>14.1</td>
<td>0.70</td>
<td>3.84</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>133.33</td>
<td>17.31</td>
<td>0.43</td>
<td></td>
<td></td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>200.00</td>
<td>21.91</td>
<td>0.55</td>
<td></td>
<td></td>
<td>2.74</td>
</tr>
<tr>
<td>160</td>
<td>10</td>
<td>66.67</td>
<td>3.42</td>
<td>0.09</td>
<td>2.92</td>
<td>0.81</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>133.33</td>
<td>6.83</td>
<td>0.17</td>
<td></td>
<td></td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>200.00</td>
<td>8.19</td>
<td>0.20</td>
<td></td>
<td></td>
<td>1.02</td>
</tr>
</tbody>
</table>
Figure 8.2 Log shear stress & log shear rate relationship of a melt polyurethane powder

Figure 8.3 Apparent viscosity & shear rate relationship of a melt polyurethane powder
The urethane-urea copolymer melt gave an almost linear relationship of log shear stress and log shear rate. The log shear stress increased with increasing log shear rate. This result was consistent with a power law relationship of Ostwald-de-Waele for pseudoplastic materials, i.e.

\[ \tau = K (\gamma)^n \]

where \( K \) is a constant value and \( n \) is the power law index. In logarithmic form the equation may be written as:

\[ \log(\tau) = \log K + n \log(\gamma) \]

When one plots the log-log of \( \tau \) versus \( \gamma \), the y-intercept is \( \log K \) and the slope of the curve is the power law index \((n)\). The \( K \) value and power law index values obtained at different temperatures are shown in Table 8.2. The \( K \) values ranging from \( 2.92 \times 10^3 \) to \( 389 \times 10^3 \) were observed as temperature increased from 130 to 160 °C, while power law index values showed changes from 0.28 to 0.81. However, these values were the results of examination over a limited shear range and should not be regarded as definitive values of the material behaviour over a wider range of flow conditions.

The apparent viscosity of the melt from the polyurethane powder decreased with increasing shear rate. The relationship of apparent viscosity and shear rates were of a power law form. However, the apparent viscosity was less effected by the shear rate at high temperatures, as seen from Figure 8.2, the change of apparent viscosity against shear rate became almost a linear relationship at 160 °C. The power law index \((n)\) value approached 1 with increasing melt temperature. This possibly indicated that at the high melt temperatures, the urethane-urea copolymers was behaving in a near-Newtonian manner, because high temperature increased the Brownian motion of the molecule chain of polymer and reduced the effect of chain interaction.

This behaviour of log shear stress against log shear rate and of apparent viscosity against shear rate clearly showed the highly pseudoplastic nature of the urethane-urea copolymer melt. The simple explanation of the high pseudoplasticity is due to the asymmetric macromolecules of the urethane-urea copolymer, extensively entangled and randomly oriented at rest. After application of shear, the molecules become oriented in the shear direction and the numbers of chain entanglements and
interactions were significantly reduced. The orientation may be opposed by disorienting effects of Brownian motion especially at higher temperatures. Therefore, higher shear stresses were obtained initially but after continuing to apply shear, the macromolecule became more oriented and ordered. The shear stress will therefore only gain from the stretching of the main macromolecules.

8.2.2 Mass output rate

The results of mass output rate, with variation of ram speed and melt temperature of urethane-urea copolymer melt are shown in Table 8.3 and Figure 8.4.

Table 8.3 Mass output rate (g/min.) at various conditions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ram speed (mm/min.)</th>
<th>Mass output rate (g/min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 (67 *)</td>
<td>20 (133 *)</td>
</tr>
<tr>
<td>130</td>
<td>3.45</td>
<td>6.41</td>
</tr>
<tr>
<td>140</td>
<td>3.47</td>
<td>6.44</td>
</tr>
<tr>
<td>150</td>
<td>3.54</td>
<td>6.60</td>
</tr>
<tr>
<td>160</td>
<td>3.57</td>
<td>6.64</td>
</tr>
</tbody>
</table>

Note: * shear rate (sec⁻¹) in the parentheses

Figure 8.4 Mass output rate at various conditions
As seen in Table 8.3 and Figure 8.4, it was found that melt temperature did not significantly alter the mass output rate and shear rate relationships, with mass output being almost independent of melt temperature. Small increases in melt temperatures only slightly increased output rate, (e.g. less than 3.5% with 10 °C increase) but the mass output rate increased more than 30% with increasing the ram speed, e.g. 10 mm/min. The former result was believed to be due to a very low activation energy of the molten polymer. This is determined by using the Arrhenius equation, viscosity-temperature relationships of a melt can be used to determine the activation energy (8.3) for viscous flow, assumed that the polymer behaviour is near-Newtonian. The Arrhenius equation is given by:

$$\mu = A e^{E/RT}$$

where A is a constant, R is the universal gas constant and E is the activation energy. The activation energy of a polymer melt can be determined by plotting the $\ln(\mu)$ against $1/T$, and the resulting slope is the activation energy over gas constant value. The activation energy is shown in Table 8.4

<table>
<thead>
<tr>
<th>Ram Speed (mm/min.)</th>
<th>Melt temperature (K)</th>
<th>Apparent viscosity (Pa.s)</th>
<th>Activation energy (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>403</td>
<td>18500</td>
<td>30.8</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td>10130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>3850</td>
<td></td>
</tr>
<tr>
<td></td>
<td>433</td>
<td>1300</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>403</td>
<td>11580</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td>6650</td>
<td></td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>3250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>433</td>
<td>1280</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>403</td>
<td>8310</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td>4830</td>
<td></td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>1280</td>
<td></td>
</tr>
<tr>
<td></td>
<td>433</td>
<td>1020</td>
<td></td>
</tr>
</tbody>
</table>

Very low values of activation energy for the urethane-urea copolymer melt i.e. from 25.3 to 30.8 kcal/mole were found. This was believed to be responsible for the small change in output rate at different temperatures.
8.2.3 Percentage die swell

Die swell is a measure of the difference of the extrudate cross section diameter compared to the die cross section diameter; normally the value of the extrudate diameter is greater than the die cross section diameter. Here, it was assumed that the polymer molecules become oriented in the die and on emergence to atmospheric pressure recoil, with a contraction in the direction of flow being offset by lateral expansion.

Die swell behaviour studied elsewhere has been found to first increase with shear, up to a limit which is near to the critical shear rate, and beyond this point die swell decreases. Second, at a fixed shear rate, die swell decreases with temperature but the maximum swelling ratio increases with temperature. However, this melt showed slightly different behaviour. Alteration of ram speed, (or shear rate) at constant temperature appeared to have no significant effect on the percentage die swell, as seen in Table 8.5. This was possibly due to the minor variation of the shear rate. The percentage die swell shown in Figure 8.5, decreased as expected with higher temperature, and results were consistent with general observations. At the highest melt temperature (i.e. 160 °C), the percentage die swell became negative. This was due to the low melt strength of the extrudate at higher melt temperatures, causing draw down of the extrudate at the die exit. In this study, the flow behaviour of polyurethane melt using the Davenport capillary rheometer, the extrudates were forced though the die, in a vertical, downward direction. There was nothing to support the extrudate so that with weak melt strength, the extrudate extended under its own weight, reducing the cross section leading to a negative value of percentage of apparent die swell.

Table 8.5 Cross section and percentage of die swell at various conditions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ram Speed (mm/min.)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 (67*)</td>
<td>20 (133*)</td>
<td>30 (200*)</td>
</tr>
<tr>
<td></td>
<td>Cross section</td>
<td>Die swell</td>
<td>Cross section</td>
<td>Die swell</td>
</tr>
<tr>
<td></td>
<td>diameter (mm)</td>
<td>(%)</td>
<td>diameter (mm)</td>
<td>(%)</td>
</tr>
<tr>
<td>130</td>
<td>3.04</td>
<td>52.2</td>
<td>3.02</td>
<td>51.0</td>
</tr>
<tr>
<td>140</td>
<td>2.83</td>
<td>41.3</td>
<td>2.83</td>
<td>41.5</td>
</tr>
<tr>
<td>150</td>
<td>2.63</td>
<td>31.4</td>
<td>2.57</td>
<td>28.5</td>
</tr>
<tr>
<td>160</td>
<td>1.83</td>
<td>-8.5</td>
<td>1.67</td>
<td>-16.5</td>
</tr>
</tbody>
</table>

Note: * shear rate (sec\(^{-1}\)) in the parentheses
8.2.4 Appearance of the extrudate

The details of the appearance of the polyurethane extrudate are given in Table 8.6. The extrudates obtained at low temperatures had a poor surface finish (i.e. shark skin) and grossly distorted shape (i.e. bambooing effect), but these characteristics were not found at either higher shear rate or higher melting temperatures. However, with very high melt temperature, the surface of the extrudate was sticky to the touch and bubbles appeared inside the extrudate: the melt strength of the extrudate was also very poor and not suitable to give satisfactory extrusion.

From these simple investigations of melt flow behaviour, some useful observations were obtained. With the low activation energy values for viscous flow temperature appeared to have little effect on flow rates between 130 and 160 °C. However, the surface condition of the extrudate suggested that the best results for injection moulding processing were likely to be obtained at temperatures of 150 °C and upwards and using high injection melt speeds.
### Table 8.6 Appearance of extrudates

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>10 (67*)</th>
<th>20 (133*)</th>
<th>30 (200*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>Poor surface finish (shark skin)</td>
<td>Poor surface finish (shark skin)</td>
<td>Poor surface finish (less shark skin)</td>
</tr>
<tr>
<td></td>
<td>Distorted shape</td>
<td>Distorted shape</td>
<td>More distorted shape</td>
</tr>
<tr>
<td></td>
<td>Transparent</td>
<td>Transparent</td>
<td>Transparent</td>
</tr>
<tr>
<td></td>
<td>130 Poor surface finish (shark skin)</td>
<td>130 Poor surface finish (shark skin)</td>
<td>130 Poor surface finish (shark skin)</td>
</tr>
<tr>
<td></td>
<td>Distorted shape</td>
<td>Distorted shape</td>
<td>More distorted shape</td>
</tr>
<tr>
<td></td>
<td>Transparent</td>
<td>Transparent</td>
<td>Transparent</td>
</tr>
<tr>
<td>140</td>
<td>Poor surface finish (shark skin)</td>
<td>Poor surface finish (few shark skins)</td>
<td>Good surface finish (few shark skins)</td>
</tr>
<tr>
<td></td>
<td>Distorted shape (better than at 130°C)</td>
<td>Distorted shape (better than at 130°C)</td>
<td>More distorted shape (better than at 130°C)</td>
</tr>
<tr>
<td></td>
<td>Transparent</td>
<td>Transparent</td>
<td>Transparent</td>
</tr>
<tr>
<td>150</td>
<td>Good surface finish Bubble in the centre</td>
<td>Good surface finish Few bubbles</td>
<td>Good surface finish</td>
</tr>
<tr>
<td></td>
<td>Poor melt strength</td>
<td>Transparent</td>
<td>No bubbles</td>
</tr>
<tr>
<td></td>
<td>Transparent</td>
<td>Transparent</td>
<td>Transparent</td>
</tr>
<tr>
<td>160</td>
<td>Good surface finish Bubble (big)</td>
<td>Good surface finish Bubbles (small)</td>
<td>Good surface finish</td>
</tr>
<tr>
<td></td>
<td>Poor melt strength</td>
<td>Poor melt strength</td>
<td>Bubbles (small)</td>
</tr>
<tr>
<td></td>
<td>Melt fracture</td>
<td>Melt fracture</td>
<td>Melt fracture</td>
</tr>
</tbody>
</table>

Note: * shear rate (sec\(^{-1}\)) in the parentheses

8.3 Injection moulding the urethane-urea copolymer powder

The techniques available for melt processing thermoplastic polyurethanes include injection moulding, extrusion, calendering and solution fabrication. Of these, the injection moulding process is the most important and satisfactory process used to manufacture thermoplastic mouldings. Usually speciality grades of polymer are produced by suppliers who also provide advice on the optimum processing conditions. Moulding conditions are generally optimised by experience and many factors can influence the quality of the final product. However, in this study only the moulding parameters, (i.e. injection melt temperature, injection speed and mould cooling times), were investigated. It was also thought likely that considerable degradation of the polymer could take place when heated to elevated temperature, resulting in a large reduction in physical strength.(8.5) In commercial practice, it is common that thermal stabilisers will be added to a polymer to reduce the effects of thermal and shear degradation. However, these were not used in this study to enable a direct comparison of a formulation used in melt processed sheet and cast films.
8.3.1 Tensile properties measurement

All injection moulded specimens (i.e. 3 mm thickness) were rubbery, slightly yellowish, (compared with cast film) and transparent. No distorted samples were obtained. A summary of the results of tensile properties are shown in Table 8.7.

Table 8.7 Tensile properties: a summary of results for injection moulding specimens from a powder.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>300 % Modulus (MPa)</th>
<th>T.S. (MPa)</th>
<th>E.B. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AVG</td>
<td>STD</td>
<td>AVG</td>
</tr>
<tr>
<td>Results from injection moulded specimens</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Series A: Effect of injection speed (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>8.3</td>
<td>0.1</td>
<td>28.0</td>
</tr>
<tr>
<td>40</td>
<td>7.5</td>
<td>0.1</td>
<td>27.3</td>
</tr>
<tr>
<td>60</td>
<td>7.1</td>
<td>0.2</td>
<td>26.9</td>
</tr>
<tr>
<td>80</td>
<td>7.3</td>
<td>0.1</td>
<td>25.7</td>
</tr>
<tr>
<td>Series B: Effect of moulding cooling time (second)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>7.8</td>
<td>0.1</td>
<td>26.9</td>
</tr>
<tr>
<td>50</td>
<td>7.8</td>
<td>0.1</td>
<td>26.8</td>
</tr>
<tr>
<td>70</td>
<td>7.8</td>
<td>0.1</td>
<td>24.7</td>
</tr>
<tr>
<td>Series C: Effect of injection temperature (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>7.8</td>
<td>0.1</td>
<td>26.9</td>
</tr>
<tr>
<td>160</td>
<td>7.7</td>
<td>0.1</td>
<td>27.8</td>
</tr>
<tr>
<td>170</td>
<td>7.3</td>
<td>0.1</td>
<td>26.3</td>
</tr>
<tr>
<td>180</td>
<td>6.7</td>
<td>0.1</td>
<td>23.3</td>
</tr>
<tr>
<td>Result from cast films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 025</td>
<td>16.2</td>
<td>0.1</td>
<td>44.4</td>
</tr>
</tbody>
</table>

Key: T.S. = Tensile strength, E.B. = Elongation at break

Series A illustrated in Figure 8.6 showed that increasing injection speed from 20 to 80 % of the maximum injection rate (i.e. 84 cm$^3$/sec. based on polystyrene) marginally decreased the values of 300% modulus and tensile strength from 8.3 to 7.3 MPa and 28.0 to 25.7 MPa respectively. The elongation at break at injection speeds of 40 to 60% had the highest value of about 1790 %. Polyurethanes are generally considered to be structurally shear sensitive materials(8.5) which can build up considerable frictional heat under high shear. Increasing injection speed, created high shear in polymer producing a deleterious effect on all the tensile properties: this was supported by these results.
With increasing mould cooling time, from 30 to 70 second, the 300% modulus remains unchanged at around 7.8 MPa but the tensile strength slightly decreased from 26.9 to 24.7 MPa, while elongation at break increased from 1655 to 1752 %, (see Figure 8.7). This may well be the result of reduced phase separation occurring in those materials which had the longest mould cooling time. Samples having shorter mould cooling time are still warm after ejection from the mould so that they subsequently cool in air at a slower rate, (cf. those which are force cooled in a cold mould at 10 °C). As a result a fuller development of polymer structure may have take place, giving enhanced phase separation which ultimately produced better tensile properties.

In series C increasing the melt injection temperature from 150 to 180 °C, produced somewhat lower 300% modulus and tensile strength values which decreased from 7.8 to 6.7 MPa and 26.9 to 23.3 MPa respectively. However, the elongation at break increased with higher injection temperature from 1655 to 1800 %, (see Table 8.7 and Figure 8.8). At higher temperatures, the specimens became distinctly yellow in colour, suggesting that some degradation had probably taken place. This degradation was also supported by the decreasing of tensile strength. The effect of degradation could perhaps be cured with the aid of a thermal stabiliser.

![Figure 8.6 Effect of injection speed on tensile properties.](image-url)
Figure 8.7 Effect of mould cooling time on tensile properties

Figure 8.8 Effect of injection temperature on tensile properties
8.3.2 Differential scanning calorimetry (DSC) analysis

A summary of results for the thermal properties of injection moulded of powders are shown on Table 8.8.

Table 8.8 DSC: Summary results of injection moulding sheet from polyurethane powders.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Tg (°C)</th>
<th>Other transitions (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Second</td>
<td>Third</td>
</tr>
<tr>
<td>Results from injection moulded specimens</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Series A : Effect of injection speed (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-77</td>
<td>81</td>
<td>222</td>
</tr>
<tr>
<td>40</td>
<td>-74</td>
<td>80</td>
<td>212</td>
</tr>
<tr>
<td>60</td>
<td>-72</td>
<td>81</td>
<td>213</td>
</tr>
<tr>
<td>80</td>
<td>-70</td>
<td>81</td>
<td>200</td>
</tr>
<tr>
<td>Series B : Effect of mould cooling time (second)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>-75</td>
<td>78</td>
<td>220</td>
</tr>
<tr>
<td>50</td>
<td>-73</td>
<td>80</td>
<td>216</td>
</tr>
<tr>
<td>70</td>
<td>-70</td>
<td>79</td>
<td>204</td>
</tr>
<tr>
<td>Series C : Effect of injection moulding temperature (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>-76</td>
<td>82</td>
<td>220</td>
</tr>
<tr>
<td>160</td>
<td>-73</td>
<td>83</td>
<td>217</td>
</tr>
<tr>
<td>170</td>
<td>-74</td>
<td>82</td>
<td>213</td>
</tr>
<tr>
<td>180</td>
<td>-71</td>
<td>84</td>
<td>215</td>
</tr>
<tr>
<td>Result from cast films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 025</td>
<td>-76</td>
<td>65</td>
<td>190</td>
</tr>
</tbody>
</table>

For series A with increasing injection speed, Tg shifted to slightly higher temperatures (i.e. from -77 to -70°C), the third transition and degradation temperature were shifted towards lower temperatures from 222 to 200 °C and 250 to 240 °C respectively, (see Figure 8.9). This was believed to be due to the higher injection speed, producing greater shear to the polymers leading to greater phase mixing between hard and soft segments within the polyurethane domains. This was indicated by the broader soft segment melting range at around 80 °C since the soft segment was less pure, with hard segment penetration into the soft segment phase. However, increasing injection speed will also generate a greater heat build up in the polyurethanes, accelerating the break down of the polymer chain, while lowering the hard segment melting range, (manifested in the relatively lower of the third transition and degradation temperatures). The decrease in tensile properties also supports this argument.
In series B on increasing the mould cooling time, Tg was shifted to a slightly higher temperature (i.e. from -75 to -70 °C). The second transition melting range was constant at around 80 °C but the curve became broader with longer mould cooling time. The third transition temperature and degradation temperature were shifted toward lower temperatures from 220 to 204 °C and from 255 to 250 °C respectively, (see Figure 8.10). This was believed to be due to the hard and soft segment phase movements of polyurethane being forced to take place at a greater level with longer mould cooling time. The polymer melted at 170 °C was then injected into a cooled mould at 10 °C, at short mould close times the samples experience less cooling than the longer mould close time. The latter samples being more forcibly cooled were likely to have a higher frozen stress level which lower the tensile properties. Further more, the hold-on time was set constant at 5 second, at longer mould close time, the polymer would have experienced longer heating in the barrel, leading to greater possibility of degradation.

Increasing the melt temperatures, Tg was found to shift slightly towards the higher temperature, (i.e. from -76 to -71 °C). The second transition melting range was almost constant at around 81 °C but the curve becomes broader in shape. The third transition and degradation temperatures were shifted toward lower values, (see Figure 8.11). This was believed to be due to the higher melt injection temperatures creating greater phase mixing, as can be seen from the broader curve at the second transition peak, before the degradation of the polymer chain took place. Since polyurethanes are heat sensitive, their chains are broken down by high heat build up at the higher injection temperature, leading to lower degradation temperatures. The poorer tensile properties also supported this argument.
Figure 8.9 DSC examination of moulded polyurethanes prepared with different injection speeds
Figure 8.10 DSC examination of moulded polyurethanes prepared with different mould cooling time.
Figure 8.11 DSC examination of moulded polyurethanes prepared with different injection moulding temperature
8.3.3 Dynamic mechanical thermal analysis (DMTA)

A summary of the results of thermal properties measured by DMTA on the urethane-urea copolymer melt are shown in Table 8.9.

Table 8.9 DMTA: A summary of results of injection moulding specimens made from a urethane-urea copolymer powder

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Tg (°C) at E' onset</th>
<th>E' at Tg (MPa)</th>
<th>First Tan δ Temp. (°C) Value</th>
<th>Second Tan δ Temp. (°C) Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results from injection moulded specimens</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Series A: Effect of injection speed (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-72</td>
<td>1023</td>
<td>-58</td>
<td>0.17</td>
</tr>
<tr>
<td>40</td>
<td>-72</td>
<td>905</td>
<td>-56</td>
<td>0.16</td>
</tr>
<tr>
<td>60</td>
<td>-70</td>
<td>834</td>
<td>-56</td>
<td>0.17</td>
</tr>
<tr>
<td>80</td>
<td>-71</td>
<td>742</td>
<td>-55</td>
<td>0.17</td>
</tr>
<tr>
<td>Series B: Effect of mould cooling time (seconds)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>-72</td>
<td>741</td>
<td>-54</td>
<td>0.17</td>
</tr>
<tr>
<td>50</td>
<td>-71</td>
<td>733</td>
<td>-54</td>
<td>0.17</td>
</tr>
<tr>
<td>70</td>
<td>-69</td>
<td>720</td>
<td>-54</td>
<td>0.17</td>
</tr>
<tr>
<td>Series C: Effect of injection temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>-75</td>
<td>1124</td>
<td>-56</td>
<td>0.17</td>
</tr>
<tr>
<td>160</td>
<td>-73</td>
<td>1059</td>
<td>-55</td>
<td>0.17</td>
</tr>
<tr>
<td>170</td>
<td>-70</td>
<td>982</td>
<td>-53</td>
<td>0.17</td>
</tr>
<tr>
<td>180</td>
<td>-70</td>
<td>868</td>
<td>-53</td>
<td>0.19</td>
</tr>
<tr>
<td>Results from cast films</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBG 020</td>
<td>-80</td>
<td>2334</td>
<td>-63</td>
<td>0.18</td>
</tr>
</tbody>
</table>

With increasing the injection speed the Tg, (obtained from the onset of change in slope of E' verses temperature) was constant at around -71 °C. However, the E' values at Tg and the E' curve moved towards lower values; (see Figure 8.12). This was believed to be due to increased shear producing more phase mixing and the possibility of polymer chains also breaking down due to heat degradation, leading to a reduction in storage modulus.

Two separated peaks in the tan δ curve were observed; (see Figure 8.13). This was quite unexpected since the cast film in the same formulation showed only a single tan δ at low temperature. This is thought to be due to the effect of the test specimen's thickness i.e. injection moulding sheets were about twice as thick as cast film. By heating a cast film above 70 °C, it become too compliant and movement could not detected by the strain transducer. The thicker moulded specimens being less compliant, enabled a fuller sensitivity of movement detection to be monitored up to 100 °C. Hence, this allowed second transitions to be observed, not detected in thinner cast films. This second tan δ peak at high
temperatures, (i.e. 60 to 80°C) was possibly due to the movement associated with side pendent carboxylic groups and methyl groups in the hard segment phase, created by the low molecular weight of the carboxylic acid (i.e. DMP A). The temperature of the lower tan δ peak, its value and shapes were almost constant, (at around -56 °C and the peak value around 0.17), since the soft segment type and the reaction block ratio were kept constant. The temperature of the higher tan δ peak dropped from 79 to 63 °C, while the tan δ value increased with higher injection speed (i.e. from 0.42 to 0.73). The tan δ curve shape also became broader. It was believed that the higher injection speed created more phase mixing, with more hard segments being mixed into the soft segment domain. The molecular structure gained greater disorder and free movement, therefore larger and broader tan δ peaks were observed. This was also consistent with the DSC results.

By increasing the mould cooling time, it was found that the E' against temperature curve was shifted to higher temperatures as can be seen from Figure 8.14. The Tg value (obtained from the onset of the change in slope of the modulus against temperature) slightly increased from -72 to -69 °C, with the 30 to 70 second increase of mould cooling time. The temperatures of the lower tan δ peak, tan δ value and its curve shape were almost constant at around -54 °C and the tan δ peak value was around 0.17. The temperature of the higher tan δ peak moved to slightly lower temperatures, (i.e. from 63 to 58 °C), indicating more phase mixing, while the tan δ value decreased from 0.50 to 0.41. The tan δ curve shape became narrower, suggesting that less pure soft segments were present in the hard segment domain, (see Figure 8.15). This was also consistent with the DSC results.

By increasing the injection melt temperature, the Tg values, (i.e. obtained from the onset E') were shifted from -75 to -70 °C. The E' value at Tg and its curve had moved to lower values, (see Figure 8.16). It was believed that at higher injection temperatures the polymer degraded further, leading to lower storage modulus values. With high melt temperatures, the lower tan δ peak was slightly shifted to a higher temperature and its value was increased from 0.17 to 0.19. The temperature of the higher tan δ peak moved to lower temperatures, (i.e. from 85 to 61 °C) and tan δ peak value increased from 0.40 to 0.59. The tan δ curve shape was unchanged. It should be noted that both tan δ peaks were moved towards each other with higher injection temperature, indicating more phase mixing of the hard and soft segments, (see Figure 8.17). This possibly indicated that on increasing the injection temperature, the hard and soft phases were mixed together before the degradation took place.
Figure 8.12 DMTA examination of moulded polyurethanes prepared with different injection speeds on $E'$

Figure 8.13 DMTA examination of moulded polyurethanes prepared with different injection speeds on $\tan \delta$
Figure 8.14 DMTA examination of moulded polyurethanes prepared with different mould cooling time on $E'$

Figure 8.15 DMTA examination of moulded polyurethanes prepared with different mould cooling time on $\tan \delta$
Figure 8.16 DMTA examination of moulded polyurethanes prepared with different injection moulding temperature on $E'$

Figure 8.17 DMTA examination of moulded polyurethanes prepared with different injection moulding temperature on $\tan \delta$
8.4 A comparison of the properties of cast film and injection moulded specimens

For comparison, the same equivalent molar block ratio of TMXDI/Terathane 2000/DMPA/MPMDA = 1/0.25/0.25/0.5 was selected. This formulation corresponded to CBG025, cast film. Since many parameters were varied in the injection moulded process a range of tensile results had been obtained. Therefore the injection conditions that gave the best tensile properties was chosen. These comparison properties are shown in Table 8.10

<table>
<thead>
<tr>
<th>Properties</th>
<th>Cast Specimens</th>
<th>Injection moulded Specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tensile properties:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300% modulus (MPa)</td>
<td>16.2</td>
<td>8.3</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>44.4</td>
<td>28.0</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>1330</td>
<td>1707</td>
</tr>
<tr>
<td><strong>Thermal properties from DSC analysis:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass transitions (°C)</td>
<td>-76</td>
<td>-77</td>
</tr>
<tr>
<td>Second transition temp.(°C)</td>
<td>65</td>
<td>81</td>
</tr>
<tr>
<td>Third transition temp.(°C)</td>
<td>190</td>
<td>222</td>
</tr>
<tr>
<td>Degradation temp. (°C)</td>
<td>242</td>
<td>250</td>
</tr>
<tr>
<td><strong>Thermal properties from DMTA:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass transitions (°C)</td>
<td>-80</td>
<td>-72</td>
</tr>
<tr>
<td>E' at Tg (MPa)</td>
<td>2334</td>
<td>1023</td>
</tr>
<tr>
<td>First tan δ temp. (°C)</td>
<td>-63</td>
<td>-58</td>
</tr>
<tr>
<td>First tan δ value</td>
<td>0.18</td>
<td>0.17</td>
</tr>
<tr>
<td>Second tan δ temp. (°C)</td>
<td>—</td>
<td>79</td>
</tr>
<tr>
<td>Second tan δ value</td>
<td>—</td>
<td>0.42</td>
</tr>
</tbody>
</table>

It was found that the 300% modulus and tensile strength of the cast films were superior to injection moulded specimens. This was believed to be due to the degradation from the melt process since these polymers are known to be both structurally shear and heat sensitive. High shear with high heat build up will initiate the degradation as observed in samples obtained by injection moulding: these were considered more yellowish than the specimens obtained by casting.

On examination of the thermal properties of the polyurethanes by DSC, it was found that there was no change in Tg, for either process method, but it was quite surprising to see that the other transitions and degradation temperature of injection moulding specimens had higher temperatures than cast films, particularly for the third transition temperature. Generally, it was expected that the injection moulded
specimens would have a lower values of third transition and degradation temperature because of degradation. In this comparison, the representative materials for DSC analysis was selected from the conditions that gave the best tensile properties, (here at 20 % injection speed). However, at higher injection speeds e.g. at 80 % or higher melt temperatures e.g. at 180 °C, the polyurethanes may be expected to follow the general trends. However, the thermal properties measurement by DSC analysis are normally strongly affected by the thermal history of specimens: since the heat treatment of cast film and injection moulding specimens were quite different, the transitions were not fully comparable.

The Tg, (from the onset of change in E') obtained from DMTA, showed that the value obtained from cast film was lower than those for injection moulding specimens. This was believed to be due to the high phase mixing of hard and soft segments of injection moulded specimens. The E' at Tg of cast films was higher than for injection moulded samples. This was consistent with the tensile properties results. It should be noted that the injection moulded film had two separated tan δ indicating clearly that phase separation had occurred between hard and soft segments, while only a single tan δ at low temperature could be detected for cast film. This is possibly a thickness factor as the injection moulding specimens had twice of the thickness of cast film. The Polymer Laboratory-DMTA equipment is not able to detect movement if the modulus falls below 10^6 dynes cm^{-2}. The thermoplastic cast films are too complaint above 70 °C to permit detection of the transitions which occur above this temperature. It was found that there were no significant differences in the low temperature tan δ, as expected, since the soft segment type and block ratio were kept the same.
References


9.1 General conclusions

Solvent-free water dispersed urethane-urea copolymers can be simply prepared by creating quaternary ammonium salt hydrophilic sites, (as dispersion stabiliser) in a urethane-urea backbone chain. This can be achieved by incorporating a small amount of polymerisable dihydroxy carboxylic acid into the formulation. The pendant carboxylic acid in the structure will then react with a water soluble tertiary amine, (e.g. triethyl amine) in aqueous conditions, forming quaternary ammonium salts. This ammonium salt provides high hydrophilicity to the polymer and therefore it does not require any organic solvent during the water dispersion stage, as in a conventional prepolymer mixing process. \( \alpha, \alpha' \)-dimethylol propionic acid (DMPA) used as the pendent carboxylic group provider because of the steric hindrance of the carboxylic group which prevents the carboxylic groups reacting rapidly with the isocyanate. The amount of DMPA used in water dispersed polyurethane preparation was optimised between 0.08 to 0.2, (DMPA equivalent molar block per total equivalent molar block ratio of TMXDI/polyol/DMPN/chain extender based polymer) to obtain stable milky white dispersions of high solids content.

The preferred synthesis temperature of the water dispersed urethane-urea copolymers based on (TMXDI/Capa or Terathane/DMPA/Aliphatic diamine) was found to be between 60 and 90 °C, with the isocyanate terminated prepolymer stage was usually carried out at 90 °C. This reaction temperature was selected on a balance factor i.e. viscosity of prepolymer, reaction time and onset of high rates of undesirable side reaction of isocyanate with dihydroxy carboxylic acids (\( \geq 100 ^\circ C \)), leading to unstable polyurethane dispersions. Neutralisation, dispersion and chain extension were carried out at 60 °C, this reaction temperature was selected on the balance of the boiling point of neutralising agent, (i.e. triethylamine), and the relative reactivity of isocyanate-water reaction and isocyanate-amine reactions.

The properties of the polyurethane dispersions were strongly affected by the concentration of carboxylic ionic emulsifiers in the polyurethane structure. With higher concentration of carboxylic ionic emulsifier, pH and dispersion viscosity were increased while particle size and surface tension were decreased. Increasing molecular
weight of the polyol component also increased the viscosity and reduced the polymer particle size.

Properties of the solid cast thermoplastic urethane-urea copolymers were mainly influenced by hard segment content and the molecular weight of soft segment (i.e. derived from the polyol). The general trends showed increases in modulus, tensile strength, glass transition temperature, secondary transition temperature, degradation temperature and hydrogen bonding with higher hard segment content or lower molecular weight of soft segment. It was possible that higher pendent carboxylic ionic emulsifier content in the polymer structure decreased its thermal stability. At room temperature, polyether (Terathane) and polyester (Capa) polyol components of similar molecular weight, imparted similar tensile properties to the polymer. Surprisingly, maximum tensile strength and elongation at break were found for polymers based on either polyol types at 2000 molecular weight.

The studies of injection moulding behaviour and the resulting properties of the mouldings of a selected polymer obtained from powder precipitated from a water based dispersion, showed that reasonable products can be obtained. In this study a limited number of melt and solid properties were examined and can only be used to draw limited number of conclusions. Much further work needs to be done to more fully explore the optimum formulation and processing conditions needed to produce moulded urethane-urea copolymers, of the quality necessary for high performance products. However, it is believed that this work indicated many potential routes to give improved products with commercial potential and these systems are well worth further investigation.

9.2 Recommendations for future work

1) In order to assist the technologist in the design of new water dispersible systems based on the current model, rate studies should be carried out on the comparative rates of reaction between isocyanate-water and isocyanate-amine, within the range of reaction temperatures, particularly for TMXDI and other, newer, suitable isocyanates.

2) Studies of reaction rates are also necessary for the reaction of isocyanate with hindered carboxylic acid containing glycols, to verify optimum conditions for preparation of water dispersible prepolymers. At the moment there is no clear
understanding of how the isocyanate tipped prepolymer is developed from its three precursor materials, (i.e. TMXDI, polyol, DMPA).

3) Investigations should be carried out on other commercial aliphatic diisocyanates, such as 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) or 4,4'-dicyclohexylmethane diisocyanate (H_{12}DMI) and also on cheaper polyols such as polypropylene glycol (PPG) or blends of polyols. These precursors would give the advantage of cheaper final products.

4) The effect of different amines used to generate the quaternary functionality, used to confer water dispersibility, could be investigated, particularly using long chain tertiary amine to give improved detergency action.

5) Studies are required on the role of carboxylic emulsifier groups on the thermal stability of polymer melts of water dispersed polyurethanes.

6) Studies are required on the choice of effective stabiliser to enable melt processing of urethane-urea copolymer powder to be carried without property degradation.
Appendices
Appendix 1

Physical properties of meta and para tetramethyl xylene diisocyanate

<table>
<thead>
<tr>
<th></th>
<th>m-TMXDI</th>
<th>p-TMXDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS registry number</td>
<td>2778-42-9</td>
<td>2778-41-8</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₁₄H₁₆N₂O₂</td>
<td>C₁₄H₁₆N₂O₂</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>244.3</td>
<td>244.3</td>
</tr>
<tr>
<td>NCO content (theory), (% by wt.)</td>
<td>34.4</td>
<td>34.4</td>
</tr>
<tr>
<td>NCO equivalent wt. (theory)</td>
<td>122.1</td>
<td>122.1</td>
</tr>
<tr>
<td>Physical form</td>
<td>colourless white crystals</td>
<td>mobile liquid</td>
</tr>
<tr>
<td>Melting point, (°C)</td>
<td>-10</td>
<td>72</td>
</tr>
<tr>
<td>Boiling point, (°C)</td>
<td>150 °/3mm</td>
<td>150 °/3mm</td>
</tr>
<tr>
<td>Vapour pressure, (mm Hg at 100 °C)</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Viscosity, (mPa.s) at 0 °C</td>
<td>25</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>20 °C</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>—</td>
</tr>
<tr>
<td>Flash point (closed cup), (°C)</td>
<td>&gt;93</td>
<td>&gt;93</td>
</tr>
<tr>
<td>Auto ignition point, (°C)</td>
<td>450</td>
<td>450</td>
</tr>
<tr>
<td>TMXDI by NCO titration, (%)</td>
<td>&gt;99</td>
<td>—</td>
</tr>
<tr>
<td>Total chlorides (ppm)</td>
<td>&lt;50</td>
<td>—</td>
</tr>
<tr>
<td>Solubility</td>
<td>Both compounds are soluble in most organic solvents, including esters, ethers, ketones and aromatic hydrocarbons.</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Physical properties of meta and para tetramethyl xylene diisocyanate
Appendix 2

Percentage of total solids content (by weight)

**Apparatus** - Tared, covered, flat-bottom glass weighing dish approximately 60 mm (2.5 in.) in diameter, balance, air circulated oven.

**Reagent** - Distilled water

**Procedure** - The sample was weighed (2.0 ± 0.2 g to the nearest 1 mg) in a tared, covered weighing dish. The cover was removed and the latex distributed over the bottom of the dish, over an area of approximately 20 cm². This was facilitated by carefully adding approximately 1 ml. of distilled water to the latex and gently swirling the dish. With the dish uncovered, the specimen was dried in a vented air oven for 2 hours at 100 ± 2 °C. Drying and weighing were repeated until the mass is constant to 1 mg or less. Tests were run in duplicate and checked within 0.15%. The average of three determinations were taken as the result.

**Calculations** - the percentage of total solids were calculated as follows:

\[
\text{Total solids content, } \% = \left(\frac{C-A}{B-A}\right)\times 100
\]

Where:

\begin{align*}
A &= \text{mass of the weighing dish, (g).} \\
B &= \text{mass of the dish plus the original sample, (g).} \\
C &= \text{mass of the dish plus the dried sample, (g).}
\end{align*}
Appendix 3

Determination of percentage of free isocyanate

Apparatus

1) Lunge pipette that can weigh a liquid by difference to the nearest 0.001 g.
2) 500 ml Erlenmeyer flask with stopper.
3) Magnetic stirrer.
4) Graduated cylinder.
5) 50 ml burette.

Reagents

1) Bromocresol green indicator solution
Using 1.5 ml of 0.1 N sodium hydroxide, extract the bromocresol green from 0.100 g of bromocresol green indicator grade powder, stirring vigorously until the amount of insoluble residue remains constant. Decant the aqueous portion into a 100 ml volumetric flask and dilute to the mark with methanol.

2) Dibutylamine solution (260g/l.)
Dilute 260 g of dry dibutylamine to 1 litre with dry toluene. Dry the solution over a Linde 4A molecular sieve.

3) Hydrochloric acid (1 N)
Prepare 1 N Hydrochloric acid and standardise frequently enough to detect changes of 0.001 N

4) Methanol

5) Toluene- Dry toluene with Linde 4A molecular sieve.

Procedure

1) The sample and blank determinations were run side-by-side. The blank determination was run exactly as described as follows but without adding the sample.
2) A magnetic stirring bar and 40 ml of dry toluene were added into a 500 ml flask. 50 ml of dibutylamine solution were then accurately added by pipette.
3) While stirring the contents of the flask, 5 g of the sample, (weighed to nearest 0.001g) was slowly added to the mixture. The sides of the flask were washed down with 10 ml of dry toluene, then the flask was stoppered loosely and allowed to stand at
room temperature for 30 minutes for the reaction to complete, (i.e. a clear solution obtained).

4) Methanol (100 ml) was added with 5 to 10 drops of bromocresol green indicator solution. The excess of the dibutylamine was then titrated with 1 N hydrochloric acid solution from a 50 ml burette while stirring the flask contents with the magnetic stirring bar. Near the end point, the hydrochloric acid was slowly added. The end point was reached when the blue colour disappeared, and a yellow colour appeared and persisted for at least 15 seconds.

Calculation

The assay percentage were calculated as follows:

\[
\text{Assay, } \% = 42 \times \frac{N(B-S)(100)}{1000W}
\]

Where:

- \(N\) = Normality of the hydrochloric acid
- \(B\) = Hydrochloric acid required for titration of the blank, (ml)
- \(S\) = Hydrochloric acid required for titration of the sample, (ml)
- \(W\) = Sample used,(g)
Appendix 4

(a) Calculation of percentage hard segment content (by weight)

For any given reaction block ratio of the polyurethane formulation, the hard segment content can be calculated as:

\[
\% \text{ Hard segment content} = \frac{\text{Total weight of hard segment}}{\text{Total weight of hard and soft segment}} \times 100
\]

For water dispersed polyurethane, the total hard segments are the sum of weight of diisocyanate, carboxylate diol and chain extender. The soft segment is the weight of polyol.

As an example of polyurethane with the reaction block ratio (TMDXI/Capa 220/DMPA/MPMDA) of 3/1/1/1.

The weight of hard segment are:
Equivalent of TMDXI = 122, therefore the weight of TMDXI = 3(122)
Equivalent of DMPA = 67, therefore the weight of DMPA = 1(67)
Equivalent of MPMDA = 58, therefore the weight of MPMDA = 1(58)

The weight of soft segment is:
Equivalent of Capa 220 = 1000, therefore the weight of Capa 220 = 1(1000)

\[
\% \text{ Hard segment in ISO 3} = \frac{3(122) + 1(67) + 1(58)}{1(1000) + 3(122) + 1(67) + 1(58)} \times 100 = 32.9
\]

(b) Calculation of percentage urea content (by weight)

For any given reaction block ratio in the polyurethane formulation, the urea content can be calculated as:

\[
\% \text{ Urea content} = \frac{\text{Total weight of amine chain extender}}{\text{Total weight of all reactants}} \times 100
\]

For water dispersed polyurethane, the total weight of all chemicals are the sum of weight of diisocyanate, polyol, carboxylate diol and amine chain extender.

As an example of polyurethane with the reaction block ratio (TMDXI/Capa 220/DMPA/MPMDA) of 3/1/1/1.
The weight of each chemical is:
Equivalent of TXMDI = 122, therefore the weight of TMXDI = 3(122)
Equivalent of DMPA = 67, therefore the weight of DMPA = 1(67)
Equivalent of MPMDA = 58, therefore the weight of MPMDA = 1(58)
Equivalent of Capa 220 = 1000, therefore the weight of Capa 220 = 1(1000)

\[
\% \text{ Urea content in ISO 3} = \frac{1(58)}{1(1000) + 3(122) + 1(67) + 1(58)} \times 100 = 3.9
\]

(c) Calculation of percentage pendent carboxylic groups content (by weight)

For any given reaction block ratio in the polyurethane formulation, the pendent carboxylic groups content can be calculated as:

\[
\% \text{ Carboxylic groups content} = \frac{\text{Equivalent weight of carboxylic groups}}{\text{Total weight of all reactants}} \times 100
\]

For water dispersed polyurethane, the total weight of all chemicals are the sum of weight of diisocyanate, polyol, carboxylate diol and amine chain extender.

As an example of polyurethane with the reaction block ratio (TMDXI/Capa 220/DMPA/MPMDA) of 3/1/1/1.

The weight of each chemical is:
Equivalent of TXMDI = 122, therefore the weight of TMXDI = 3(122)
Equivalent of DMPA = 67, therefore the weight of DMPA = 1(67)
Equivalent of MPMDA = 58, therefore the weight of MPMDA = 1(58)
Equivalent of Capa 220 = 1000, therefore the weight of Capa 220 = 1(1000)

The equivalent weight of carboxylic groups is the multiply of equivalent molar of DMPA and equivalent of carboxylic groups (45).

Equivalent weight of carboxylic groups = 1 x 45 = 45

\[
\% \text{ Carboxylic groups content} = \frac{1(45)}{1(1000) + 3(122) + 1(67) + 1(58)} \times 100 = 3.0
\]
Appendix 5

The calculation of shear stress & shear rate relationships

The measurement of the shear stress-shear rate function as well as the viscosity functional relationship, Newtonian flow behaviour is assumed initially and the apparent quantities (i.e. apparent viscosity) is obtained for the pseudoplastic materials investigated by this following equations:

\[ \tau = \frac{\Delta P \cdot R}{2L} \]

\[ \gamma = \frac{4Q}{\pi R^3} \]

Where

- \( R \) = radius of the capillary (1 mm.)
- \( L \) = length of the capillary (20 mm.)
- \( \Delta P \) = pressure drop (psi)
- \( Q \) = volumetric flow rate = \( \pi r^2 V \)
- \( r \) = radius of the barrel (10 mm.)
- \( V \) = ram speed (mm/min.)

The equations which have been proposed to describe pseudoplastic behaviour is the power law equation, (also know as the Ostwald-de Waele equation). This equation takes the form:

\[ \tau = K \gamma^n \]

In logarithmic form, it can be written

\[ \log \tau = \log K + n \log \gamma \]
In log-log plots of $\tau$ versus $\gamma$ will yield a straight line. $\log K$ is a y intercept and $n$ is the slope of the curve.

At this stage, the relationship between apparent viscosity ($\mu_a$) and the power law constants, $K$ and $n$.

Now

\[ \mu_a = \frac{\tau}{\gamma} \quad \text{by definition} \]

and

\[ \tau = K(\gamma)^n \quad \text{the power law equation} \]

combining these two equations,

\[ \mu_a = K(\gamma)^{n-1} \]