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THE STRUCTURE-PROPERTY RELATIONSHIPS OF URETHANE-ACRYLIC TEPHRMOSETTING SYSTEMS

By
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A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of The Loughborough University of Technology May 1995

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Institute of Polymer Technology and Materials Engineering

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To my dear parents, brother and sisters
ACKNOWLEDGEMENTS

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SYNOPSIS

Urethane-acrylic copolymers have found increasing use as a radiation curable materials in the recent years. These copolymers are highly crosslinked through the use of acrylic monomers having more than one double bond. Stirling Lloyd had discovered such materials to be a successful alternative to the urethane or acrylics coatings as waterproof membrane coatings. In this project, structure-property relationships of UA copolymer systems were studied. These were peroxide cured at room temperature.

A series of urethane-acrylic copolymers were made by varying the types and concentrations of the acrylic monomers, isocyanate and polyol components. These include use of polyol blends and polyols of varying molecular weight. In order to achieve a better co-relation of a copolymer properties with its components, acrylic monomers having single double bond were used to achieve a less crosslinked structure. The copolymers were synthesised through a combination of step reaction to produce the intermediate products (i.e. NCO terminated urethane prepolymer and acrylated-urethane oligomers) followed by free radical polymerisation to form a crosslinked network.

Evaluation of the system included characterisation of the raw materials and intermediate products. The effect of compositional variables on copolymers’ properties and morphology were assessed. The main conclusions drawn from this project were:

i) All intermediate products consisted of chain extended products. The viscosities of the intermediate products were strongly influenced by the hydrogen bonding forces present in the system.

ii) The reactivities of the reactants influenced the total curing of the copolymers, mainly through the induction period. Influence from acrylic content was significant only when the reactants had low reactivities.

iii) The molecular weight of the acrylated urethane oligomers (AUOs) had a significant influence on the crosslink density of the system, while the acrylic content hardly had any influence.

iv) The mechanical properties of the copolymers were determined mainly by the average molecular weight of the AUOs. However, adjustments could be made to these by selecting appropriate hard segment types. Increasing the amount of rigid acrylic used can enhance the polymer strength but will have little influence on the elongational properties except when polyol blends were used. For this latter type of copolymers, greater variation in mechanical properties were observed depending on the method with which the polyol blends were introduced. Tough copolymers properties could be achieved through proper combination of the hard segment and soft segment types.

v) Glass transition temperatures, Tgs, of the soft segment and hard segment were interdependent on each other as a result of crosslinking. Flexibility (or low temperature properties) of the copolymers was determined by the molecular weight of the polyol chain. The use of flexible acrylic monomers such as butyl-methacrylate could also increase the elongational properties.

vi) Morphology studies indicated a 2-phase system with no evidence of phase aggregation. However, copolymers based on higher polyol molecular weight (e.g. PPG 4000) showed capability of limited hard segment phase reinforcement when subjected to appropriate thermal conditioning.
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CHAPTER 1

INTRODUCTION
Chapter 1

1.1 Waterproofing of Bridge Decks

It is generally agreed that the main cause of bridge deck deterioration is due to spalling of concrete resulting from corrosion of the reinforcement steel [1]. When steel rusts, it expands and thereby creating high compression forces on the concrete, causing it to crack [2]. Corrosion of the steel reinforcement arises in part from water permeating through the pores and cracks in the concrete.

There are only a few ways of providing resistance to such deterioration of bridge decks [3]. The most preferred method is to apply a layer of waterproof membrane over the concrete [1]. The current conventional method involves bonding a suitable sheet material onto the substrate using adhesive. However, the success of this is very dependent on the quality of the adhesive bond between the sheet material and the substrate; and irregular surfaces may lead to problems. In addition, there are fabrication problems in tailoring of sheet materials, and it is a labour intensive, time consuming method [4]. An alternative to this is to spray coat the substrate with a layer of polymerisable material capable of forming a waterproof membrane in situ [5].

1.2 Waterproof Membrane Systems

The requirements for a polymeric coating to be used as waterproof membrane for bridge decks are as follows [3]:

1. be impermeable to water under all conditions.

2. be sufficiently flexible, even at low temperature, to accommodate for deflection and movements of the bridge, including thermal expansion/contraction.

3. exhibit good weather resistance properties.

4. be of a "tough" material i.e. good mechanical properties.

5. have good abrasion resistance.
6. be quick and easy to apply/lay, even under adverse weather conditions, by workmen possessing a moderate degree of skill.

The main polymer types that can be used for this purpose are polyurethanes (PU), acrylics, and epoxies [4, private communication 1989]. The first two are the most versatile, being available in a large number of chemical varieties. Both are used since they can be catalysed to react in a very short time and at temperature as low as -10 °C. They are also superior to epoxy based coatings in terms of weathering resistance and low temperature flexibility performance [4, 6]. Epoxy based coatings tend to have longer curing times, although their main advantage is better adhesion to the concrete [4] and a variety of other substrates in adverse conditions (e.g. surface water, oil).

1.3 Urethane-acrylic Coating System

Both urethane and acrylic coatings serve well as waterproof membrane systems with their excellent properties and formulation flexibility in terms of compositions (refer to Literature Survey, Sections 2.1 and 2.2), etc. However, there are application disadvantages in using these coatings for bridge decks:

A Urethane Coatings

Curing of the coatings in situ is not favoured due to problems associated with the volatility and health hazard of the low molecular weight polyisocyanates. In addition, as the properties of the polyurethanes are known to be very dependent on the composition of their reactants [7, 8], the relative amounts of the prepolymer (usually isocyanate-tipped) and curative (e.g. a polyol or isocyanate compound) of the two pack system has to be determined and held within close tolerances in order to obtain consistent, desired mechanical properties. Incompetent ratioing and mixing in situ arising from employing unskilled labour or other errors may result in deviation from the required stoichiometry of the reactants, and hence coatings of varying properties. Application should be on dry substrate because of NCO/H₂O reaction.
B Acrylic Coatings

With reference specifically to the conventional acrylic or acrylate coating systems. For those based on solvent thinners, the emission of volatile solvent poses a health hazard. Besides, the cost of using solvent can be expensive too. The water based emulsions are also available but not normally capable of producing a thick coating (e.g. 1mm) in one pass.

Stirling Lloyd, the company supporting this research project, has developed a waterproof membrane system based on acrylated-urethane oligomers and methacrylate monomers. Curing is carried in situ through free radical mechanism, initiated by benzoyl peroxide (BPO) and accelerator dimethyl para-toluidine (DMPT) initiating system. The material contains no free isocyanate or solvent thinners.

Acrylated-urethane oligomers (AUO) can be described as urethane prepolymer having acrylic functional groups. They are included in one type of acrylate modified oligomers that was developed in the early seventies for use mainly as radiation curable materials (see Sections 2.2.6 and 2.3.1). However, radiation curing by this method is currently still limited to thin films (i.e. < 1mm thickness). Several application advantages can be gained by adopting the urethane-acrylic system for conventional curing process, i.e. by peroxide curing. These include:

I As they can be cured by a free radical mechanism, full crosslinking can be achieved rapidly [9], even at low temperature with the use of the right initiating system, e.g. room temperature initiating peroxide catalysts.

II They can be formulated to a 100% solids content system consisting predominantly of the oligomers and monomers (i.e. acting as reactive diluents). Hence they are less health hazardous than the conventional solvent based systems. Although some acrylic monomers may be relatively toxic, it has been shown that the addition of a wax can help to reduce monomer evaporation significantly [9]. In addition, the curing process is fast and does not involve external heat other than the heat of polymerisation, which can be dissipated quickly from thin films to substrates.
Hence, volatile loss of the monomers is minimal, reducing pollution effects [9 p110].

III Mixing of the reactive diluents, i.e. the acrylic monomers, and oligomers can be achieved in the controlled environment of the factory while catalysis and curing of the system will be carried out on site. Unlike the epoxides or PU system, dispersion of the catalyst does not have to be thorough, although this helps. Once catalyst free radicals have been formed, the reaction is initiated by free radical formation of the monomers followed by chain propagation into the bulk of reactants without the presence of additional catalyst. Research [10] has shown that variations in the catalyst concentrations over a reasonable range does not produce too much undue effect on the mechanical properties of the resulting coating. Hence, this eliminates many problems on site, that may arise from uneven mixing of the initiating systems due to unskilled labour, otherwise evident with 2 pack urethane or epoxide formulations.

1.4 Objectives

Considerable studies have been carried out on the urethane-acrylic copolymers systems in the recent years. However, most of these were on thin film systems cured by radiation, due to increasing industrial use of these materials. In spite of this, literature reviews (see Section 2.3.3) have indicated that the structure-property relationships of these polymers are still not well understood. Some investigators have even reported different findings on similar formulations. This variation might be explained by the large number of influencing factors resulting from the different combinations of reactive diluents and oligomers types. Unfortunately, several general studies of urethane-acrylic systems had little discussion or detailed analysis [11-14].

The aim of this project is to examine an important group of urethane-acrylic copolymers cured using a BPO / DMPT initiating system. Unlike the radiation curing
system which often requires the use of multifunctional acrylate\(^1\) as the reactive diluent monomers (see Section on 2.3.1), methyl and/or butyl methacrylate with single terminal double bond (termed as functional monomers in this case), were used in this project, to keep the formulation as simple as possible. Studies were carried out on a range including factors influencing the viscosity and cure rate of the oligomers, and to the effect of compositional variables on the properties of the cured polymers. The variables included:

a) Isocyanate index, i.e. the actual amount of isocyanate used over the theoretical or stoichiometric amount.

b) Hydroxyl propyl methacrylate (HPMA) content. HPMA monomer was used to react with the isocyanate tipped urethane oligomers (see Figure 3.3 and Section 3.3.1 for details).

c) Soft segment length of the urethane component.

d) Soft segment length distribution, by using polyol blends.

e) Reactive diluent types and concentrations.

\(^1\) This refers to acrylate monomers having more than 1 C=C.
Chapter 2

2.1 Polyurethanes

2.1.1 Introduction

Polyurethane (PU) is a term given to polymers having urethane groups in their polymer chains [15]. These polymers normally contain other groups such as ester, ether, urea, amide, biuret, allophanate, etc. as well. The urethane linkages are formed from the polyaddition (or step rearrangement) reactions between isocyanate groups (—NCO) and hydroxyl groups (—OH) as shown in Figure 2.1, and they may not be repeating in a regular order. PU can be formed by a variety of methods, such as from the reaction of chloroformic esters with diamines and of carbamic esters with diols [16]. However, the commercial development of PU has been based on the reaction of di- or polyfunctional hydroxyl compounds with di- or polyfunctional isocyanates [15, 16]. Figure 2.2 shows the general structure of PU derived from reactions of dihydroxy (HO–R–OH) and diisocyanate (OCN–R'–NCO) compounds. These may be further reacted with a diol or amine chain extender, in the chain extension reaction, to form thermoplastic polyurethane (TPU) as shown in Figure 2.3.

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

Isocyanate Hydroxyl Urethane

Figure 2.1: Formation of urethane linkage
2 OCN—R'—NCO + HO—R''—OH →

Diisocyanate       Polyol

OCN—R'—NH—C—O—R''—O C—NH—R'—NCO

Isocyanate-terminated prepolymer

Figure 2.2: Urethane prepolymer formation

Reaction of PU prepolymer with:

I. diol chain extender, (n) HOR''OH

II. amine chain extender, (n) NH₂—R''—NH₂

Figure 2.3: Reactions of polyurethane prepolymers with chain extenders
PU are available as fibres, soft and hard elastomers, flexible and rigid foams, coatings, adhesives and sealants [17]. Coatings based on urethane materials range from varnishes and paints, e.g. used on furniture, to sprayable coatings with high abrasion and corrosion resistance [7], e.g. primer and topcoats in the automotive industries [18]. In recent years, polyurethanes have been widely utilised as engineering materials in many industries [18, 19]. The wide range of properties achievable with PUs is due to a number of factors [17]:

a) the ability of isocyanate to react with a broad range of "active hydrogen" containing reactants.

b) the availability of a considerable number of hydroxylated materials, which are also available in a wide range of molecular weights, affecting the chain flexibility, intermolecular forces, etc..

c) the great formulation flexibility of PUs, enabling the chemist to vary degree of crosslinking, chain flexibility and intermolecular forces widely and almost independently by carrying by altering the functionality or the relative ratio of the reactants [17].

The main factors that contribute to the popularity of polyurethanes are their outstanding properties and ease of fabrication. Among their many good properties are good adhesion, abrasion-resistance, toughness, high tear resistance and high load bearing ability [7,18]. The limitations of polyurethane can often be by passed because of the ability to tailor-make these materials to suit various applications [7, 18, 8].

2.1.2 Polyurethane Chemistry

The chemistry of PU is based mainly on the chemistry of isocyanates. This is well documented in several texts [15, 16, 20, 21]. The isocyanates are highly reactive because of the presence of the highly unsaturated $-N=\text{C}=O$ groups [16]. Reactivities of commercial isocyanates can vary from batch to batch, e.g. due to chloride
contamination. This section provides an introduction to the polymer chemistry relevant to the work reported later in this thesis.

2.1.2.1 Reaction of Isocyanates.

Although a large number of isocyanate reactions are possible with almost any compound containing active hydrogen, only a relatively small number of these reactions are of major significance to the commercial production of polyurethanes. However, only those reactions which are essential to the understanding of the urethane prepolymer synthesis will be discussed here. These are classified into:

I. Primary reactions

a) Reactions with alcohols to form urethanes (or carbamates)

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

The reaction is readily catalysed by mild and strong bases (e.g. amines, secondary and tertiary amines), many metal soaps, and weakly by acids, although phosphoric acid is known to inhibit the urethane reaction.

b) Reaction with water

\[ R'\text{-NCO} + H_2O \rightarrow R'\text{-NH-COOH} \quad \text{Carbamic acid (unstable)} \]
\[ R'\text{-NH-COOH} \rightarrow R'\text{-NH}_2 + CO_2 \quad \text{Amine} \]

The reaction of isocyanate with water is not as simple as the formation of a urethane. Carbamic acid is produced as an intermediate but being unstable, it is cleaved into amine and carbon dioxide. The amine thus formed is capable of reacting further with isocyanate, normally at an even faster rate than does the water, with certain exceptions, to form substituted ureas (see (c)). This reaction is the basis for production of flexible foams and moisture cured coatings. The
reaction of water with isocyanate can be catalysed by tertiary amine, many other bases, and certain metal compounds.

c) Reaction with amine

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

The reactions between isocyanate and the amines to form substituted urea, being inherently fast, are not strongly influenced by catalysts (as compared to the slower isocyanate reactions). The reactivity of the amine increases as its basicity increases unless steric hindrance becomes excessive. The relative reactivities of the amine are in the following descending order:

**Primary amine > secondary amine, aromatic primary amine > secondary aromatic amines**

II. Secondary reactions to form crosslinked species.

d) Reaction with urea to form a biuret or substituted urea.

\[
\text{R'}^-\text{NH}-\text{CO}-\text{NH}-\text{R''}^- + \text{OCN-}R' \rightarrow \text{R'}^-\text{N}^-\text{CO}-\text{NH}-\text{R''}^- \quad \text{biuret or substituted urea}
\]

e) Reaction with urethane to form allophanate

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

Urethanes are generally less reactive than ureas toward isocyanates, and the reaction is promoted by specific catalysts or elevated reaction temperature.
The secondary reactions are slower than the primary reactions. Generally, the relative reactivities of the hydrogen containing compounds with isocyanates can be placed in the following descending order:

For primary reactions:

Aliphatic NH₂ > aromatic NH₂ > primary OH > water > secondary OH > tertiary OH > phenolic OH > COOH

For secondary reactions:

R-NH-CO-NH-R > R-CO-NH-R > R-NH-CO-OR

Urea amide urethane

The secondary reactions are so called because they result from the combination of isocyanate with an initial reaction product from a primary reaction. As both ureas and urethanes still possess hydrogen atoms, they can react further with isocyanates under suitable reaction conditions to give biurets and allophanates linkages respectively. These secondary reactions are not strongly catalysed by most tertiary amines although stronger bases and certain metal compounds may be effective. A temperature of about 120 °C or higher is required to give a significant reaction rate in an uncatalysed system. However, at this reaction temperature many other side reactions can also occur, resulting in a variety of polyaddition and dissociation products.

The secondary reactions are particularly important in polyurethane chemistry as they will lead to increased branching, if permitted to occur. Hence, a linear polyurethane prepared from a diol and a diisocyanate may be branched by allophanate formations. However, when a crosslinked polymer is desired, it is usually obtained with best control by using a trifunctional reactant such as a triol and catalysing only the NCO — OH reaction. The crosslink thus obtained will also have a better thermal stability than the biuret or allophanate crosslink.
2.1.2.2 Poly-addition Reactions

Isocyanates are also capable of self condensation to form carbodiimides, giving off CO$_2$:

$$R'^{-}\text{NCO} + \text{OCN-R'} \longrightarrow R'^{-}\text{N=C=N-R'} + \text{CO}_2$$

Self condensation carbodiimide + carbon dioxide

They can undergo dimerisation and trimerisation under certain catalytic conditions to form uretidiones and isocyanurates respectively:

$$\text{Dimerisation} \quad \text{Uretidione}$$

$$3R'^{-}\text{NCO} \longrightarrow R'^{-}\text{N-N-R'}$$

Trimerisation isocyanurate

However, with aliphatic isocyanates, only trimerisation occurs. The trimers exhibit a characteristic infrared peak of the isocyanurate carbonyl groups at 5.85μm to 5.92μm (1709 cm$^{-1}$ to 1689 cm$^{-1}$) [16].
With certain aromatic isocyanates such as monomeric 4,4’-diphenyl methane diisocyanate (MDI), dimerisation occurs slowly on standing even at ambient temperature and in the absence of catalysts. The consequence of this is a limited storage life as the MDI loses its activity slowly. To minimise this problem, MDI has to be stored under refrigerated conditions. The rate of dimerisation will be greatly retarded if there is an ortho substituent on the aromatic ring. Hence, dimerisation at room temperature is not a problem with 2,4-toluene diisocyanate [16].

2.1.3 Raw Materials

The materials used in the synthesis of polyurethanes are basically classified into:

1. Polyols
2. Isocyanates
3. Chain Extenders
4. Catalysts

2.1.3.1 Polyols

Generally, polyols are hydroxy terminated intermediate molecular weight oligomers, having molecular weights between 300 to 4000 and functionality of 2 or 3. They may be branch or linear polymers. The polyols that are widely used in polyurethane manufacture are divided into two classes:

a. The polyether based polyols, namely polypropylene glycols (PPG) and polytetramethylene ether glycols (PTMO) [7]. Polyethylene glycols (PEG) are employed for specialised applications of PUs.

b. The polyester based polyols such as polyethylene adipate diols (PEA) and polycaprolactone diols (PC)
The choice of polyol has a large influence on the final properties of polyurethane produced. PUs produced from polyester based polyols generally have better mechanical properties, e.g. toughness, abrasion resistance, tear strength, etc. [22, 16 p73], and oxidative stability [23] than those based on polyether. However, they have poorer hydrolytic stability due to the presence of the active polar ester groups $-\text{CO-O-}$, which are capable of interacting with polar substances such as water. Study carried out on variation in polyester structures on the properties of urethane products [24] has shown that greater ester group separation yielded improved low temperature flexibility but lower tear strength. Closer ester group spacing was observed to produce polymers with reduced flexibility at low temperature, but at room temperature, it favoured higher hardness values, modulus, with a marked increase in permanent elongation. These effects were attributed to increased attractive forces (e.g. polar forces, hydrogen bonding, etc.). The presence of side chains in polyester also resulted in PUs of much lower tensile strength than that obtained from linear polyesters. This is thought to be due to the effect of the side chain in preventing or hindering stress induced crystallisation of the polyesters upon extension [16 p52].

Among the polyether polyols, PTMO based PUs give the best physical properties due to the regularity of chain structure and their ability to crystallise upon extension [16]. PTMO polyols impart better low temperature performance than other polyols [25] and are so-called premium types of polyether. PPG polyols are known as the low cost polyether types [7]. Inspite of their low cost, the relative ease to vary and modify molecular structure and ready availability, PPGs are seldom used in TPUs and performance elastomers [26] but are used significantly in foam formulations. This is probably because PPG based TPUs are inferior in mechanical strength, processibility and do not show any special properties, as compared to TPUs prepared from other polyols [26]. Data collected by O' Shea has indicated a poorer low temperature properties as well as poorer resistance to heat distortion than the corresponding PTMO based PUs [27]. The side chain methyl group in PPG prevents crystallisation of the flexible segments and increases interchain separation [16]. The resulting weaker interchain attractive forces however, allows increased chain slippage and disentanglement and consequently accounts for higher elongation at break.
The reactivity of PPG can be increased by post reacting a PPG polyol with a small amount of ethylene oxide so as to convert the secondary hydroxyl groups of PPG to the more reactive primary hydroxyl groups [16]. The structure-properties relationships of thermoplastic polyurethanes (TPU) based on these 'tipped' PPG polyols has been studied by O' Shea [27].

According to Bayer [28], the hydroxyl-polyethers, which are obtained by alkoxylation, are used in greater quantities than hydroxyl-polyesters obtained by esterification. The presence of trace catalysts used in the synthesis of the polyols can confer several effects either in the synthesis of PU or in the final properties of PU. Trace residues of some of the catalysts used in the esterification process can have an adverse effects on the hydrolytic stability of the final urethane products. With polyether polyol, the presence of residual alkaline catalyst such as potassium hydroxide can results in difficulties in the subsequent PU synthesis process as this is a strong catalyst for the isocyanate trimerisation reaction [8, 29].

The polyols are described by their hydroxyl number (OHV) or their equivalent weight [28] where equivalent weight = 56100/OHV, and by their functionality.

2.1.3.2 Isocyanates

The most common commercial isocyanates used in this field are 4,4'-diphenyl methane diisocyanate (MDI) and the isomers of toluene diisocyanate (TDI) [7, 28]. MDI is usually used in rigid foam production whereas TDI is largely used when producing flexible foams. TDI is commonly used as a mixture of 2,4 and 2,6 isomers, in the ratio of 80:20 or 65:35. For many purposes, the 80:20 mixture is most widely preferred.

Other isocyanates that are also of commercial interest are : 1,5-naphthalene diisocyanate (NDI), isophorone diisocyanate (IPDI), 4,4-dicyclohexylmethane diisocyanate (H12 MDI) and hexamethylene diisocyanate (HDI). IPDI is widely used
in the coating industry in the production of transparent and moisture curing sealants. The structural formulae of these isocyanates are as shown in Figure 2.4.

Polyurethanes produced from aromatic isocyanates are known to have poorer light stability than that based on aliphatic isocyanates. The double bonds of the aromatic rings are capable of being photo-oxidised to quinone-imide structures which are responsible for the yellowing and embrittlement seen when aromatic based PUs are exposed to ultraviolet (UV) radiation [30, 31]. Figure 2.5 illustrates an example of an aromatic based PU exposed to UV radiation.
2,4-TDI

Toluene diisocyanate (TDI)

4,4'-Diphenylmethane diisocyanate (MDI)

1,5-Naphthalene diisocyanate (NDI)

3-Isocyanatomethyl 3,5,5-trimethyl-cyclohexyl isocyanate
(Isophorone diisocyanate, IPDI)

Figure 2.4: Diisocyanates commonly used in polyurethane syntheses.
Figure 2.4: continued

Meta-Tetramethyl xylene diisocyanate (m-TMXDI)

\[
\text{OCN(CH}_2\text{)}_6\text{NCO}
\]

1,6-Hexamethylene diisocyanate (HDI)

\[
\text{OCN}-\text{CH}_2\text{-CH}_2\text{-HC-CH}_2\text{-CH}_2\text{-HC-NCO}
\]

4,4'-Dicyclohexylmethane diisocyanate (H\textsubscript{12 MDI})
(available in isomeric mixtures)

\[
\text{OCN}\text{-}
\]

Cyclohexyl diisocyanate (CHDI)

\[
\text{OCN-}
\]

para-Phenylene diisocyanate (PPDI)
It has been reported that the recently developed pseudo-aliphatic diisocyanates, i.e. meta- and para-tetramethyl xylene diisocyanates (m- and p- TMXDI), have the characteristics typical of aliphatic diisocyanates, such as light stability, even though they have of aromatic structures (see Figure 2.4) [32]. These isocyanates have low reactivity with water, permitting stable water based emulsion polymerisation to be carried out. They can also be used to produce transparent products. The paraphenylene diisocyanate (PPDI) and 1,4-cyclohexane diisocyanate (CHDI), under the trade name Elate 160 and Elate 166 respectively, are also recent additions to the commercially available isocyanate family. These are claimed to produced elastomers of better physical properties and thermal stability up to 260 °C via the isocyanurate crosslinking mechanism [33, 34].

Pigol et al. [24] working on the effect of various type of isocyanate structures on the mechanical properties of PU have observed that generally polymers of higher tensile strength, tensile modulus, tear strength and hardness are associated with diisocyanate molecules of greatest symmetry and rigidity. The present of methyl substituents will induced spartial separation of adjacent polymer chain and increased mobility of local segment. This produced a softer and more elastic polymers. Studies on the effect of isocyanate structure on the properties of cast PU was also carried out by Pandya et al. [35].
The isocyanates are characterised by their NCO content (in %), and in some cases also by their equivalent weight whereby

\[
\text{equivalent weight} = \frac{\text{molecular weight}}{\text{Valency}} = \frac{42}{\% \text{NCO}} \times 100
\]

### 2.1.3.3 Catalysts

Catalysts play an important role in urethane formulations, including coatings [23, 36, 37 p1005, 38]. They may be employed in the preparation of prepolymer but are most widely used in the curing reactions. They are used to increase the reaction rate and to bring about a complete or adequate cure. As the functionality of reactants increase, complete reaction becomes progressively more difficult to obtain. However, complete cure can be obtained in many instances by the use of a catalyst and heat (i.e. at 100 °C or above). High prolonged heating also leads to the formation of small amounts of carbodiimide [38].

Catalysts exert a considerable influence on the ultimate properties as they direct the polymer forming process. Therefore selection of catalysts is critical to ensure desired primary reactions at accelerated rates. The use of catalyst may also introduce other reactions such as trimerisation and carbodiimide formation [15 p274]. In general, the tertiary amines favour NCO/OH and NCO/H2O reactions. Tertiary amines, for instance, with exposed electron pairs in their structures (e.g. Triethylene diamine-DABCO) will promote the rearrangement of isocyanate structure permitting reaction with alcohol and formation of urethane. The catalytic reactivity of the tertiary amine increases with base strength, but it is also influenced by structural effects such as steric hinderance (i.e. steric shielding of the amino N) which can result in a reduction in activity.

The organotin catalysts are most effective for the NCO/OH reaction, in preference to the reaction with water. However, it is also effective in influencing urea and biuret reactions. Unlike the strong bases, tin catalysts do not promote isocyanurate
formation. In certain applications, mixtures of tertiary amines and tin catalysts are used to achieve a very fast reaction or to obtain the appropriate balance of chain extension and crosslinking as in foam production. Such combinations are also known to produce synergistic effects [15, 16].

It is known that residual amine or metal compound catalyst will accelerate UV/oxygen and thermo-oxidative degradation of aromatic isocyanate based PUs [16].

2.1.3.4 Chain Extenders

These are usually low molecular weight glycols or diamines, assumed to have functionality of 2. The action of these chain extension agents is to provide the rigid or hard segments in the PU by reacting with the free isocyanates in the prepolymer. The use of low molecular weight diols promote three effects:

a) increased amount of isocyanate used in the reaction, which in turn leads to

b) more rigid isocyanate-derived component in the unit length of polymer chain,
   increased urethane repeat group (i.e. increasing chain stiffness)

c) short diol derived components (i.e. again increasing chain stiffness).

The hard segments formed are interconnected with the flexible polyol segment through reaction with the NCO groups. The ability of these urethane linkages to form hydrogen bonding has played a significant role, as discussed in a later section.

Chain extender choice can influence elastomer properties considerately. When a rigid and bulky diol is used as chain extender, harder elastomers of higher modulus are produced [16 p56]. Generally, with aromatic glycols, the properties obtained indicated lower tensile and higher tear, modulus and hardness than for specimens extended with aliphatic glycols. These changes may be attributable to the greater rigidity of the aromatic glycols. The most widely used chain extension agents are ethylene glycol, dipropylene glycol, 1,4-butane diol and 3,3'-dichloro-4,4'-diamino phenyl methane
The use of diamine extenders will result in polyurea segments which are known to possess high hydrogen-bonding interactions. Consequently, elastomers produced from diamines extenders have a better mechanical properties and higher hardness than if diol are used. The influence of chain extenders is not as pronounced as that of varying the polyols or diisocyanates. This was undoubtedly due to the relatively small quantity of extender used in comparison to the ether constituents, but within the limits noted, useful changes were obtained by varying the extender [24].

2.1.4 Health and Safety

The hazards associated with PUs have been primarily associated with the isocyanates. Isocyanates are hazardous materials as they are respiratory irritants and can cause asthmatic-like attack in persons exposed to isocyanate vapours. Many isocyanates are skin irritants, leading to dermatitis. The general health hazards associated with isocyanates can be found in several texts such as that written by C. Hepburn [16, chapter 13], and by J.H. Saunders [15 p30] and A. Bayer [28 p27]. MDI, usually liquid in its crude form, is considerably safer to use at room temperature than TDI, as it is less volatile. Derived products containing residual isocyanate groups such as polymerised diisocyanate or polyfunction isocyanate of some basic diisocyanates are also available on a commercial scale. These give low to non-volatile products.

The hazards associated with catalysts are also summarised by A.G. Bayer. The organotin compounds are less toxic than the tertiary amine catalysts. Certain diols (e.g. ethylene glycols) are toxic while polyols less so.

2.1.5 Synthesis

Strictly, the required amount of isocyanate to react with all the active hydrogen species available in the co-reactants must be calculated, i.e. giving the stoichiometric proportion of reactants. For instance, in simple two component systems, stoichiometry will be calculated from the equivalent weight of isocyanate and diol.
In practice, industry uses "isocyanate index", i.e. the degree to which actual ratios of ingredients deviate from the stoichiometric value. That is,

\[
\text{Iso Index} = \frac{\text{Actual amount of isocyanate used}}{\text{Stoichiometric amount of isocyanate}} \times 100
\]

Iso index equals to 100 when the actual amount used is the same as the determined stoichiometric amount of isocyanate.

The techniques generally used in the synthesis of PUs are: prepolymer, quasi-prepolymer and 1 shot methods, as illustrated in Figure 2.6.
I. Prepolymer

Polyol → Diisocyanate → Prepolymer → Chain Extender → Final Polymer

II. Quasi-prepolymers

Polyol (part A) → Diisocyanate → Quasi Prepolymer → Polyol (Part B) → Chain Extender → Final Polymer

III. One-shot System

Polyol → Diisocyanate → Chain Extender → Final Polymer

Figure 2.6: Polyurethane Synthesis Techniques
2.1.5.1 Prepolymer Method

This is the most widely used method especially for PU elastomer systems as it provides better handling, controlled processing and consequently better properties. It is also used in production of moisture cure coatings, TPU's and for some flexible foam formulations.

In this method, the prepolymer is obtained by reacting the polyol with an excess of isocyanate to give intermediate molecular weight NCO-tipped prepolymer which may be in the form of a viscous liquid or low melting solid at room temperature. Typically, the molar ratio is 2:1, although other ratios can be employed. The prepolymer can be prepared either by melt polymerisation or solution polymerisation. Further reaction of the prepolymer with chain extender gives the final product (see Figure 2.6 I). Strictly, the prepolymer should be free of any residual original isocyanate (e.g. removed by vacuum stripping).

The presence of excess NCO causes difficulties in controlling the pot life of the resin. Hence, storage of these prepolymer has to be careful to prevent photodegradation, dimerisation or premature curing (resulting from moisture contact with NCO). These are usually stored in the dark under dry nitrogen or air.

The method "eliminates" the differences in reactivity between the secondary hydroxyl group of the polyol and the primary hydroxyl group of the chain [27]. In structure-property studies of PU with monodisperse segment length distribution, the prepolymer and multi-step procedure were used to achieve narrow hard and/or soft segment length distribution [40].

2.1.5.2 Quasi-prepolymer

In this method, only part of the polyol is reacted with all the diisocyanate to form the semi- or partial (quasi) prepolymer (i.e. having excess free isocyanate). The final
product is obtained by reacting the prepolymer with the remaining portion of the polyol that has been mixed with a chain extender (see Figure 2.6 II).

2.1.5.3 One-shot Method

This method is used for economical reasons and is generally used in the manufacture of foams. The method involves mixing of all the reactants, e.g. the polyol, the chain extender and the NCO together at the same time to produce the final product (see Figure 2.6 III). The disadvantage of this method is that there is no control over reaction priority and therefore random PU structures are produced.

Therefore, it may be stated that two shot reactions lead to block urethane copolymer, while one shot reactions lead to random copolymers.

2.1.6 Structure-morphology-property Relationships

TPUs are actually block copolymers of the \( -(\text{-A-B-})_n \) type, where A represents the soft segment and B corresponds to the hard segment (see Figure 2.3). The soft segment comes from the long and flexible polyether or polyester chains, while the hard segment is composed from a series of urethane linkages formed from the reactions between isocyanates and low molecular weight diols such as 1,4-butane diol (BD). These segments are linked chemically to each other by reactions with diisocyanates.

As with other polymers, the mechanical properties of PU are influenced by the molecular structure of the reactants and the resulting polymer. Structural influence from selected reactants such as chain stiffness, crystallisation ability of the soft segments are as discussed in Section 2.1.3.

In addition to structural influence, it is has been recognized that the enhanced mechanical properties of thermoplastic polyurethanes (TPU) are a direct result of their
2 phase microstructures [42] and are determined to a large extent by the degree of phase separation and perfection of domain organisation [43, 44, 172-175].

In general, the effect of molecular weight on Tg of a homopolymer is [44] such that the Tg of the polymer reduces as the molecular weight decreases due to the additional free volume associated with the chain ends of the molecules and is therefore proportional to their concentration. However, in PUs, the chain ends of the soft segments do not possess increased mobility due to chemical attachment to the rigid hard segment of the molecules. Increasing sequence length of the soft segment tends to reduce the hardness, tensile modulus and tear properties of the polymers while its ultimate elongation increases. In a study made on the effects of increasing soft segments molecular weight on Tgs, Seefried et al. [41] observed that increasing the soft segment length by using a higher molecular weight diol will actually reduce the Tg of the PU elastomer as the restrictive influences of the hard segment become less important.

The incompatibility between the hard and soft segments due to large thermodynamic differences, such as in polarity, interfacial effects and solubility parameters, tend to induce segregation of these segments to form a 2-phase morphology. This contributed to the elastomeric properties of the polymer, with the hard segment acting as a reinforcing filler or physical crosslinker restricting viscous flow and to mechanically reinforce the copolymer. A typical polyurethane elastomers have a high extensibility and modulus 3 to 4 times greater than that of natural rubber [45].

Generally, the elastic nature of a PU and its low temperature performance are influenced by the soft segments while the rigid hard segments determine the high temperature performance, by their ability to remain associated at elevated temperatures. It is known that the strong polar interactions, such as hydrogen bonding, between the urethane units can lead to a supermolecular organisation with aggregated structures which may be in the form of glassy domains or crystallites [16]. Hence, TPU has a morphology of phase separated microstructures of discrete or semi-
continuous glassy or crystalline hard segment domains dispersed throughout a continuous rubbery 'soft' segment amorphous phase [26]. A. F. Galambos et al. [46] observed that the hard segment becomes the continuous phase when its content exceeded 60%.

Experimental evidence has shown that the phase separation in PU is incomplete [47] and the soft phase may contain some 'dissolved' hard segment [48]. Studies have shown that the Tg of the soft segment is dependent on the hard segment to soft segment interaction, i.e. on the extent of phase separation [25, 48-51, 172-173]. At low level of phase separation, increasing the hard segment content increases the soft segment glass transition temperature. However, once maximum phase separation is achieved, through use of either longer soft segment length [49] or better hard segment aggregation [43, 44, 50, 52, 173], the Tg of the soft segment will remain relatively constant despite changes in variables such as increased hard segment content.

The degree of phase separation is interdependent on a number of factors, namely [17, 48, 51, 53]:

I. The chemical structure of the reactants.

II. The chemical composition of the reactants.

III. The thermal history of the polymer.

IV. The method of preparation.

I. Chemical structure of the reactants

The effect of changing the soft segment type of the PU was investigated by L. L. Benmel and G. M. Stack [54]. They prepared a series of PUs based on a polar polyester, polycaprolactone diol (PCL); a less polar polyether, polymethylene oxide glycol (PTMO), and non polar polybutadiene diol (HCHT-PBD). The PCL based PUs have the possibility of hydrogen bonding between both the hard and soft
segment, whereas the other two types of PUs will only be hydrogen bonded between hard segments. They observed that the increased ability for hydrogen bonding in PCL based PU had resulted in a greater source of mechanical loss peaks, tan δ due to greater amount of mixing.

In phase separation studies of PUs using thermal transitions, Paik Sung et al. [25] observed that the Tg values of polybutylene adipate based PUs are higher than those of PTMO based PUs having the same soft segment molecular weights. He attributed this to the fact that the urethane to the polyester hydrogen bonding has led to a lower degree of phase separations. Similar analysis of this nature was also reported by O’Shea [27], who ascribed the poorer low temperature and high temperature properties obtained with polypropylene glycol (PPG) based PU (compared to PTMO based PU) to be due to better compatibility of PPG with MDI/BD hard segment. B. Bengston et al have observed that the use of butadiene soft segment results in Tg very close to that of free hydroxyl terminated butadiene and independent of hard segment content indicating complete or very nearly complete phase segregation [137].

The effect of hard segment on the morphology of urethane polymers depends on the symmetry of the diisocyanate as well as the chain extender [24, 44, 54, 55]. Generally, structures that result in a weaker packing of the hard segment cause a somewhat higher proportion of it to be dissolved in the soft segment matrix, and consequently less of it to be present in the hard domains [16]. Improvement in phase separation is achieved if the hard segments are capable of closer association with each other through probably its capabilities for self crystallisation or stronger urethane interactions among themselves. This consequently leads to a higher room temperature modulus [16, 24, 44, 54] resulting from improved mechanical reinforcement effect of the hard segment.

Seefried et al. [44] investigating into the effect of isocyanate structures on the properties of PUs have also proved this point. They observed better mechanical
properties with 4,4'-MDI based polymers than with isomeric mixtures of 2,4- and 2,6- TDI based PU (i.e. higher hardness, tensile strength and tear resistance values although ultimate elongation decreased) and attributed this to the fact that hard segment based on 4,4'-MDI possess a more perfect domain organisation due to their crystalline nature. The NCO groups of 4,4'-MDI being symmetrically situated at the para position of the aromatic rings, allows relatively close association of these segment when reacted in a urethane. This improves the ability of the hard segment to separate from the soft segment. This higher degree of phase separation also reduces the influence of the hard segments on the glass transition temperature of the amorphous soft segment. With 2,4- and 2,6-TDI mixture, the amorphous characteristic of the hard segments containing the isomeric TDI units result in considerable intermixing of the hard and soft segment. This produces restrictions on the relatively mobility of the soft segment due to the effect of hydrogen bonded crosslinks and consequently increase the Tg of the urethane polymer. A similar concept was also given by Benmel and stack on their works based on tetramethyl meta and para xylene diisocyanate [54]. It is expected that the 2,4- isomer of MDI will demonstrate worse phase separation properties. This could be the basis for the use of such isocyanate tipped prepolymer to react with water to make carbon dioxide blown foam (private communication).

Pigott et al. [24] have concluded from their studies using various isocyanate types that the NCO structure plays a major role in governing the tendency of chains to orient within the polymer and thus exhibits an important influence on the Van der Waal forces and hydrogen bonding potential within the polymer. He also observed that the influence of the diisocyanate structure on the low temperature properties of the urethane elastomer was only moderate when compared to other variables.

The influence of chain extender on hard segment aggregation and mechanical properties was noted by several workers [48, 50, 57-59]. Chain extenders (diols) that contain pendent groups such as 1,3-butane diol promote phase mixing, leading to higher soft segment Tg's while preventing hard segment crystallisation [57, 58].
Chein et al. [50] has shown from hot stage microscopy studies, that the changes of chain extender type, from a symmetrical to an asymmetrical structure (e.g. in their case, it's from 1,4-BD to N,N'-bis(2-hydroxyethyl) terephthalamide), may cause a large reduction in hard segment crystallisation because of mixing-in domains. This also causes the Tg of the soft segment to increase. He noticed that domain separation is strongly dependent on the amount of hard segment in the polymer. The commonly used 1,4-butane diol being unbranched, and is therefore symmetrically structured so is capable of providing efficient hydrogen bonding and chain alignment. However, the use of longer polymethylene sequence of the 1,6-hexane diol results in a poorer hard segment fit. This can also slow down realignment and rubbery crystallisation [27].

Wang and Cooper [48] have reported that the use of amine chain extenders lead to unusually strong hard domain cohesion due to the stronger association of the hard segment as a result of stronger three dimensional hydrogen bonding presence within the hard domain produced when urea group is present.

II. The chemical composition of reactants

The composition of the reactants determine the relative size of the hard and soft segments. For example, increasing the ratio of diisocyanate and chain extender to flexible block increases the size of the rigid block of polyurethane. Variation in segmental sizes affect the degree of phase segregation, phase mixing, hard segment domain organisation; and accordingly, the polymer properties of the segmented PU block copolymers. X-ray studies on segmented polyether-MDI-butane diol based urethanes revealed that hard segment crystallisation occurs at high hard segment content (of 45%) [60]. Other morphological changes also take place as the hard segment fraction is increased. The texture changes from that in which little domain content exists at low hard segment levels (15%), to that in which the polymer has as interlocking domain morphology at high hard segment content (i.e. 35 to 45%). Elastomeric properties are obtained when isolated hard segment domains exist (25% hard segment) [60]. Chien et al. [50] has also observed that at low hard
segment content (<30%), a PU will act as a non-crosslinked elastomer and that
domain separation is strongly dependent on the amount of hard segment.

From the work of Lee et al. [61], they observed that the mechanical properties of
polyurethane-ureas (PUUs) depend primarily on the degree of order in the hard
domain. They have also showed that this order can be improved by increasing
either the hard segment content at constant molecular weight of the soft segment,
or soft segment molecular weight at the same hard segment content. In PUUs
where the hard segment cohesion is stronger than that in PU due to the urea
groups, increasing hard segment content is observed to result in a change in
morphology from interconnecting hard and soft segment domains to isolated hard
segment domains in a soft segment [48].

Increasing soft segment length also increases the chances of soft segment
crystallisation [57] as observed by Seefried et al. [41] when the molecular weight
average number, Mn, of PCL is increased to above 3000. While the capacity for
crystallisation of the flexible segment is a stimulating factor for segregation process
in segmental PUs, it is, however, undesirable to have polyol such as some long
molecule polyesters to crystallise and to produce cold hardening in PU elastomers.
However, the ability of the flexible polyester segments to crystallise upon extension
of the elastomer is a desirable feature since the strength of the material is thereby
increased [16].

Studies made by other workers on this factor, have also indicated that as the soft
segment length increases, the level of phase separation is increases. This leads to a
shift in the Tg of the soft segment to a lower temperature [41, 48, 49, 55, 61-63].
For example, several studies have shown that TPU based on 2000 molecular
weight polycaprolactone soft segment exhibited a better defined microphase
separation than that based on 830 molecular weight polycaprolactone of the same
hard segment length [44, 49, 55].
III. The thermal history of polymers

Studies have shown that the thermal transitions observed in differential scanning calorimetry (DSC) studies are sensitive to changes in thermal history and annealing conditions [46, 47, 60, 64-68]. The relation between thermal transitions and degree of phase separations have been given by several researchers as shall be further illustrated in section 2.1.7.1. It has been reported that annealing increases the cohesive forces of the hard domains, thereby increasing their mechanical integrity [42]. Y. Camberlin et al. [65] noticed that the soft segment Tg of PUs decreased with annealing time and they attributed this to progressive enrichment of soft segment (i.e. purity from hard segment) within the soft phase.

In a study of the thermal stability of domain structures of several PU systems, Wilkes et al. observed a considerable upward shift in Tgs of the soft segment following heat treatment [66]. They also found that endothermic behaviour (of the samples) that occurred above Tg is lost immediately after heat treatment. However, these phenomena are reversible as the transitional behaviours recovers slowly with time at room temperature. They concluded that thermal treatment of a TPU causes it to loose some of its domain or microphase separation character, resulting in a more mixed system of hard and soft segment materials. This structure, in turn, will return to the more well developed domain structure with time at a rate depending on a number of factors such as temperature, Tg, degree of hydrogen bonding, crystallisation, solubility parameter differences, etc. In follow-up studies on MDI based PUs with polyether and polyester soft segment [67], they observed that the degree of phase mixing, and therefore the transitional behaviours, immediately after heat treatment are very dependent on annealing temperature when this temperature is above 120 °C. They also deduced that the presence of hydrogen bonding capabilities in urethane are not the only factor in determining whether partial mixing of the hard and soft segment will occur or not, but it does apparently play an important role in determining the kinetics of the Tg return following annealing. They observed that the kinetics of the changing Tgs are faster for polyether than polyesters and is also faster the higher the soft segment
molecular weight. In another paper [60], these authors reported that the recovery with time is also composition dependent. In general, crystalline domains, when present, are disrupted the least while fastest recovery is displayed by samples with noncrystalline domain texture.

Galambos et al. [46] has also observed that thermal treatment of a MDI/BD/polyether PU at various temperatures results in appreciable differences in the morphology of these materials, as evidenced by large changes in DSC behaviour with the annealing of samples. Using a combination of thermal analysis with real time small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) analysis to determine the morphological transition associated with these various endotherms, he observed that the structure developed during annealing was a strong function of annealing temperature in three basic temperature regions. Kinetic studies revealed that at annealing temperatures at or below 130 °C, rapid development of phase separated structure occurred with little evidence of ordered hard segment crystalline structure. At annealing temperatures between 130 °C and 185 °C, this was typified by development of both phase separated and crystalline structure. As the temperature is increased further, the kinetics of structural development slowed markedly, until at 187 °C, no further development was observed after one hour of annealing. Here, the melting and phase mixing behaviour of the annealed sample is similar to that of specimens annealed at or below 130 °C. Similar observations were made by Koberstein et al. [47] in a similar DSC annealing- quenching studies on polyether/MDI/BD PU.

The effect of annealing has also been demonstrated by MacKnight et al. [68] using a combination of infrared spectrometry (IR) and differential scanning calorimetry (DSC) techniques. Working on model compound synthesised from 1,4-BD with each of the 3 types of diisocyanates : 2,4-MDI, 2,6-TDI and 2,4-TDI, they observed that both MDI and 2,6-TDI showed strong dependence on the annealing times with NH stretching band, and the size and shape of the melt endotherm becoming narrower and more intense with longer annealing times. However, the
2,4-TDI BD polymer did not show a change in the organisation or hydrogen bonding properties upon annealing. Hence the effect of annealing will also depend on the ability and ease at which crystallisation and/or segregation of the repeat units occurred (i.e. it is influenced by the chemical structure, and size of both the soft and hard segment material, composition, etc.).

IV. The method of preparation

The reason behind this can be understood from Section 2.1.5. Under appropriate material variables, the prepolymer method will tends to provide a better degree of phase separation. Abouzahr and Wilkes [53] reported that in their studies on a polyester based TPU, the one-stage synthesis process yielded materials with somewhat poorer physical properties than for a two-stage technique. They attributed this to a higher soft-hard segment interaction and mutual solubility of the segments brought about by a possible broader molecular weight distribution of hard segments produced in the one-stage reaction. Also working on polyether based TPU, they observed that the polymerisation technique was more influential on properties when the soft segment was a polyester than when it was a polyether. For this, they explained that the effect of the polymerisation method appeared to be largely offset by higher incompatibility of the hard and soft components.

2.1.7 Crosslinked Polyurethanes

Chemical crosslinking in non-cellular PU can be achieved by:

1. reaction of terminal isocyanate or excess isocyanate groups with urethane groups to form allophanate linkages [69, 134]

2. use of isocyanates with functionality (f) > 2; pure tri and higher functional isocyanates are not common.

3. substituting a glycol chain extender with a tri- or multi-functional hydroxyl compound [71].
4. use of amine (f = 3 or more) to form biuret structure.

The different type and relative amount of these chemical crosslinkings were reported to have a pronounced effect on most properties [23]. On contrary to crosslinking of hydrocarbon elastomers, where increased crosslinking results in an increase of many mechanical properties (e.g. modulus), the introduction of chemical crosslinking can cause a general weakening of the polymer when the level of crosslinking is relatively low [24,16]. This has been explained as to be due to spatial separation of chains resulting in reduction in intermolecular attractions, namely the hydrogen bonding. Pigott et al. [24] showed that the modulus of a polyester/ MDI/BD/TMP (Trimethylol propane) PU decreased with increased crosslinking from Me values 21000 to 5300. However, after passing through a minimum, the modulus was observed to increase as the degree of crosslinking is increased from Me values 5300 to 2100. The glass transition temperature temperature will shift to a higher temperature as the degree of crosslinking increases. A similar observation was also made by Xiao Hu and R. J. Young [19] in their study on highly crosslinked PU where crosslinking is achieved by varying the polyol/triol chain extender ratio. The increase in Tg has been attributed to loss of chain flexibility as the network becoming more tightly packed. They observed that increasing crosslink density resulted in not only in an increasing modulus and Tg, but also lead to more brittle products. However, a tougher material was obtained at higher polyol content.

Analysis carried out on a series of PU elastomer by Konton, et al. [69] using IR, DSC and tensile testing has lead to the conclusion that the crosslink elastomer PU (achieved by increasing isocyanate index) are more homogeneous than an equivalent thermoplastic PU, as evidenced from a reduction in the average hydrogen bond strength, a narrower distribution of hydrogen bond strength, the lack of endotherms above Tg and the closer to ideal rubber stress-strain curves obtained as an increasingly crosslinked product is produced.
However, morphology studies carried out by Lagasse using microscopy and SAXS techniques [70] on a chemically crosslinked urethane elastomer having butadiene soft segment, has shown the existence of microdomain structure to be similar to that seen in uncrosslinked TPU elastomers. The crosslinking, in this case, was achieved through using multi-functional polybutadiene prepolymer. He also noticed that thermal treatment of the cross-linked elastomer caused a time-dependent change in its room temperature modulus although the magnitude of this change is generally less than that observed previously with linear system. In a recent study by Petrovic, et al. [71], they observed that if chemical crosslinks are introduced via combination of linear and tri or multifunctional polyols, the effect is different. The crosslinked products obtained showed distinct two-phase structures. Chemical crosslinking was found to increase the tensile stress and the strain at break, but did not affect appreciably the tear strength, hardness and soft segment glass transition nor the melting point of the hard segment domains in this case.

Radiation crosslinking has also been reported by R. A. Assink [72]. Generally, he did not find much difference in the increased in mechanical strength of these coating as compared to the conventional coating method.

2.1.8 Characterisation Methods for Polyurethane Materials

Several methods such as IR, DSC, X-ray diffraction, dynamic mechanical measurements, wide angle X-ray scattering, optical and electron microscopy have been used to determine the structure and morphology of urethane elastomers [43, 46, 51, 62, 73-75, 77]. In this section, only a review of the DSC and IR studies are made.

2.1.8.1 Differential Scanning Calorimetry

The morphology of PU has been explored by a variety of methods. The most commonly used techniques being the IR and DSC [25, 43, 46-48, 50, 61, 64-68, 73, 76, 78, 172]. As PUs are known to exhibit a two-phase morphology, one would expect these materials to have 2 glass transition values corresponding to the soft and
hard segments. However, according to Camberlin et al. [65], usually only the Tg of the soft phase can be observed by DSC because the change of heat capacity of amorphous hard blocks at glass transition, whether in segmented copolymers or alone, is too small to be observed. Instead, the occurrence of endothermic behaviour above the glass transition values has been reported in non-crystalline and semicrystalline segmented urethanes [e.g. 46, 47, 67].

Generally, 2 to 3 characteristic endotherms above Tg may be observed in the DSC thermograms and these have been suggested to be due to the reordering within hard segment domains. Koberstein et al. [47, 64] in their studies on multiple endothermic behaviour in polyether/MDI/BD based PU using SAXS and DSC has described the following:

a) The low temperature endotherm, T_I, found at temperatures 20 °C to 40 °C above the annealing temperature (which was below 140 °C). This endotherm is due to short range (local) reorganisation of hard segments within the hard domains and is time dependent with peak magnitude increasing slowly during the annealing process. For a fixed annealing temperature, T_I increases with increase in hard segment content.

b) The intermediate temperature endotherm, T_II, found generally in the range 140 °C to 210 °C. This has been associated with the disruption of the disordered crystalline and/or noncrystalline hard micro-domain structure and possibly forming a homogeneous mixed phase, i.e. onset of a microphase separation transition to a homogenous phase. This increases with hard segment content but under conditions which are unfavourable for hard segment crystallisation.

c) A high temperature endotherm (above 200 °C) attributed to the melting of microcrystalline region within the hard domains. Hence, this occurs in crystalline material and only when the hard segment content is sufficiently high to allow for hard segment crystallisation.
Working in a similar area using a combination of SAXS, WAXD and DSC techniques, Gambos et al. [46] have also made similar observations to Koberstein et al. [47] in that T_{II} and T_{III} temperatures were seen at annealing temperature at or below 130 °C while the T_{III} endotherm temperature is promoted by annealing in the temperature range between about 135 °C and 185 °C. He noticed that the T_{I} endotherm temperature increased with increasing annealing temperature until it merges with a higher temperature peak at an annealing temperature of 180 °C. However, T_{II} intermediate endotherm does not move with annealing temperature. Rather, it simply disappears as annealing temperature is increased and crystalline structure begins to develop in the system.

Wilkes et al. [67] studying the time dependence of thermal and mechanical properties of segmented urethanes following thermal treatment, have also suggested that there are at least two sources of hard segments available to mix with the elastomeric soft segment and which differ in their thermal stability and morphology. One comes from partial thermal disruption of the microcrystalline or glassy domains at annealing temperatures above 120 °C, and the other from the less ordered amorphous hard segments at intermediate annealing temperatures greater than 60 °C.

In the past, DSC endotherms have been interpreted primarily in terms of hydrogen bond disruption [169, 79] mainly because studies carried out in the past has shown hydrogen bonding to be temperature dependent. H. Ishihara et al. [89] observed that breakage of hydrogen bond between NH groups and ether O occurred up to 100 °C while inter-urethane hydrogen bonding in the soft segment begin to break at about 140 °C [52, 78, 79]. A DSC endotherm in the region of 80 °C has been ascribed to the dissociation of urethane-soft segment hydrogen bonds, while an endotherm terms around 150 °C to 170 °C is related to the dissociation temperature of inter-urethane hydrogen bonds. In addition, with materials having longer aromatic urethane segments, a higher melting endotherm from microcrystalline hard segments is observed [101 and references therein]. However, recent studies have indicated that such endotherms are strongly dependent on thermal history and annealing condition of the
samples [66, 67, 101, 135]. Independent IR experiments carried out by Seymour and Cooper [68] indicated that there is no relationship between the dissociation of hydrogen bonding in these materials and the transitions observed in DSC experiments. The morphological changes that accompany these changes in thermal properties has also been studied using a combination of X-ray scattering and thermal analysis techniques [46, 50]

2.1.8.2 Infrared Analysis (IR)

Infrared spectroscopy is a very useful technique for studying the chemical bonding states of atoms or atomic groups. The difference in bonding state of atoms or atomic groups is observed as changes of absorption peak position, peak width and peak height [81]. Based on this concept and the fact that PU is characterised by extensive hydrogen bonding, IR spectroscopy has been used as a method of assessing the degree of phase separation in segmented PU by several investigators [52, 63, 68, 78-83] as well as in several temperature dependence studies of hydrogen bonding [79, 84-86].

The region of importance in the IR spectra of PU are that due to the NH and the C=O stretching absorptions at (3000 to 3500 cm\(^{-1}\)) and (1750 to 1700 cm\(^{-1}\)) respectively. IR spectra of PU have indicated that almost all the NH groups of the urethane linkages are found to be in the hydrogen bonded state [79, 83]. It is claimed that hydrogen bonding was found to exist between the hard segments as well as in the hard-soft segment. Generally, 3 types of hydrogen bonding are possible in PU [87-90]:

![Figure 2.7](image-url)  

**Figure 2.7**: Hydrogen bonding between: I urethane units, II urethane and ester and III urethane and ether.
The relative proportion of each of these types is dependent on the proton accepting ability and the relative molar proportion of each acceptor [90]. Generally, the relative strength of these hydrogen bond formed are in the order of I > II > III [78, 79, 90]. However, Colemen et al. [52, 88] have reported that the strength of the hydrogen bond formed between NH and O is comparable to that between NH and C=O, as they found that the 2 types of hydrogen-bonded NH absorption bands are superimposed almost exactly on each other.

The strength of the hydrogen bond is reflected in the absorption frequency. Reduction in hydrogen bond strength results in a frequency shift of the NH and C=O stretching absorption band to a higher frequency [84, 90, 91]. IR studies have shown that hydrogen bonds of varies strength exist in PU [80, 81]. These were attributed to the differences in the circumstances forming the hydrogen bonds, i.e. on the inside of the hard and soft segment domains or the interface between the hard and soft segment domains. Yamamoto et al. [81] viewed these to be indicative of the degree of phase mixing, i.e. the dispersion of hard segments in the soft segment matrix, and the cohesive force in the hard segment domain. Both Harthcock et al. and Tanaka et al. have observed that the strength of the hydrogen bond is influenced by the hard and soft segment length [80, 90]. Harthcock et al. have observed a shift of the C=O absorbance peak as hard segment length is increased while Tanaka et al. observed that when the NH in polyether-based urethane is small, most of the NH of urethane will form hydrogen bonds with ether units of polyether chains such as in a situation where the PU is prepared from polyethers of considerably high molecular weight. The broadness of the hydrogen-bonded NH bands (or C=O band) is a reflection of the distribution of hydrogen-bonded NH groups (or C=O groups) of varying strength, dictated by distances and geometries of the hydrogen bonds formed between the NH groups and the proton acceptors [84-86].

In a study on model compounds based on different NCO systems, Brunette and MacKnight et al. [169] attributed the differences in breadth and intensity of the NH absorption band to be due to differences in packing and the ability and ease with which
crystallisation and/or reorganisation of the repeat unit occurred. In a separate paper, MacKnight et al. [83] also mentioned that quantitative analysis of the hydrogen bonds from data collected on the NH stretching bond, is complicated by the significant band overlap which may result from the large differences in inherent coefficient as a function of hydrogen bond strength.

Coleman and coworkers in a series of IR studies on hydrogen bonding have concluded that using NH stretching region of the infrared spectrum to obtain accurate quantitative data concerning the fraction of ‘free’ and hydrogen bonded NH groups can lead to large errors because:

a) the initial concentration of ‘free’ NH groups in PU is considerably less than the hydrogen bonding groups (< 20% at room temperature), and

b) the absorption coefficient is a strong function of the strength of hydrogen bond. It decreases with decreasing hydrogen bond strength. Hence, infrared band attributed to the ‘free’ NH stretching vibration has an absorption coefficient that is much smaller than the hydrogen bonded NH stretching band.

An alternative to the above problem, as proposed, is to study the C=O stretching region because:

a) the ‘free’ C=O stretching band is well separated from the disordered hydrogen bonded C=O,

b) the absorption coefficients for those bonds varies only slightly.

H. S. Lee et al. [83] have used spectroscopic techniques to study phase separation in PUs. They noticed that quantitative analysis of the hydrogen bonds from data collected on the NH stretching bond is complicated by the significant band overlap which may result from the large differences in inherent coefficient as a function of hydrogen bond strength.
2.1.8.3 Other Techniques

Other characterisation techniques used in morphology studies include scanning electron microscopy (SEM), differential mechanical thermal analysis (DMTA), etc. In DMTA, the magnitude of the mechanical loss peak, $\tan \delta$, usually reflects the relative amount of amorphous material in the polymer undergoing the transition from the glass to the rubbery. A lower $T_g$ is seen as a shift of this modulus to lower temperature [41]. The relative concentration of the hard and soft segments affects the level of the plateau modulus at temperatures between the major relaxation regions.
2.2 Acrylate Polymers

2.2.1 Introduction

Many acrylate polymers are derived from either acrylate or methacrylate esters and represented by the general formula:

\[
\begin{align*}
\text{CH}_2 - \text{CH} & \quad (\text{R'}_n) \\
\text{C}=\text{O} & \\
\text{OR} &
\end{align*}
\]

where \( R' = \text{H} \) for polyacrylate

and \( R' = \text{CH}_3 \) for polymethacrylate

Acrylate polymers can range in physical properties from soft elastomers (\( T_g < -40 \, ^\circ\text{C} \)) to hard plastics such as PMMA (\( T_g = 105 \, ^\circ\text{C} \)). These materials have excellent weatherability, being stable to visible and UV radiation and do not readily discolour on aging or otherwise degrade on outdoor exposure. They have good heat resistance. The properties of these polymers are strongly influenced by the:

1. chemical nature of the \( R' \) group on the \( \alpha \)-carbon.

2. chemical nature and length of the ester side chain.

3. presence or certain functional groups in the ester side chain.

Literature reviews on this topic [92-98, 101-111, 135, 170, 182] in the next section provided an understanding to the wide variety of properties obtainable from the acrylate family of esters, various polymerisation techniques employed and the applications of these polymers [92-94].
2.2.2 Polymerisation routes of acrylates [103, 106, 109]

Polymerisation of acrylic monomer range is extremely versatile in terms of polymerisation mechanism which can be:

a) free radical mechanism: thermal, anaerobic, high energy irradiation.

b) anionic mechanism.

c) cationic mechanism

For example, polymerisation of cyanoacrylates (a highly electrophilic material) to give adhesives of enormous strength is based on anionic mechanism in the presence of a suitable electron donor, A\(^-\), (a Lewis base catalyst) as briefly illustrated below:

\[
\begin{align*}
&\text{CN} \\
&\text{CH}_2=\text{C} - \text{COOR} + A^- \rightarrow \text{A} - \text{CH}_2 - \text{C} \_ - \text{COOR} \ \\
&\rightarrow + \ \\
&\text{CN} \\
&\text{CH}_2=\text{C} - \text{COOR} \ \\
&\rightarrow
\end{align*}
\]

Further reaction

\[
\begin{align*}
&\text{CN} \\
&\text{A} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} \_ - \text{COOR} \ \\
&\rightarrow \text{Thermoplastic material}
\end{align*}
\]

Commercial production of polymethacrylate is based on a free radical mechanism. All industrial polymerisation processes are carried out at elevated temperature in the presence of catalyst such as tertiary butyl perbenzoate (C\(_4\)H\(_9\) OOOC C\(_6\)H\(_5\)). The polymerisation can be carried out in bulk, solution, aqueous suspensions or in emulsions. The molecular weight and rate of polymerisation can be controlled by the use of a suitable concentration of catalyst. Acrylic resins with low molecular weight
and narrow molecular weight distribution, an essential criteria for use as high solids coating [94], can be produced by use of tertiary amyl peroxide catalyst. High loadings of catalyst may encourage initiation, limited propagation and premature termination.

The free radical mechanism involving 3 steps is as illustrated below:

I Initiation

\[ \text{I} : \text{I} \rightarrow 2 \text{I}^- \]

\[ \text{I}^- + \text{M} \rightarrow \text{IM}^- \]

The initiator (I), may be peroxides, azo compounds or hydroperoxides, is readily decomposed, at temperatures dependent on the type of initiator used, to produce free radicals (I\(^-\)). The resultant free radicals then react to open the double bond of the acrylic monomers (M) to form acrylic radicals (M\(^-\)).

II Propagation

\[ \text{IM}^- + n \text{M} \rightarrow \text{IM}_n \text{M}^- \]

Chain propagation proceeds with the acrylic radicals adding on to the acrylic monomers to form macroradicals.

III Termination

a) \[ \text{IM}_n \text{M}^- + \text{MM}_m \text{I} \rightarrow \text{IM}_{n+1} : \text{M}_{m+1} \text{I} \]

Combination

b) \[ \text{IM}_n \text{M}^- + \text{MM}_m \text{I} \rightarrow \text{IM}_n \text{MH} + \text{M} = \text{M}_m \text{I} \]

Disproportionation

where H is an hydrogen atom abstracted from the other acrylic macro-radical.
The termination step is achieved by a mixture of combination and disproportionation between the acrylic macro-radicals.

However, all polymerisations by free radical mechanism are subjected to oxygen inhibition at initiation stage. This arises from oxygen dissolved in monomers at the air/monomer interface [95-101]. Oxygen in the ground or unexcited state is itself a radical and is highly reactive with other radicals. Thus, chain growth can be terminated by the oxygen radical, resulting in uncured, often tacky surfaces. Several methods have been suggested for reducing the oxygen inhibition effect such as uses of waxes, more reactive diluents, etc. [95, 96, 99].

The free radical mechanism is also employed in a variety of non thermal polymerisation methods (using initiator system as described in above) for industrial use. Common examples are:

1. Acrylates cured in anaerobic composition

   These are defined as polymerisable compositions and are intended to polymerise spontaneously in the absence of oxygen, since the reaction is otherwise substantially inhibited by the presence of dissolved in oxygen. Polyethylene glycol dimethacrylates are typical of the range of the monomers capable of polymerisation by this method. Catalysis is via breakdown of the hydroperoxide group, to reform the free radical species.

2. By high energy irradiation

   High energy irradiation, e.g. ultraviolet or electron beam radiation, of acrylic monomers is commonly used to initiate free radical chain reactions. Photoinitiators (i.e. Norish and hydrogen abstracting types) are usually used for greater efficiency as it readily form free radicals on exposure to energetic radiation. Anionic photo-initiators may also be used.
The versatility in polymerisation method is further extended by some acrylic monomers having dual functional groups. Such monomers, e.g. hydroxy ethyl methacrylate, glycidyl methacrylate, etc., may be homo-polymerised or copolymerised with other vinyl or acrylic monomers such as styrene, methyl methacrylate, etc. to give linear polymers with pendant functional groups such as hydroxyl or epoxy groups. These polymers are capable of further reaction with di- or poly-functional compounds, e.g. polyisocyanates, isocyanate tipped urethane prepolymers, conventional epoxies, etc., having groups that can react with the pendant functional groups, forming a cross-linked product. The thermosetting acrylic compositions mainly rely on such mechanisms.

Alternatively, the pendant functional groups of such monomers may be made to react with the functional groups of a condensation or vinyl polymers to form an acrylic terminated polymer with residual double bonds. An example of such is the anaerobic structural adhesives [103] which are based on either

a) those obtained by addition of 2 moles of a hydroxy alkyl methacrylate to 1 mole of diisocyanate or/

b) via a prepolymer obtained from the reaction of a diol with a diisocyanate (1:2 molar) and subsequent capping with hydroxy alky methacrylates.

The synthesis of radiation curable oligomers are also based on this latter method (i.e. method b). Such polymers are capable of further polymerisation or crosslinking with other vinyl or acrylic monomers, through the double bonds by free radical mechanism.

2.2.3 Structure-property Relationship

1. Mechanical properties

Generally, acrylic polymers with glass transition temperature values (Tg) greater than room temperature are characterised as having high tensile strength and low elongation, whereas those with Tg below room temperature have low tensile
strength and high ultimate elongation. The best compromise for maximum toughness is achieved by polymer composition with Tg values around room temperature, although this leads to strain rate dependence failure (i.e. ductile / brittle) in such polymers. The effect of molecular structure on the Tg of the polymers are namely:

a) Chain stiffness

b) Side chain effects

The substitution of the α-hydrogen by the methyl group on the main chain results in steric hinderance to the segmental rotation of the polymer backbone, causing its Tg to increase.

Variations due to side chain effects relate specially to relative side chain length, its flexibility, bulkiness and crystallisability. As the length of the ester side chain increases, the polymer chains are forced further apart, resulting in greater segmental mobility and hence, a lower Tg. However, at relatively long side chain lengths (to approximately 12 carbon atoms), crystallisation of the side chains results, hence higher Tg polymer is obtained. Increasing the bulkiness or rigidity of the alkyl side group also restricts the motion of the backbone polymer chains, thereby causing an increase in the Tg of the polymers.

2. Chemical Properties

The nature of the side groups determines to a large extent the type of solvent necessary to solubilise the polymer. Acrylic polymers with polar side groups or short side chains are relatively polar and are soluble in polar solvent such as ketones, ether or alcohols. The water and chemical resistance of the polymers are also related to the chemical nature of the side group. Introducing hydrophobic constituents such as styrene or high side chain length results in polymers having better resistance to polar solvents. The presence of certain types of functional group on the ester side chain also impart specific characteristic properties such as
increased adhesion. Hence, specific end use requirements (e.g. flexibility, hardness, adhesion, etc.), of the acrylic polymers can be tailor-made accordingly by proper selection of the monomers type. The physical properties of the acrylic esters and their derived polymers can be found in several texts. [92, 97, 103-105, 111].

Acrylics are known to possess excellent weather properties and are not readily attacked by acids or bases. The reasons for these properties are attributed to the chemical nature of the polymer backbone. The polymer backbone is comprised entirely of C–C single bonds that are relatively inert and not susceptible to hydrolysis. Even though the ester side chains can be hydrolysed, with difficulty, this still leaves the C–C backbone intact. Another reason for superior durability is that the polymers are transparent in the spectral region between 3500 and 3000 Å, which is one of the most photochemically active region of the solar spectrum. The durability of the acrylic polymers is increased with longer ester chain length as the increased flexibility and hydrophobicity of the softer polymers enable them to withstand dimensional changes in the substrate more readily without cracking, while having greater water repellence property.

Generally, in comparison to acrylate polymers, the methacrylate polymers have superior resistance to light and chemical degradation because the methyl group in the α-carbon of the main chain is less reactive than the tertiary hydrogen in the acrylate. Consequently, free radical intermediate contributing to chain scission is less readily formed.

2.2.4 Storage and Handling [107]

Due to the unstable double bond, all acrylic monomers are potentially reactive and capable of undergoing polymerisation under relatively mild conditions. Hence, acrylic monomers are normally stabilised with inhibitors such as hydroquinone or hydroquinone monomethyl ether to prevent polymerisation (initiated from e.g. presence of foreign matter) during storage.
The hazards associated with acrylic monomers vary considerably depending upon the monomers used [107]. For example, methyl methacrylate (MMA) monomer is of low acute toxicity and only slightly irritating to the skin, eyes and respiratory system. However, hydroxy propyl acrylate (HPA) is irritating and corrosive to all parts of the human body and harmful amounts may be absorbed through the skin.

2.2.5 Applications [103, 105, 106]

Acrylic homopolymer or copolymers are used in a wide range of applications such as:

1. Sheets, rods, etc. by casting techniques.

2. Moulding powders, e.g., for melt shaping, powder coatings, etc.

3. Rubbers or latexes which are used in, examples, automotive gasket and sealant applications. The latexes may also be used in adhesive and coating applications.

4. Resin syrup, e.g. polymer dissolved in monomer, used in many adhesive and coating applications.

5. Interpenetrating network (IPN) systems.

2.2.5.6 Polyacrylate Elastomers [103, 105, 106, 108]

Polyacrylate elastomer chains are normally made up of substantial amount of homopolymer of ethyl or butyl acrylate copolymerised with a small proportion of a monomer containing an appropriate substituents (e.g. –CN, –COOH) or providing a residual double bonds (e.g. a diene). The polymerisation is radical-initiated and is usually carried out in aqueous emulsion followed by coagulation, or by a suspension method yielding the elastomer directly as granules. The rubbers are normally vulcanised with amines (e.g. triethyl-trimethylene-triamine). Reinforcing fillers (e.g. carbon black) are needed to impart the best physical properties, with tensile strength up to 1.7 kgf / mm² and breaking elongation 500%.
2.2.5.7 Acrylic Coatings

For the past 50 to 60 years, protective and decorative coatings based acrylic resins have found increasing use in a variety of industrial and consumer applications such as seamless flooring, automotive finishes and refinishes, aircraft finishes, paints, fabric coatings, etc. These resins are homo- or co-polymers of alkyl esters of acrylic or methacrylic acid, made commercially in a variety of forms such as solution acrylics and acrylic emulsions. In many applications, acrylic copolymers are preferred as they enable coatings to be tailor-made accordingly to requirements (refer to Section 2.2.3).

Acrylic coatings can be classified into thermoplastic or thermosetting systems. Thermosetting acrylic coatings are based on low molecular weight copolymers of two and occasionally three monomers. These are usually the acrylic or methacrylic esters or styrene-based monomers and functionally reactive monomers, such as acrylic or methacrylic acid [109]. Curing of these resins is based on polycondensation or polyaddition reactions, as described in greater details under Section 2.2.2. The selection of a particular thermosetting formulation will depend on the process and end requirements such as cure temperature, properties, etc..

2.2.5.8 Interpenetrating Networks (IPN)

IPN is the term used to describe the combination of two or more different polymer networks which consist of purely physical entanglements of the polymer chains synthesised either simultaneously or sequentially with respect to each other [110, 181]. The sequential-IPNs (SIPN) are prepared by swelling a crosslinked polymer with monomer and the crosslinking agent of another polymer, and curing the swollen polymer in situ. The simultaneous IPN (SIN) are prepared by blending the linear polymers, prepolymers, or monomers in some liquid form (latex, solution, or bulk) together with the respective crosslinking agents, evaporating the vehicle (if any), and curing the component polymers simultaneously [177].
2.2.6 Recent Trends in Acrylic Coatings

As a result of growing concern over air pollution, occupational safety and health hazards in the mid sixties, efforts have been made to develop low-emission acrylics coatings. These coatings, available in thermoplastic or thermosetting forms, can be classified into:

A. water-based coatings, e.g. emulsion types.
B. high-solids coatings.

The high solids coatings can be subdivided into three general categories:

I. Oligomeric form

These are low molecular weight thermosetting entities with molecular weight lower than that of the conventional solvent-based coating, ranging from $10^2$ to $10^4$. It has been found that unless the molecular weight distribution is quite narrow, the cured film does not develop adequate properties.

II. Powder coatings [93, 112-115]

These are applied as solid particles of thermoplastic or thermosetting polymers by electrostatic spray and subsequently fused into a continuous film by heat.

III. Radiation-cured coatings [11-14, 113-119, 121-132, 176]

These coatings are used in applications such as board coating and printing inks. They are based on acrylate modified oligomers [93, 94, 112-115], namely,

a. Epoxy acrylate:
   -- prepared by adding acrylic acid to a polyepoxide (see Figure 2.8)
b. Urethane acrylate:

-- prepared, for example, by adding hydroxyalkyl acrylate, via multifunctional isocyanates, to an hydroxyl terminated polyester or polyether (see Figure 2.9)

c. Polyester acrylate:

-- prepared by transesterification of polyester resins (see Figure 2.10).

These may be thinned using a reactive diluent (usually multifunctional), e.g. MMA. The basic chemistry of such systems involves the initiation of the cross-linking reaction (often with the aid of photoinitiator) by ultraviolet radiation or electron bombardment [112, 114]. The polymerisation then proceeds rapidly to completion. Depending on the types of photoinitiator used, the reactions are usually based on free radical mechanism. UV radiation source should be tuned to a wavelength equivalent to that which produces photo-initiated degradation of the photoinitiator.
Figure 2.8: Synthesis reaction of epoxy acrylate oligomer.

Figure 2.9: Urethane acrylate oligomer.

Figure 2.10: Polyester acrylate oligomer.
2.3 Urethane - Acrylic System

Urethane-acrylic polymers can exist as IPN [177-181] or copolymers. As this project is concern with urethane-acrylic copolymers, the literature survey in the next section refers only to the copolymers.

2.3.1 Acrylated Urethane Oligomers (AUO)

AUO have typical molecular weights in the 500 to 3000 range [112]. They may have one or more acrylic components at any point along the oligomer chain. Various types of AUO have been described in several patents, such as in:

a) US 3 700 643 [116] ----based on polycaprolactone diol

b) US 3 782 961 [117]----based on polyether polyols

c) US 4 131 602 [118]---based on a mixture of organic diol and organic tri and / tetrol

AUO commonly encountered in literature are those having typical structural formula as shown in Figure 2.9. The synthesis of these AUO can be carried out by either a one - step [117] or a two-step procedures. The latter method is often chosen, whereby the polyols are reacted with excess isocyanates to form isocyanate- terminated urethane prepolymer. These are further reacted with hydroxy alkyl acrylic esters to form AUO [118-120] and the resin is isocyanate free. Alternatively, the isocyanates can react first with a deficiency of the hydroxy alkyl acrylic compounds and subsequently with the polyols [22, 121, 122].

In AUO, the hard segment is derived from the diisocyanate, the urethane linkages and the acrylate groups [14]. The soft segment which imparts flexibility to the urethane acrylate is derived from the polyol, with molecular weight usually in the range 1000 to 2000.
Although AUO may be used in some other applications, such as in anaerobic structural adhesives [103] their importance arises from being popular materials used in radiation curing process (both uv and electron beam) [99, 102, 112-119, 121-132, 176]. For this reason, the acrylic components are normally based on acrylate rather than methacrylate as the former is more responsive to radiation curing. Although radiation curable by itself (i.e. without a reactive diluent) to form urethane-acrylic polymers, it is usually dissolved in some di- or multi- functional acrylate monomers [22, 99, 112, 123, 124] for the following reasons:

1. to reduce the viscosity of the resin to a workable level (these monomers constitute about 20% to 60% of the total formulation),

2. to increase the curing process (for this purpose, the di- or multi- functional acrylate monomers are preferred as they provide the highest response to the radiation as compared to its monofunctional species or to methacrylate or vinyl or allyl functionalities [124]).

The monomers also participated in the polymerisation / curing reaction to become part of the urethane-acrylic polymer network. Hence, they will constitute to the development of film properties such as improved adhesion, hardness, resistance to weathering, etc. [125, 126].

2.3.2 Urethane-acrylic Copolymers (UA copolymers)

UA copolymers are known to be capable of providing a combination of properties that are related both to polyurethanes (e.g. high abrasion and certain chemical resistance) and to acrylic polymers (e.g. superior weatherability and transparency), together with a good balance of flexibility and hardness [121, 124]. Hence, they are the preferred choice for a variety of applications, such as coatings, high quality wood finishes, floor coatings, etc.. The ultimate performances and properties of the coatings will depend on the chemical design of the polymers. Coatings with tensile strength over 250
kg/cm² and elongation at break of over 100%, combined with excellent abrasion resistance are obtainable with these polymers [124].

As mentioned earlier, UA copolymers are formed from reaction between AUO and acrylate monomers. As such, curing of the AUO with mono-functional acrylic monomers through the vinyl double bond, would actually result in a AB crosslinked copolymer type (known as ABCP), whereby polymer chain A is crosslinked to polymer chains B as illustrated in Figure 2.11. An example of such a crosslink copolymer type is that based on polyester resins and styrene monomers. For UA copolymers, literature survey of several publications and texts on polymer compatibility, blends, alloys, multicomponent polymers, etc. seemed to indicate that very few studies have been made on the ABCP systems [120, 133, 136, 154, 183-188]. To the author's knowledge, studies that have so far been carried out were mainly those of the radiation curable systems, in which multifunctional acrylate monomers were used [11, 13, 22, 121, 122, 125-132]. Such systems are therefore highly crosslinked and complicated. In the next section, a literature reviews of structure-property studies on UAP as an ABCP and radiation cured coatings will be discussed. In these studies, the hard segments were composed of the urethane-acrylate groups and the (meth)acrylate components. There were also attempts made to introduce hard blocks made from a series of isocyanate and short diol chain extender units into the AUO [122, 132] but very little information of such systems has been found and these will not be mentioned here.

![Figure 2.11: A ABCP network](image-url)
2.3.3 Structure - property Studies

2.3.3.1 Urethane-acrylic Crosslinked Polymers (ABCPs)

Ying et al. [133] have reported from their studies on ABCPs based on hydroxyethyl methacrylate (HEMA) terminated castor oil polyurethane (COPU) and polymethyl methacrylate (PMMA), that the AB crosslinked polymers exhibit semi-compatibility (i.e. partial compatibility). Based on dynamic mechanical (DM) spectra, they have concluded that the compatibility of the two components decreased with increasing hard segment content. This was indicated by the shift in Tg of the tan δ peak to a higher temperature with gradual change of the tan δ curve from a symmetric to an unsymmetrical curve, with a shoulder attributed to the COPU soft segment. The transmission electron microscopy (TEM) results have also indicated a 2 phase morphology but the phase separation was not clear. The COPU soft segment is thought to formed the continuous phase with phase inversion occurring when PMMA content is above 50%. They also reported that increasing the crosslink density of the ABCP, by adding divinyl benzene to adjust the average molecular weights between crosslinked points, increased the compatibility of the two components.

Liu et al. [120] working on ABCPs based on hydroxyethyl acrylate (HEA) terminated polypropylene glycol polyurethanes (PGPU) or COPU with a variety of vinyl monomers such as methyl methacrylate, butyl methacrylate, vinyl acetate, etc. at 50% weight ratio, have also observed a 2-phase morphology with the PU-rich domains forming the separated phase as seen on the electron micrographs. The PU-rich domains were irregular in shapes and had a highly polydisperse distribution with the average diameter of the domains depending on the molecular weight of the prepolymer PPG. They observed that highly crosslinked structures will produce large numbers of very small domains. They found that ABCP based on COPU showed better compatibility than those based on PGPU. This was ascribed to the higher crosslink density of the COPU based ABCP.
In a separate study based on HEMA-terminated polyethylene adipate urethane and methyl methyacrylate ABCPs, Liu et al. [136] have also observed a 2-phase morphology as evident from TEM and DM studies. They reported that the inwards shifted of the two Tgs (corresponding to the urethane and the acrylate components) in the ABCP as evident from the DM spectra has indicated that the chemical crosslinking between the two components increased the mutual miscibility.

2.3.3.2 Radiation Cured Polymers

Studies carried out by several investigators have revealed that the highly crosslinked radiation cured urethane-acrylic polymers were capable of phase separation under suitable conditions [14, 22, 121]. These morphological studies done mainly by dynamic mechanical thermal analysis technique (DMTA). The variables that affect the morphology and properties of the polymers were shown to be divided basically into:

A. Oligomer structure and molecular weight

It was generally recognised that the oligomers have a greater influence on the mechanical properties of the cured polymers than the reactive diluent monomers (which are usually multifunctional) [13, 14, 125]. From their work on some multifunctional oligomers, Noren et al. observed that the molecular weight of the reactive oligomer was the most significant variable in controlling the mechanical properties of the polymer. Several studies [11, 14, 22, 125, 127] have reported where oligomers made from higher molecular weight diols resulted in polymers of lower tensile strength and modulus while giving increased elongation. These have been ascribed to increased chain flexibility, reduction both in hard segment content and effective crosslink density of the system.

The ability of the system to undergoes phase separation also appears to be dependent on the polyol types and molecular weight used. Wadhwa et al. [128] reported that films (thickness of approximately = 0.2 mm maximum) formed by curing a variety of toluene diisocyanate (TDI) - ester based oligomers (of 1000 to
6000 molecular weight) exhibited a single phase morphology in which the hard segments and the soft polyester segments were homogeneously mixed. Dai et al. [14] working on films cured from TDI-PPG (of molecular weight, Mn = 1180) based oligomers have also found, from DSC, SEM, etc. studies, that these copolymers exhibited phase separation. However, both Speckhard et al. [121] and Koshiba et al. [22] have reported that polymers based on polytetramethylene oxide (PTMO) of 2000 molecular weight have a two phase morphology, distinguished by the presence of a low temperature soft segment Tg and a high temperature hard segment Tg in the DM spectra. They also found that those based on a lower molecular weight PTMO (Mn = 650) showed only a single Tg, indicating a single phase morphology where the hard and soft segments were mixed homogeneously. Working with three different molecular weights of PTMO, Koshiba et al. concluded that increasing the molecular weight of the polyol soft segment increased the degree of phase separation. The low temperature Tg of the urethane-acrylate polymer is determined mainly by molecular weight of the polyol.

Based on Ando et al.'s [131] work, also on film cured without the use of reactive diluents, it appeared that the use of higher molecular oligomers would encourage crystallisation of crystallisable oligomers. However, this seemed to depend on the curing temperature. Chiang et al. [130] reported that semi-crystalline films cured at temperatures below the melting temperature (Tm) of the oligomers had a higher breaking strength, Young's modulus, and a higher Tg, but a lower elongation at break, compared to those cured above Tm. In their studies, reactive diluents were used. They observed that crosslinking, which occurred at the acryloyl double bond did not destroy the crystalline phase of the prepolymer.

The properties of urethane-acrylate oligomers are dominated by the polyol component. Hence, it is expected that polyol based on polyester segments will impart toughness, abrasion resistance, tear strength and polarity to the resin system while that based on polyethers will impart improved low temperature properties and hydrolytic stability. Koshiba et al. reported that coatings based on PTMO
exhibited better phase separation than those based on polycaprolactone diol, (both having a molecular weight of 2000). They attributed this to the higher polarity of PCL compared to PTMO, thereby resulting in better compatibility of the former with the polar acrylic hard segments and consequently a lower degree of phase separation. Dai et al. [14] have described the superior mechanical properties of PTMO based polymers as compared to the PPO based polymers to the crystallisability of PTMO. According to him, PPO chains lack symmetry and are difficult to crystallise. The presence of crystalline regions have played a similar role to the crosslinks in improving the mechanical properties of PTMO based polymers.

Noren et al. have reported that the effects of polyol structure for multifunctional oligomers were similar to those reported for difunctional oligomers. The presence of urea groups increased the percent elongation and tensile strength. They observed that the tensile strength and modulus of the polymers decreased according to the polyol series:

polyester > polytetramethylene glycol > polycarbonate > polycaprolactone > polypropylene glycol

Chiang et al. [19] also showed that the tensile properties of the cured polymers were affected by the polyol structure.

Very few studies have been made on the effect of isocyanate structures, and those reported appear confusing. McConnell et al. [11] concluded from their works that polymers from TDI based oligomers (polyol type not given) gave higher tensile but lower modulus and elongation than those based on isophorone diisocyanate (IPDI). They ascribed these effects to the less flexible aromatic structure of TDI isocyanates. However, Dai et al. [14] also reported that the IPDI based polymers showed higher Young's modulus and stress at break as compared to the TDI or p-xylene diisocyanate (XDI) based polymers. In their works, no significant differences in the elongation at break was observed. They thought that this could
be related to the higher IPDI-HEMA (2-hydroxyethyl methacrylate) hard segment content as the IPDI had the highest molecular weight of the three components. Both McConnell et al. and Dai et al. carried on work on pure oligomer systems i.e. without using reactive diluents. In Koshiba et al.'s works, the films were prepared from a series of urethane oligomers dissolved in varying amount of reactive diluents (i.e. 0%, 10% and 20% weight). They found that there was no trends indicating that the TDI based films have a better properties than the IPDI based film. Hence, they concluded that the properties of these 2 types of films were probably the same.

Most acrylated urethane oligomers were based on hydroxy ethyl (or propyl) acrylate or their corresponding methacrylates. Noren et al. [125], reported little or no effect on the physical properties of the cured films had been observed when changing from acrylate to methacrylate functionality. As far as can be ascertained, no studies of 4,4'-diphenyl methane diisocyanate based acrylated urethanes have been reported.

B. Reactive diluent types and concentrations

Oraby and Walsh [127] have postulated that curing an oligomer by polymerising the double bonds at each of its ends would result in a multirayed, star-shaped crosslink structure where the average crosslink functionality would equal the average degree of polymerisation of the double bonds (see Figure 2.11). They hoped that copolymerising the oligomers with a reactive diluent would serve to break up the star-shaped crosslinking and thereby increase the flexibility and elongation of the material. However, except for N,N'-diethylaminoethyl acrylate (DEAEA), the addition of the monofunctional reactive diluents employed in their studies generally led to a slight decrease or no change in the elongation at break. The improvement in elongation at break seen with DEAEA was attributed to its significant chain transfer constant. The effect of these diluents on the tensile strength of the cured polymer varies as well, with some causing an increase while others having little effect.
Figure 2.12: Multirayed star-shaped crosslink structure [127].

However, studies carried out by several other investigators, have shown that the addition of reactive diluents, both mono and multifunctional, generally resulted in an increased in tensile strength and Young's modulus, accompanied by a reduction in elongation at break [13, 14, 22, 119, 121, 125]. From their studies based on monofunctional reactive diluents, Noren et al. [125] observed that certain diluents caused a greater increase in tensile strength and modulus than the others, and would be accompanied by a corresponding greater reduction in elongation at break. These properties did not appear to be related to the Tg of the reactive diluent monomers.

Some investigators have ascribed the properties changes to an increase in the hard segment content and crosslink density of the system [13, 14, 22]. Steven et al. [13] observed that polymers cured with the reactive diluent hexane diol diacrylate (HDDA), gave a greater tensile strength, but poorer elongation, than that using tripropylene glycol diacrylate (TPGDA). They attributed this to a greater effective crosslink density achieved with HDDA, thereby causing a greater restriction to the chain movement in the cured film.

Chiang et al. [119] made a study on a series of monomers having a similar backbone structure but a different methacrylic functionality. They observed that
the Young's modulus and the breaking strength of the cured films increased with increasing functionality of the monomers, while the elongation at break decreased. They also worked on some monofunctional diluents, observing that the tensile properties of the cured polymers were affected by the stiffness and flexibility of the monofunctional monomer chains used in their studies.

Both Koshiba et al. [22] and Speckhard et al. [121] also believed that the effect of a reactive diluent on the polymer properties was also related to the Tg of its homopolymer. Working on PTMO based oligomer (with PTMO molecular weight, \( M_n = 2000 \)), they observed that increasing crosslinker content, using either polyethylene glycol diacrylate (PEGDA) or N-vinyl-2-pyrrolidone (NVP), resulted in increase in Young's modulus and ultimate tensile strength. However, improvement in "toughness" (i.e. related to the elongation at break as toughness, as defined as area under stress-strain curve) was observed only with NVP crosslinker. Dynamic mechanical analysis (DMA) of these polymers revealed that increasing NVP content caused the hard segment Tg to increase in magnitude and to shift to a higher temperature while the Tg of the soft segment remained constant. However, with increasing PEGDA content, DMA result showed only an increase in the magnitude of the hard segment transition without changing its Tg. Hence, they deduced that the improved toughness observed with NVP based polymers was due to NVP having a higher Tg than PEGDA.

Koshiba et al. have also found that the effect of NVP or the polymer properties was also dependent on the morphology of the system. With the single phase system (i.e. those based on PTMO molecular weight of 650), increasing NVP content resulted in a reduction in the elongation at break instead and the material become more brittle at higher levels of NVP content. The DMA spectra has shown that increasing the NVP content also caused the single Tg of the single phase material to shift to a higher temperature. With the two-phase systems (i.e. those based on PTMO molecular weight of 2000), they attributed the improved toughness observed to the increase in volume fraction of the hard segment
domains, as indicated by the increase in the magnitude of the hard segment transition peak with increasing NVP content.

Speckhard et al. [121] carried out a much more detailed study on this aspect than most other investigators and ascribed the varying effects of the different reactive diluents on the physical properties of the cured polymers, to the relative compatibility of the reactive diluents with the hard and soft segments of the urethane-acrylate segments. They believed that this was accountable for the mechanical properties derived consequently, since the choice of reactive diluents has an influence on the degree of phase separation and on the extent of copolymerisation of the reactive diluent with the urethane acrylate groups, was accountable for the mechanical properties derived consequently. For example, they observed that the Young's modulus and tensile strength, as well as the room temperature storage modulus of the two-phase polymers based on one of the three reactive diluents (i.e. PEGDA, triethylene glycol diacrylate (TEGDA) and diethylene glycol diacrylate (DEGDA)), appeared to increase with reactive diluent types in the order PEGDA < TEGDA < DEGDA. They attributed this to the better compatibility of the shorter chain reactive diluent (where the C=O groups are closer to each other) with the urethane-acrylate phase, leading to a greater proportion of the hard segment phase and a greater likelihood of copolymerisation of the reactive diluent and the acrylate groups. The trend of increased crosslink density with reactive diluent type in the order DEGDA > TEGDA > PEGDA was also attributed more to the differences in compatibility of the reactive diluents with the oligomer and / or the effectiveness of the reactive diluents acting as a chain transfer agent, rather than to the differences in the chain length of the reactive diluents: the differences in the chain length are fairly small. However, they pointed out that it is difficult to directly relate the property differences to the differences in the chemical structures between the oligomers and the various reactive diluent, since the many different factors (as mentioned earlier) will also affect the physical properties of the materials. For example, polymers cured with NVP showed superior tensile strength, modulus and elongation than those cured with the diacrylate reactive diluents mentioned earlier. They ascribed this effect to:
(i) possibility of its (NVP) better compatibility with the hard segment (urethane-acrylate group), thereby leading to a higher degree of phase separation.

(ii) higher Tg of NVP.

(iii) NVP is probably a better chain transfer agent.

Speckhard et al. have also reported that the addition of reactive diluent to a single phase or a poorly phase separated systems (i.e. usually those based on low polyol molecular weight of e.g. $< 1000$) served to increase the degree of phase separation and the amount of urethane acrylate / reactive diluent phase. For materials with a well-defined two-phase morphology (i.e. usually those based on a higher polyol molecular weight of e.g. 2000), the addition of reactive diluent served primarily to increase the amount of the urethane acrylate / reactive diluent phase.

Puskas et al.'s work [12] was based on polyisobutylene urethane-acrylate polymers. They observed from the DSC traces that the high temperature Tgs, at approximately 65 °C, associated with the acrylate domains, were less distinct due to the relatively low amount of acrylate content used. Nevertheless, a slightly higher hard segment Tg was observed when a higher acrylate content was used.
CHAPTER 3

EXPERIMENTAL WORK
3.1 Introductions / Experimental Approach

This chapter deals with the various materials used and the experimental work carried out in this project. It also covers on the type of equipment used with their basic working principles, the purpose of carrying out the various characterisation tests, the test procedures and the sample preparations involved. The main experimental work was divided into:

a) synthesis of urethane-acrylate (UA) copolymers.

b) characterisations of the raw materials, intermediates, and final products.

Syntheses of acrylic homopolymers, i.e. polymethyl methacrylate (PMMA) and polybutyl methacrylate (PBMA) and crosslinked polyurethanes (PUs) were also made. These were used as reference materials in studying the effect of introducing the various variables to the UA copolymers.

The experimental approach adopted for this project is summarised in the flow chart shown in Figure 3.1. The flow chart does not include the synthesis of acrylate homopolymers.
Chapter 3

Isocyanates (MDI, TDI)

- DSC for melting point.
- Purity assessment by industrial method.
- GPC

Polyols (PPG, PEG)

- Trace catalyst removal for PEG
- OH content by Acetic anhydride acetylation
- GPC for molecular weight and molecular weight distributions
- DSC

NCO-prepolymers

Route B: synthesis of Crosslinked Polyurethanes

- GPC analysis to deduce structure of prepolymer and to select synthesis conditions (e.g. temperature, use of catalysts, etc.) there from.
- Methods of following reactions, i.e. by IR or wet analysis using dibutyl amine.
- Viscosity measurements by cone and plate.
- Characterisations including DSC, IR analysis.

Route A: synthesis of UA Copolymers

Figure 3.1: Flow chart showing experimental approach, including synthesis and characterisation routes taken.
Figure 3.1 cont’d.

**Route A:**

- HPMA
  - Moisture content by Karl Fischer
  - Acrylated-urethane Oligomers (AUO)
    - Selection of synthesis conditions and variables (e.g. temperature, percentage of excess HPMA, etc.).
    - Methods of following reactions.
    - Characterisations such as GPC analysis (for rough indication of reaction products), DSC, IR and viscosity measurements with respect to temperature.
    - UA copolymers
    - Casting temperatures.
    - Variables to introduce, e.g. methacrylates types and content, use of AUO blends, etc.
    - Characterisations included DSC, DMTA, IR, Tensile measurements, SEM, TEM, solvent extractions.

**Route B:**

- Glycerol
  - Crosslinked PUs
    - Selection of casting conditions.
    - Variables to introduce, e.g. polyol blends, etc.
    - Characterisations included DSC, DMTA, IR, Tensile measurements.
UA copolymers were made by free radical copolymerisation of acrylated-urethane oligomers (AUO) with monofunctional acrylate monomers (i.e. with single C=C unsaturation group), as shown in Figure 3.3

In order to achieve a better control of the reaction products in synthesis of the AUO, a two-step reaction procedure was adopted. First, isocyanate-terminated urethane prepolymer (NCO-prepolymers) were synthesised by reacting difunctional polyols with excess isocyanate. These were subsequently reacted with hydroxyl propyl methacrylate (HPMA) to produce a AUO (see Figure 3.2)

From basic urethane theory and the literature survey on radiation curable UA copolymers discussed in Chapter 2, the soft segment of UA copolymer was derived from the polyol component while the hard segment was derived from the diisocyanate, urethane linkages and acrylate components (see Figures 3.2 and 3.3). Hence, to understand the structure-property relationship of urethane acrylate copolymers, it was decided to include the synthesis variables:

a) Polyol chemical type and molecular weight (eg. to vary soft segment length).

b) Polyols or AUO blends to give specific molecular weight averages (eg. to vary soft segment length distribution).

c) Isocyanate types (eg. to influence urethane hard segment structure).

d) Methacrylate monomer types and concentrations.

e) Use of excess isocyanate i.e. varying isocyanate index.

f) Use of excess hydroxyl propyl methacrylate.

UA copolymers having two different PPG chain lengths in their soft segment components were mostly prepared by first blending AUO made from PPGs of different molecular weights before reacting with the methacrylate monomers (see Section 3.3.2). However, to check on how this method of producing might differ from
using NCO-prepolymer that was already made up of different PPG chain length, one lot of the latter was also produced and converted into its corresponding AUO before reacting with the methacrylate monomers (see Section 3.3.1 on synthesis of NCO-prepolymers).

Cast sheets of the methacrylate homopolymers, and crosslinked PU cured with glycerol were also made and used as reference materials. For crosslinked PU system, variables described in a, b, c and e were introduced to produce various crosslinked PU types.

Characterisation techniques employed to characterise the raw materials, the intermediate and the final products were conducted at various stages of the synthesis process, (see flow chart in page 69 to 70). The characterisation of the raw materials included hydroxyl measurement (OH value), molecular weight and molecular weight distribution assessment of the polyols, Karl Fischer measurement for moisture content of HPMA; melting point determination by DSC for solid materials such as 4,4'-diphenyl methane diisocyanate (MDI) and polyethylene glycol (PEG). Characterisation of the intermediate products (i.e. NCO-prepolymer and AUO) involved studies on the effect of synthesis conditions and variables on the nature of the reaction products (i.e. namely the chain extension reactions) by gel permeation chromatography (GPC) techniques, the effects of varying polyol segment length on their viscosities, and curing rate when copolymerised with methacrylate monomer to form UA copolymers. The effects of varying methacrylate monomer types and concentrations on the cure rate were also examined.

As the viscosities of the prepolymers were surprisingly observed to decrease with increasing molecular weight polyol (for the range used), the factors influencing viscosity were also assessed using differential scanning calorimeter (DSC), infra-red (IR), GPC and viscosity measurements with respect to temperature.
The effect of structural variables on UA copolymers were examined by a number of characterisation techniques. These included tensile testing, Tg measurement by DSC and dynamic mechanical thermal analyser (DMTA). Attempts were made to determine the morphology and relative compatibility of the urethane and methacrylate components of the UA copolymers, using IR, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Both DSC and DMTA were also used to assess the compatibility of the systems. The relative degree of crosslinking in selective UA copolymer were compared by measuring the percentage extractables obtained after solvent treatment.

In addition to the above, supporting experimental work was also conducted so as to achieve a better understanding and accuracy in sample preparation for final characterisation works. These are described in Sections 3.5.
3.2 Materials: Selection and Preparation

The materials used in the synthesis of urethane and urethane-acrylate polymers are listed in Table 3.1, which also provided information of suppliers, structural formulae and some general descriptions.

3.2.1 Isocyanates

Pure monomeric 4,4'-diphenyl methane diisocyanate (MDI) was used in the majority of the synthesis work. The Desmodur 44MS (ex Bayer) was the particular grade used. MDI was used for the following reasons:

a) It was received as solid flakes and therefore posed less health hazard as compared to liquid isocyanates such as toluene diisocyanate (TDI) at room temperature. However, it should be noted that at the reaction temperature used, the volatility of pure MDI could lead to health problems.

b) It has linear symmetrical structure and the two isocyanates (NCO) groups on the two aromatic rings have the same reactivities [16]. Hence, molecular development of the urethane polymer is more controlled, enabling subsequent structure-property interpretation to be conducted with greater reliability.

The MDI was divided into small portions in plastic bags and kept in 200ml containers. It was then stored at below 4 °C to prevent dimerisation. Each time MDI was required, the estimated portion of the MDI was then allowed to warm to room temperature within the closed plastic bag and container prior to being weighed to the required amount. This precaution was taken to minimise moisture contamination when MDI was being taken out from the freezer. The MDI was used in solid form without further drying. A quick check on the purity of the isocyanate was carried out using a method widely practised in the urethane industries. As recommended by the supplier of MDI, the isocyanate was heated in a test tube over a beaker of hot tap water. MDI of high purity melts to form a clear transparent liquid while a cloudy liquid indicated that substantial dimerisation has occurred. The above method of handling the stored
MDI was found to give a clear transparent liquid when the test was done on it. As recommended by the supplier, MDI was discarded once storage period exceeded six months in order to ensure 99% purity (i.e. in terms of reactivity).

Mixed toluene diisocyanate (TDI) isomers at 80:20 ratio of 2,4- and 2,6-TDI were used in selected cases in order to study the effect of isocyanate structure on UA copolymer. Isomers were used instead of pure TDI due to difficulty in obtaining sample of the latter at the time of work.

3.2.2 Polyols

Polypropylene glycols (PPG) were selected as they were already used commercially by the project's sponsor, Stirling Lloyd, in their products. These are difunctional and liquid at room temperature. Polyethylene glycols (PEG) were also selected as the alternative soft segment type. These are semi-crystalline materials and normally used in PU formulations where hydrophilicity is required.

Three different molecular weights of each polyol type were examined, i.e. 1000, 2000 and 4000. The polyols were designated codes in such that for examples, PPG 1 and PEG 2 represents PPG of molecular weight 1000 and PEG of molecular weight 2000 respectively. The same batches of polyols were used throughout the project in order to minimise batch to batch variations (eg. trace catalyst content can exert a large catalytic effect on the isocyanate-hydroxyl reaction [see Section 2.1.3.1, 16 p31]). The hydroxyl contents of the polyols were determined, as described in Section 3.6.1, so as to determine their exact molecular weights (or equivalent weights). The PEGs were found to be contaminated with trace Na OH catalyst (used for conversion of ethylene oxide to PEG) and addition of MDI to the PEGs resulted in very rapid solidification, as it was thought isocyanurate ring was formed. It was recommended that the PEGs be sent to Smiths and Newphew to be cleaned by ion exchange to remove the trace catalyst. The hydroxyl content of the ion exchanged polyols were subsequently determined by the company.
The PPGs were supplied by Shell Chemicals while the PEGs were supplied by Lancaster Chemicals.

3.2.3 Chain Extenders and Crosslinking Agents

HPMA was used to introduce terminal double bonds to the NCO-prepolymers. HPMA was selected in preference to hydroxyl ethyl methacrylate (HEMA), as it was thought that the more linear HEMA structure would produce comparatively more rigid network structures due to better packing: this would not be desirable for low temperature properties. HPMA is a hygroscopic material and had to be stored in an air-tight container over about 25% by volume of molecular sieve of size 4A types for about two weeks to reduce its moisture content to a low value before usage (i.e. \(< 0.02%\) water). The effect of storage conditions on the moisture content of the HPMA was assessed as described in Section 3.6.2. Zeolith T-powder (often used in the PU industry for drying purpose) was not chosen for drying of the ingredients, since it could not be filter out and would remain within the cured system.

Methyl methacrylate (MMA) and n-butyl methacrylate (n-BMA) were employed as reactive diluents, i.e. to reduce oligomer viscosity and to then promote copolymerisation through crosslinking reactions. MMA is cheap. Homopolymers of MMA and n-BMA have Tgs of 105 °C and 20 °C respectively [11]: hence, MMA was expected to impart the greater rigidity to the system. They were used as received for this work. All the acrylic monomers used were from ICI.

Analytical grade glycerol (functionality = 3), purchased from Fisons, was used to produce crosslinked PU from NCO-prepolymer. It was pre-dried in the small quantities required for each castings (5g was more than sufficient). Drying was carried out in vacuum oven, set at 65 °C, for 1 hour followed by cooling under vacuum to about 30 to 35 °C. The glycerol was then removed from the vacuum oven and kept in desiccator ready for use.
3.2.4 Catalyst and Initiating Systems

The catalyst dibutyl tin dilaurate (DBTL) was used mainly in the synthesis of urethane-acrylate oligomers and urethane polymers to promote isocyanate-hydroxyl (NCO-OH) reactions. DBTL is a light-yellowish liquid at room temperature and is readily miscible into the polyl.

Catalyst benzoyl peroxide (BPO) and accelerator N,N-dimethyl-p-toluidene (DMPT) were used as the room temperature initiation system to produce free radical polymerisation / crosslinking of urethane-acrylate copolymers. The above catalyst and accelerator can be purchased from Fisons.
3.3 Formulations

Formulations related to the synthesis of the various products produced in this work are given in Tables 3.2 and 3.5 (see pages 114-118). Codes assigned to these are explained in page 115.

3.3.1 Intermediate Products

The intermediate products were namely the isocyanate-terminated urethane prepolymer (NCO-prepolymers) and the acrylated-urethane oligomers (AUO). The relative amount of isocyanate to polyol reactants used in the synthesis of the various intermediates are given in Tables 3.2 and 3.3.

3.3.1.1 Synthesis of the Isocyanate Terminated Prepolymers

These were based on an NCO/OH ratio of 2:1, expressed in equivalent weights. The equivalent weight of the isocyanates were calculated from their molecular weight (see Section 2.3.1.2). Most of the formulations were based on an isocyanate index of 105, for two main reasons:

   a) to account for isocyanate losses that may have occurred through reaction with impurities or participation in minor side reactions.

   b) to account for any inaccuracy in hydroxyl (OH) measurements.

Appendix A: 1A shows sample calculation for determining the quantity of reactant required in the synthesis of NCO-prepolymers. Catalyst was not used in the synthesis of MDI-based prepolymer due to difficulty in controlling the inherently fast MDI-OH reaction. However, for synthesis using TDI, catalyst DBTL concentration of approximately 0.025% was used to accelerate the reaction.
For NCO-prepolymer based on a mixture of two PPGs of molecular weight, the relative quantities of the individual PPG needed to give the required average polyol soft segment length were added together prior to reaction with the isocyanate. “S-Prep 142” was prepared by this method. Table 3.3 shows the relative amount of PPG 1 and PPG 4 required to produce the NCO-prepolymer (i.e. “S-Prep 142”, having an average PPG soft segment of 2000). See Appendix A: 1B for sample calculation.

3.3.1.2 Synthesis of Acrylated-Urethane Oligomers

In the synthesis of AUO, the amount of HPMA required was based on the amount of unreacted NCO groups left in the NCO-prepolymers. An equal molar ratio of NCO to HPMA was used (i.e. 42g NCO : 144g HPMA). Unless specified, 1% excess HPMA was included in the calculations to compensate mainly for losses through evaporation during synthesis of the MDI-based NCO-prepolymers. DBTL concentration of approximately 0.025% of total AUO content was used to accelerate the reaction. AUO with 10% and 20% excess of HP 1 were made by adding in the additional specified excess amount of HPMA. The TDI-based NCO-prepolymer had a 2% excess HPMA added instead, to account for higher evaporation losses due to longer reaction time.

3.3.2 Urethane-acrylate Copolymers

UA copolymers were prepared by copolymerising acrylated-urethane oligomers (as listed in Table 3.2 and 3.3) with varying amount of MMA or BMA monomers as shown in Table 3.4. The amount of BMA used was based on the number of moles of MMA it has to replace in the corresponding MMA series. For example, 60g of MMA which corresponds to 0.6 moles was replaced by the equivalent moles of BMA, weighing 85.2g.

For UA copolymers based on a mixture of MMA and BMA, the above concept was adopted and variations were made with respect to 100 phr of MMA. Acrylated-
urethane oligomer based on PPG 2 was selected for this work. Table 3.5 shows the formulations used.

For UA copolymers consisting of two different polyol soft segment lengths, acrylated-urethane oligomers made from polyol of the respective molecular weights were blend in such proportions as to produce a specific desired average soft segment chain length. These were then reacted with the methacrylate monomers to produce the final UA copolymers. Table 3.3 shows the relative proportions of the specific acrylated-urethane oligomers required to produce the desired products. See Appendix A: 3 for sample calculation.

The amounts of BPO and DMPT used were based on 4 and 2 phr respectively of the total HPMA and MMA components present in the system. That is, when BMA was used, the amount of the initiating system required was still based on that needed for the corresponding equivalent moles of MMA. Table 3.4 shows the amounts of BPO and DMPT required for copolymers syntheses at various acrylate contents and AUO types. See Appendix A: 5 for sample calculation.

3.3.3 Crosslinked PUs and Methacrylate Homopolymers

Crosslinked PUs were prepared using glycerol as crosslinker at an equal NCO to OH equivalent weight ratio of 1, (see Appendix A: 4 for sample calculation). Various types of crosslinked PU synthesised included:

1. PU of varying polyol soft segment length (i.e. different PPG molecular weight).

2. PU based on a blend of two NCO-prepolymers. The relative amount of respective NCO-prepolymers used are also shown in Table 3.3.

3. PU based on polyol blends of PPG 1 and PPG 4 to give an average polyol soft segment length equivalent to that based on PPG 2. This serve the same purpose as point 2 except that the method of producing PU of two different polyol soft
segment length is different. This is to check on the effect of synthesis method on
the final products.

4. PU based on PPG 2 and at varying excess of isocyanate content (i.e. at varying
isocyanate index of 100, 105, 110 and 115).

5. PU based on PPG 2 using 80:20 mixture of 2,4- and 2,6- TDI isomers.

The above PUs were to be used as references in studying the effect of the above
variables on the PUs as compared to the UA copolymers. DBTL catalyst
concentration of 0.0003 % to 0.0004 % was used to increase cure rate so as to prevent
glycerol from phase separating out of the system and also to react with atmospheric
moisture. For TDI based NCO-prepolymer which already contained DBTL, added in
the previous stage, no additional DBTL was used when curing with glycerol.

Homopolymers of MMA and n-BMA (i.e. PMMA and PBMA respectively) were
casted at 2 and 4 phr of BPO and DMPT respectively.
3.4 Synthesis Procedures

3.4.1 NCO-prepolymers

A typical laboratory apparatus used for the synthesis process is shown in Figure 3.4. The synthesis was carried under a blanket of nitrogen. Nitrogen entering the reaction flask was dried by passing it through a test tube of dried silica gel, fitted to the inlet socket of the reaction flask. During the synthesis process, the flow rate of the nitrogen was kept to a minimum with the aid of a flow indicator attached to the outlet of the reaction flask. When vacuum was required, the flow indicator was replaced by a gas trap consisting simply of a test tube cooled by some sawdust coated ice in a thermoflask. The function of the gas trap was to prevent any toxic gases and other volatiles being released into the atmosphere during the vacuum operation. Heating was achieved by means of a temperature controlled oil bath. An anchor stirrer, fixed to a variable speed constant torque stirrer motor, was used. Unless specified, stirring speed was set at approximately 200 rpm. Standard synthesis conditions were established after some preliminarily synthesis and characterisations of NCO-prepolymers investigations using GPC, as described in Section 3.7.4. Synthesis was carried out in fume cupboard and the following procedures were followed:

a) Polyol was weighed into a dry reaction flask and vacuum dried with constant stirring, for at least 2 hours and at approximately 70 °C [16]. Normally 250g to 500g of polyols were used, depending on the size of the reaction flask.

b) At the end of the drying operation, dried nitrogen gas was flushed into the flask for a few seconds and stirring stopped.

c) The required amount of isocyanate was weighed and charged into the reaction flask. Where catalyst DBTL was used, this was added after 2 to 3 minutes of mixing.

d) The mixture was stirred again continuously under nitrogen gas and the temperature of the system was reduced to about 55 °C by lowering the temperature of the oil bath.
e) When the reaction time of the system concerned approached the estimated completion time (shown in Table 3.6), the NCO content of the prepolymer was determined by method described in ASTM D2572-80 using di-n-butylamine solution (DBA) of 0.2 N. NCO content was assumed to be based on unreacted original isocyanate and isocyanate reacted to chain ends.

f) The reaction was stopped when the NCO content of the prepolymer reached about 3% below its expected NCO content, given in Table 3.2

The synthesis temperature for PEG-based prepolymers was set at about 80 °C (PEG 4 melts at 62 °C).

The total reaction time of the various systems depended greatly on the molecular weight of the polyols and the type of isocyanate used. In order to achieve synthesis efficiency, the estimated total reaction time for MDI-based system were determined from the first trial runs of the system with the aid of an IR spectrophotometer. In these trial runs, when the OH absorbance peak of the IR spectrum (of NCO-prepolymers) has reduced significantly, the NCO content of the prepolymers was followed at 45 minutes to 1 hour intervals by the di-n-butylamine back-titration method, until it reached its expected NCO content.

The "expected NCO content" refers to the amount of unreacted NCO groups expected to remain in the prepolymers in a completed reaction, basing on the assumption that all the isocyanate was used only in reaction with the hydroxyl groups of the polyols. A sample calculation for this is given in Appendix A: 2. These values served to provide a rough indication as to when the reaction was considered completed.

However, it was observed that the NCO content of the prepolymers do not come down to a steady value as expected. Hence, a separate experiment was also carried out to look into the effect of extending the reaction time on the final UA copolymer, (see Section 3.5.6).
To maintain consistency in NCO measurements of the prepolymers in subsequent synthesis, sample sizes (of the various prepolymers) required for DBA titration were kept within a consistent range, as shown in Table 3.6.

Quantitative IR analysis was not used to follow the reaction because it was difficult (and time consuming) to obtain a good calibration and sample spectrum [to refer to reference 171 for method]. The reference peak (i.e. \(-\text{CH}_2-\) or \(-\text{O}-\)) that could be selected for the job was very strong as compared to the NH or OH peaks. Hence, control of the prepolymer coating thickness on the sodium chloride disc in order to get these peaks within the spectrums became extremely difficult. This was particularly so with the more viscous prepolymers. Similar problems have also been reported by a previous researcher [138].

3.4.2 Acrylated-urethane Oligomers

Syntheses of the AUOs were carried out immediately after the preparation of the NCO-prepolymers. The following procedures were followed:

a) The amount of dried HPMA (by storing over molecular sieves, see Section 3.2.3) required was dissolved into the NCO-prepolymer with constant stirring under nitrogen gas. The temperature of the system was held at about 50 °C to 55 °C.

b) Once a clear solution was achieved, DBTL was added immediately by means of a pastor pipette. To reduce HPMA evaporative losses through the stream of nitrogen leaving the reaction flask, the nitrogen supply was cut off and the reaction was allowed to proceed, with very slow stirring, under HPMA vapour.

c) The reaction was followed using a IR technique (see Section 3.6.6). The disappearance of NCO absorbance peak at 2270 cm\(^{-1}\) signified a complete reaction.
The total reaction for the MDI based AUO were completed within an hour while the TDI-based AUO (using PPG 2) took approximately 12 hours. This is could be due to the use of the less reactive TDI [15, 16].

3.4.3 Casting UA Copolymers and Methacrylate Homopolymers

The UA copolymers were casted using the mould shown in Figure 3.5. This was made of polyethylene terephthalate (PET) film lined with wax strips of 2 mm thickness to form a rectangular enclosure on top of it. The PET film was sprayed with "Ambersil PU", a silicone release agent, and placed on top of a glass panel which will serve to provide a flat surface for casting. Casting was carried out according to the following procedure:

a) AUO (150g) was weighed into a paper cup, covered with aluminium foil and warmed in an oven (set at 80 °C) for about 3 to 10 minutes (depending on AUO types: AUO based on lower molecular weight PPG was observed to take a longer time), to reduce its viscosity.

b) The required amount of methacrylate monomers were then added to the oligomer and the mixture was stirred to form a solution.

c) The solution was cooled to room temperature and reweighed. Any loss in methacrylate monomers (through evaporation), as reflected from the weight loss, was replaced.

d) BPO was dissolved into the solution, followed by DMPT. Care was taken not to blend BPO and DMPT together at the same time, because of explosion risk.

e) The mixture was left in the cup for a while to allow for some trapped air bubbles to rise and escape at the top. It was then poured into the mould once it started to exotherm and felt warm, (this was easily detected by holding the cup). For TDI, 0.013% DBTL concentration was used.

f) A second piece of PET sheet which has been sprayed with the release agent was then carefully placed on top of the resin, with the wax strips serving as its support.
Care was taken not to trap any bubbles while doing this and to try to push any remaining tiny surface bubbles to the side. Another glass panel was then placed on top of the PET sheet to provide a flat top coating.

g) The coating was allowed to cure and cool at room temperature before stripping it off from the mould. This took about 15 minutes.

Casting was carried out on the PET sheet instead of the glass panel, as this permitted a faster and easier removal of the cast sheets. The above technique enabled bubble free coatings with smooth surfaces and even thicknesses to be obtained. Step (f) helped to overcome oxygen inhibition which would otherwise resulted in coatings with sticky surfaces. It was found to be a more effective method in preventing oxygen inhibition than using a wax (which was normally added at 1% of the total methacrylate content, as recommended by Stirling Lloyd in their formulations).

Casting of the methacrylate homopolymers was carried out as above, except that the resin once catalysed, was poured straight into the mold, covered and left to set overnight. As the monomers was of low viscosity, there was no problems of trapped air bubbles.

### 3.4.4 Crosslinked Polyurethanes

The apparatus set up remained the same as shown in Figure 3.4. The mould used was made of aluminium sheet shaped to form a rectangular tray. Bubble free cast sheets of crosslinked PU were obtained as according to the following procedure:

a) NCO-prepolymer (300g) was weighed into a 1 litre reaction flask.

b) The required amount of vacuum dried glycerol (weighed to 4 decimal places) was added to the prepolymer.

c) The mixture was heated in an oil bath to about 50-55 °C, under nitrogen, to reduce viscosity.
d) Meanwhile, an rectangular aluminium tray (about 20 cm by 15 cm) which has been preheated in an oven (80 to 90 °C), was sprayed with the silicone release agent. Any noticeable excess of the release agent was wiped off with a tissue paper. The tray was put back into the oven to keep it hot.

e) Once the viscosity of the resin-glycercol mix was reduced (this was noticeable from stirring), about 0.0003 to 0.0004% of DBTL was added.

f) The mixture was stirred at maximum speed (i.e. approximately 350 rpm) for one minute before vacuum was applied to remove the resulting trapped nitrogen bubbles.

g) A minute after the vacuum was applied, the stirrer speed was reduced to avoid further generation of bubbles and vaporisation of any volatile unreacted components (e.g. unreacted excess isocyanate). The whole vacuum operation was kept short (about 5 minutes) for the same latter reason. When the vacuum was released, nitrogen gas was flushed into the system and stirring was stopped.

h) About 130g of the content was carefully poured into the hot tray tilted at an angle to avoid catching air bubbles. The hot tray, coupled with the low viscosity of the content (at 50 °C) enabled only trapped bubbles in the mixture to rise to the top.

i) The tray was allowed to cool slightly so as to increase the viscosity of the mixture. This would then enabled the air bubbles that had risen to the surfaces be scraped off by means of a spatula.

j) The reactants were then cured in an circulating hot air oven at 65 °C for 3 days.

The low catalyst concentration was achieved by diluting small quantities of DBTL in some PPG 4 before use. PPG 4 was selected because it gave the least number of OH groups per unit weight (than PPG 2 or PPG 1). The dilution was also prepared in such that only 1 to 2 drops (by pastor pipette) of the catalysed polyol was required to give the desired catalyst concentration. These measures were taken so as to reduce any
possibility of upsetting the stoichiometry balance of the glycerol and NCO-prepolymer mixture.

The cured PU sheets were stored in sealed polyethylene bags and in the dark at room temperature for at least 2 months before further testings.

3.5 Other Experimental Work

3.5.1 Selection of Synthesis Conditions for NCO-prepolymer synthesis

Synthesis of NCO prepolymer from PPG 4 took a long time (approximately 43 hours). Hence, in order to reduce the synthesis time, the use of DBTL catalyst was examined. The reaction products were tested on a GPC to compare uncatalysed and catalysed prepolymer, (refer to Section 3.6.4 for more details). This experiment showed a need for further GPC analysis of the MDI-based prepolymer synthesised under various conditions, so as to achieve a better understanding of the relationship between synthesis conditions and reaction products. The various synthesis conditions examined were:

a) Different reaction temperatures, i.e. 55 °C and 78 °C, in the absence of catalyst. PPG 1 was selected for this study as it was more reactive than the other longer chain polyols. Hence it was expected to be more responsive to changes in temperature. The prepolymer were then cured with glycerol to form cross-linked PU. Tensile strengths of these cross-linked PUs measured and compared.

b) At varying amount of catalyst concentrations of 0.01%, 0.001% and 0.0004%. Reaction temperature were kept at 55 °C and prep 2 was selected for this study. Such low catalyst concentration were studied due to difficulty in controlling the synthesis process when level higher than these were used.

c) At different synthesis environments: NCO-prepolymer based on PPG 4 was synthesised under two enviroments, i.e. under a blanket of nitrogen and in vacuum.
PPG 4 was selected because it has the longest reaction time and was likely to be more influenced by the synthesis environment than the other NCO-prepolymer types.

d) Effect of using excess MDI (i.e. varying iso index), HPMA, as well as the extent of reaction time on the nature of the reactions products.

### 3.5.2 Selection of Synthesis Conditions for Crosslinked Polyurethanes

In investigating the casting conditions for crosslinked PU, MDI tipped prepolymerms based on PPG 1 and PPG 2 were cured with glycerol under the following conditions:

a) At various casting temperatures. These included room temperature casting, casting at 65 °C for 72 hours, at 113 °C for first 4 hours (to set the casting) followed by conditioning of the cast sheet at 65 °C for the remaining 68 hrs. High temperature is known to promote crosslinking reaction through secondary reactions. Hence, the latter temperature was selected to assess how this would influence the final properties of the cast sheets.

b) At various DBTL catalyst concentrations of 0.0001%, 0.0002%, 0.0003% and 0.00035% (based on total prepolymer weight) for crosslinked PU based on PPG 2. Castings became impossible at concentrations higher than these, due to rapid setting. For crosslinked PU based on PPG 1, catalyst concentration of 0.00005%, 0.0001% and 0.00015% were used.

c) At different casting environments, whereby an attempted made to cure PPG 2-based crosslinked PU under vacuum, to compare it with that cured in hot air oven.

Casting conditions were then selected after due consideration given to the tensile properties obtained and the practicability of the casting conditions under which the test sheets were produced. Casting was also made with NCO-prepolymer (based on PPG 1) that was synthesised at 78 °C. This was casted at 65 °C for 3 days.
3.5.3 Effect of Casting Temperature for UA Copolymers

As mentioned in Section 3.4.3, both AUO and methacrylate monomers had to be made into solution before being cast into sheets. This was aided by heating the oligomers, so reducing their viscosities prior to mixing. In order to assess the effect of solution temperature (hence its direct influence on the casting temperature), on the products' properties, 2 lots of AUO (based on PPG 1) mixed with 80 and 100 phr of MMA were cast at solution temperature of approximately 40 °C, and conditioned for 14 days prior to tensile test.

3.5.4 Effect of Storage Time on State of Cure of UA Copolymers.

The effect of conditioning period prior to testing was assessed by carrying out tensile testings on UA copolymer based on PPG 2 at 48 hours, 2 weeks and 6 weeks after synthesis.

3.5.5 Assessments of Lot Variations in Intermediate Synthesis

The effect of batch variation on the intermediate products was assessed by casting UA copolymers (based on PPG 2) from different batches of oligomers. The tensile properties of these UA copolymers were then compared after cure and conditioning for 14 days.

3.5.6 Effect of Extent of Reaction in NCO-prepolymer Synthesis on Final UA Copolymer Properties.

As mentioned in Section 3.4.1, NCO-prepolymer synthesis continued until a specific NCO content was achieved. However, the assumption made in this NCO value provided little allowance for any MDI that may have be used in side reactions and thereby resulting in some unreacted polyols. This possibility was further enhanced by the fact that the NCO content of the prepolymers did not appear to come to a steady value despite of increasing reaction time by several hours, (indicating that the reaction
between the polyol and the MDI is probably still continuing). The end product of such reaction was a more viscous prepolymer. Hence, to study the effect of such variables on the final polymers derived from it, a batch of NCO-prepolymer based on PPG 4 was prepared under similar conditions, but the reaction was allowed to continue until the expected NCO content had reached 1.8% (i.e. reaction time was increased). This new value of NCO content took in consideration that all excess MDI (i.e. 5% since iso index is 105) was also used up in side reactions.

A GPC analysis of the prepolymer was carried out. Tensile properties of crosslinked PU and UA copolymers made from this batch were determined and compared. In addition, a comparison of these properties was made with another lot of PPG 4 based NCO-prepolymer synthesised using an exact amount of MDI. This has an actual NCO content of 1.8% (as compared to its calculated "expect NCO content" of 1.82%).

3.5.7 Synthesis of UA Copolymer at Low MMA Content

An attempt was also made to cast AUO with a low level (40 phr) of MMA but was unsuccessful as the mixture thickened without gelation.

3.6 Characterisation Methods

3.6.1 Hydroxyl Value Determination

The hydroxyl content of the polyols was measured by the acetic anhydride acetylation method as described in ASTM E222 method B, but some with slight modifications, i.e. as follows:

a) The reflux time for PEG and PPG were 2½ and 3½ hours respectively in order to ensure a complete reaction at a reflux temperature of 65 to 70 °C.

b) Titrant, (which was an aqueous solution of sodium hydroxide), concentration for PPG was adjusted to 0.1 N in order to prevent precipitation during titration.
An average of two readings were taken for each sample tested. The equivalent weights of the polyols were calculated from the hydroxyl number (OH No.) using the following formula [16]:

\[
\text{Equivalent weight} = \frac{56100}{\text{OH No.}}
\]

The molecular weight of a difunctional polyol = 2 X the equivalent weight.

3.6.2 Karl Fischer Measurement

The effect of storage conditions on the moisture content of the hygroscopic HPMA was examined by storing HPMA both in the presence and absence of molecular sieves. The moisture content of the HPMA was then determined by Karl Fischer method. For HPMA stored with molecular sieve, the efficiencies of drying at storage period of 1 day and 3 weeks were compared.

The principle of this test is as described in ASTM E203-75. Basically, this is a titration method using a modified Karl Fischer reagent (ex Fisons) against the moisture content of the sample. Anhydrous iso-propyl alcohol was used as the solvent medium for the titration. A known amount of water was also titrated against the reagent and thereafter, the amount of water corresponding to 1 ml of the reagent was determined. This was then used to calculate the moisture content of the test samples.

3.6.3 Viscosity

The viscosities, \( \eta \), of the oligomers were measured at 40 °C, 60 °C and 80 °C using a Haake Rotor visco RV2 viscometer with a cone and plate sensor system PK I, 10. A shear rate of 136 sec\(^{-1}\) was selected. Since hydrogen bonding was suspected to occur in some of the oligomers, their viscosities against temperature were determined. From these, an Arrhenius plot of \( \ln \eta \) versus \( \ln 1/T \) plot was obtained. Other characterisation techniques such as DSC, GPC, IR were also employed in assessing the factors that contribute to the high viscosity.
Viscosity measurements were also taken on the following intermediate products:

1. NCO-prepolymer based on PPG I, synthesised at 55 °C and 78 °C

2. AUO based on PPG I, with 10% and 20% excess HPMA

3. AUO based on PPG I and 4, blended in such proportion as to give an average PPG chain length of 2000. In this case, the effect of soft segment length distribution on the viscosity was observed.

3.6.4 Gel Permeation Chromatography

Gel permeation chromatography is a method used to determine the molecular weight averages and distribution of the polymers. The species are separated into molecular weight fractions based on hydrodynamic volume whereby various polymer molecules of a polymer sample were separated according to their size with the larger molecules eluting out of the separation column before the smaller molecules [139, 142]. These are monitored by a detector, usually a refractometer, as a function of the elution volume.

In a gel permeation chromatogram, a peak may represent more than a single species, if their hydrodynamic volumes are similar. In addition, most GPC calibrations are based on polystyrene standards, as the construction of a primary calibration curve for a specific groups of polymers is very difficulty (i.e. such series of well characterised, narrow molecular weight fraction of the polymer are rare). Hence, molecular weight of a polymer determined by GPC may not be its true molecular weight. An improvement to this is to obtain a universal calibration [139, 140]. Even so, there is still a possibility of error occuring in using this method [140, 141].

The syntheses of UA copolymers involved synthesis of the base resin (i.e. the intermediate product) before conversion into the final solid state polymer. Hence, it was thought useful to understand the factors that may influence the type of reaction
products from the synthesis of the NCO-prepolymers. GPC analysis of the reaction products was employed to give a rough guide to the nature of the reaction products obtained. This approach had also been adopted by Papez et al. [194] for quality control of urethane coating production. In this case, GPC was used only to provide the molecular weight distributions of the polyols, the relative molecular weight and molecular weight distribution of the NCO-prep produced under various synthesis conditions. For this purpose, the constituents of the NCO-prepolymers studied, such as MDI, HPMA, etc. were also run on the GPC individually. GPC traces of selective AUOs were also collected and compared with its corresponding NCO-prepolymers. The procedure followed was:

Prior to analysis on GPC, all samples that were thought to contain free NCO groups were rendered inactive by reaction with an excess amount of dibutylamine. This precaution was necessary to ensure that the NCO groups do not react with any hydrogen containing compounds that may be present in the column. Diluted and filtered solution of each of the samples (0.1 to 0.2% (w/v) in THF) was then injected into a 5 μm mixed gel column on a GPC (obtained from Polymer Laboratories) equipped with a refractive index detector. The column was run at room temperature (approximately 22 °C) using a flow rate of 1 ml/min of THF and pressure of less than 50 kg/cm². The GPC equipment was connected to a BBC microcomputer which subsequently analysed and reported the results based on a calibration curve prepared from a series of monodisperse polystyrene standards of molecular weights 3, 500 000, 1 750 000, 450 000, 9 000 and 1200.

### 3.6.5 Cure Rate

The cure behaviour (i.e. namely the setting rate of the free radical copolymerisation system) of selective UA copolymer systems (i.e. with varying amount of MMA and/or BMA) were assessed using a vibrating needle curometer developed in IPTME. The vibrating needle was immersed into a disposable test tube containing approximately 50 ml of the catalysed resin-monomer mixture, prepared according to Section 3.4.3 (see Figure 3.6). The amperage required to maintain the vibrating needle at a pre-set
frequency was recorded manually with respect to time at a regular intervals. These were plotted on a x-y axis to produce a curing profile. In order for the results to be compared, the depth at which the needle penetrated into the catalysed resin-monomer mixture was kept at approximately 2 cm and the recording time was started immediately after BPO and DMPT were added and mixed.

3.6.6 Infrared Spectroscopy

Infrared frequencies in the wavelength range of 1 to 50\mu m are associated with the vibration and vibrational-rotational modes of a molecule or atom. In infra red spectroscopy (IR) of polymers, the sample is irradiated with electromagnetic radiation in the infra red region of the spectrum (i.e. 2.5\mu m to 50\mu m). The molecules or group of atom will undergo transitions between the various vibrational - rotational quantum states when the energy of the wavelength corresponds to the energy differences between the two states. However, infra red absorption spectra can be observed only when there is a net dipole moment changes of a definite bond or of the molecule as a whole due to vibration. These absorptions are recorded and constitute the sample’s IR spectrum. The IR spectra are usually expressed in wave number where

\[
\text{wave number ( cm}^{-1} \text{ ) } = \frac{10000}{\lambda \text{ in } \mu m}
\]

The frequency of an IR peak can be used to identify for the presence of characteristic groups such as C=O, OH, and NH. References on spectra collections can be found in references 144-146. A list if other such literatures can also be found on reference 147. For further reading on this topic, see references 142, 147 (chapter 8, p223) and 148 (Chapter 2, p64).

In PU characterisation, the IR technique is often used to examine the degree of hydrogen bonding in the polymer and to subsequently relate it to the extent of phase separation in the polymer system. This can be carried out by noting the precise location of the NH and C=O absorption bands. An increase in hydrogen bonding is
associated with a decreased in absorbance frequency. This is also accompanied by increased absorbance intensity. However, some researchers have cast doubts on the use of NH absorption intensity for quantitative determination of hydrogen bonding [see literature survey Section 2.1.7.2].

In this project, 3 types of IR spectrometers (i.e. the grating type, Fourier transform infra red spectrometry (FTIR) and attenuated total reflectance (ATR)) were used. The differences between these lies mainly in the method by which the spectrum is collected. In the grating type and FTIR, irradiation of the sample was by the transmission mode and the spectra was collected as percent absorption or transmission (see Figure 3.7I). In ATR, the spectra was obtained from reflection of radiation from the surface of a sample (see Figure 3.7II) [147, 148]. This latter technique was used on samples where transmission mode was not possible. Samples to be analysed by this technique had to make good contact with the prism cell.

For the project, the grating type (Unicam) IR was used to follow the synthesis reaction of AUO as it was the only one available at the time. The spectra was recorded between 4000 cm⁻¹ and 600 cm⁻¹ using the normal scanning mode. The disappearance of the NCO peaks denoted completion of a reaction, (see Appendix II). Hydrogen bonding studies on AUO, UA copolymers and PU were carried out on the more accurate, newer Mattson 3000 FTIR spectrometry, fitted with an attachment for ATR analysis. The spectrum were collected at 64 scans, 4 resolutions. Spectrums enlargement (by computer) were made on frequencies associated with the C=O band.

Room temperature FTIR studies were made on AUO of varying polyol length, different polyol blends, different isocyanate structures, isocyanate index, and its corresponding UA copolymers at 60 and 100 phr of MMA. Selective PU and PMMA systems were also scanned. Thin layers of NCO-prepolymers and AUO to be analysed, were coated onto one side of the sodium chloride disc. Another sodium chloride disc was used to form a sandwich and these were mounted onto a support ready for scanning. For UA copolymer that were too stiff to give good contact with the ATR
crystals, microtomed section (i.e. 25 µm thick) were examined, (these were mainly the UA copolymers based on 100 phr of MMA and those based on PPG 1).

IR spectra of AUOs of PPG 1 and PPG 4 heated at 150 °C for about 15 minute and when they have cooled to room temperature, were also collected immediately after the treatment.

3.6.7 Differential Scanning Calorimetry (DSC)

DSC is a common method used in the thermal analysis of polymers. It records the changes in thermal response of the sample as a result of changes in its morphological behaviour, such as melting of crystallite regions in a semi-crystalline material, transition of an amorphous glassy polymer to a rubbery state, i.e. Tg (see Figure 3.8). The Tg of a material indicates the temperature at which the polymer changes from a glassy state to a flexible state or vice versa. This softening point is frequently used as an index of flexibility [149]. Materials with low temperature flexibility are noted by the presence of low glass transitions temperature.

In DSC analysis, the sample (contained in a metal pan, usually made of aluminium) and a reference (an empty pan) were placed in a cell sitting on a high conductivity disc. A cross sectional view of a standard DSC cell is as shown in Figure 3.9. Both the sample and the reference were subjected to controlled heating or cooling in a controlled atmosphere. As heat will transferred through the disk to the sample and reference pans, the resulting differential heat flow was measured by a highly sensitive area thermocouple amplified and recorded for the determination of transition temperatures, melting points, specific heats and other heat-related phenomena [150]. More sample applications of this technique can be found in references 151, 152, 196.

In this project, DSC thermograms of various selected UA copolymers were measured on a Dupont standard DSC cell 910 equipped with a thermal analysis data station, model 2000. In order to interpret the thermograms, DSC thermograms of the major
constituents of the UA copolymers, such as the corresponding polyols, MDI, intermediates products as well as the resulting PUs, PMMA and PBMA were also collected. It should be noted that most of these samples had been stored for more than 1 month. The scanning temperature range covered was from -150 °C to 200 °C depending on the sample tested and the purpose of the test. Cooling to the low temperature was achieved using liquid nitrogen into a steel jacket surrounding the cell. Heating was carried out at a rate of 10 °C/min. under a nitrogen purge. The samples sizes used were within the range of 10 mg to 15 mg. Additionally selected copolymers (i.e. those based on PPG 1 and PPG 4 at 100 phr of MMA) were conditioned at 100 °C for 1½ hours to allow for phase mixing, (since initial DSC showed maximum transition temperature at about 60 °C), followed by 40 °C for 14 hours to encourage phase separation or crystallisation, if any. For reference, PMMA was also subjected to the same conditioning. Confirmation of DSC thermograms was carried out by running analysis two to three times for each sample: in some cases, reruns were made on the same samples. The Tgs were recorded at the temperature which corresponded to the onset of the discontinuity in the heat capacity, i.e. the onset of a transition, while an endothermic peak, if present, gave the Tm value.

3.6.8 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical tests are extremely useful in studying the structure of high polymers, since their mechanical properties are dependent on glass transitions, crystallinity, crosslinking, phase separation, molecular aggregations and many other features of the molecular structure of polymer chains and the morphology of the bulk materials [153 p139 chapter 7]. Among several available techniques of carrying out these types of tests, DMTA is reported to be one of the most sensitive techniques for characterising and interpreting the mechanical behaviour of materials [153, 165].

Polymers are viscoelastic materials exhibiting elastic and viscous properties. When a sinusoidal stress loading is applied to such a material, the deformation of the elastic component (i.e. the strain) will respond exactly in phase with the applied stress while the viscous component will lag behind the applied stress by some angle, $\delta$ where $\delta <$
90° depending on the amount of internal motion occurring in the same frequency range as the imposed strain. That is, for a given material, this will vary according to the test conditions (i.e. frequency, temperature). The DMTA technique is based on the measurement of viscoelastic response of a material that has been subjected to an oscillating strain. Such measurements enable the calculation of storage modulus \( E' \), loss modulus \( E'' \) and loss tan \( \delta \) where:

\( E' \) corresponds to the elastic response and it represents the stored elastic energy in the sample.

\( E'' \) is the viscous response and it corresponds to the amount of energy dissipated as heat during the deformation of the material.

Tan \( \delta \) indicates the significance of viscous dissipation in the material (at a given test temperature and frequency) and is equal to the ratio of energy lost to energy stored per cycle. It is a direct measure of the amount of energy dissipated as heat [149].

These are related to the complex modulus, \( E^* \), of the material by the following equations:

\[
E^* = E' + iE''
\]

\[
\tan \delta = \frac{E''}{E'} \quad \text{and is dimensionless}
\]

The \( E' \) and \( E'' \) are measured as:

\[
E' = \frac{\text{amplitude of in phase stress component}}{\text{strain amplitude}}
\]

\[
E'' = \frac{\text{amplitude of out of phase stress component}}{\text{strain amplitude}}
\]

The dynamic mechanical data are usually collected either at constant frequency (or time) over a broad range of temperatures (i.e. isochronal measurement), or at constant
temperature over a range of frequencies (i.e. isothermal measurement). Generally, isochronal measurement allows most rapid characterisation of a full range of viscoelastic behaviour, while the isothermal measurement normally cannot be made over a sufficiently broad range of time or frequency to encompass the full range of viscous behaviour [154 p355]. According to reference L.E. Nielsen [153 chapter 7, p138], a low frequency (such as 1 Hz) is preferred for isochronal measurements, since secondary transitions and other structural features may be more easily detected and the data collected are more readily related to transitions measured by other techniques. A loss maxima is observed at the temperature where the frequency of a motional process in the material coincides with the imposed frequency. Increasing the imposed frequency will result in loss peak occurring at a higher temperature. Further readings on this topic and related topics can be found in references 155 to 165. References 58, 61, 62, 161 to 165, 167, 168, 192 give several case studies and applications of dynamic mechanical testing.

In this project, dynamic mechanical properties of PMMA, PBMA, the crosslinked PU series (all, except those based on crosslinked PPG 4 which was too soft and sticky to be handled) and UA copolymers (of various PPG molecular weight and combination) at 60 and 100 phr of MMA or equivalent amount of BMA, as well as those based on a mixture of MMA and BMA, were studied on a Polymer Laboratories - DMTA interfaced to a microprocessor for data analysis. This was selected in preference to Du Pont 980 dynamic mechanical analyser (DMA) because the latter has been designed to measure very small changes in damping and is therefore more sensitive to harder materials than soft materials [162]. Polymer Laboratories' DMTA, on the other hand, has been reported to be suitable for study of coatings [149]. The DMTA measuring head assembly of this equipment is shown in Figure 3.10 (refer to reference 163 for detail description). An oscillating strain was applied from a vibrating head to a rectangular test sample (2 mm x 10 mm x 4 mm) at a frequency of 1 Hz. The temperature range studied was from -110 °C to 120 °C at a heating rate of 5 °C/min. Liquid nitrogen was used as the coolant in bringing the temperature down to about -120 °C. The samples were cooled to about -60 °C before the clamps were tightened so as to avoid shape deformation. A dual cantilever clamp was used. Tightening was accomplished
using a torque driver set at 6 N/mm. Detail descriptions of the procedure are given in reference 163. The Tg (or Tg's) of the copolymer was taken as the temperature corresponding to the maxima in $E''$ or tan $\delta$ at the main relaxation [154 p195].

In order to achieve a better understanding to the microphase structure of UA copolymers, samples of HP 1 M100 and HP 4 M100 which had been conditioned at 95° C in an air circulating oven for about 2 hours, followed by slow-cooling to room temperature at an average rate of approximately 1 to 2 °C/ min., were also tested. These samples were selected as representing the extreme range of hard and soft samples at 100 phr MMA content. However, as these samples were tested at a much later date, the corresponding unconditioned samples were also tested. The test parameters were also slightly altered. A single cantilever was used as it had been subsequently recommended as one giving greater accuracy: scanning rate of 10 °C/ min. was used to reduce the test time. Additional DMTA test was also conducted on a quench cooled sample of HP 4 M100 (achieved by rapid cooling at approximately 10 °C/ min.).

3.6.9 Mechanical Properties

The tensile properties of all the polymer products synthesised were determined at room temperature (about 20 °C) on a Houndsfield tensometer, (Model H50KM), which was interfaced to a microprocessor for data analysis. UA copolymers, PMMA and PBMA were conditioned at room temperature for two weeks following casting. This conditioning time was set after some preliminary investigations into the effects of storage time on the tensile properties, (see Section 3.5.4 and Table 5.3). The crosslinked PUs were conditioned at room temperature for about 2 months, since these polymer with soft segment greater than 2000, were found to be still slightly tacky to the touch even after 2 weeks.

The test specimens were stamped out using a die cutter, according to ASTM D412, a day before the testing. Samples that were too tough to be stamped out (i.e. the HP 1
series) were softened by heating them in an oven set at 100 °C for about 45 seconds to 90 seconds. All test specimens were strained to fracture using a crosshead speed of 500 mm/min. and their extension was followed by means of a laser extensometer. This strain rate was selected initially because of the original elastomeric UA copolymers produced. This rate is also used by the sponsoring company, Stirling Lloyds. At least 5 tests were carried out for each set of samples and the medium result of these tests were presented. The following parameters were determined:

\[
\text{Tensile strength} = \frac{\text{Tensile force at break}}{\text{Cross-sectional area}} \quad (N / m^2)
\]

\[
\text{Elongation at break} = \frac{\text{Changes in gauge length, } \Delta L}{\text{Original gauge length, } L} \times 100 \quad (%)
\]

\[
\text{Modulus at 5 } \% \text{ elongation} = \frac{\text{Stress}}{\text{Strain} \text{ taken at 5 } \% \text{ elongation}} \quad (N / m^2)
\]

The tensile strength and elongation taken at the yield and break points.

3.6.10 Scanning Electron Microscopy (SEM)

SEM studies on the fracture surfaces of PMMA, PBMA, crosslinked-PUs (based on PPG 1 and PPG 2) and selective UA copolymers were carried out using Cambridge Stereoscan Mark S360 SEM. These specimens were fractured by tensile pulling at a speed of 500 mm/min. The fracture surfaces were coated with a thin film of light conducting vapourized gold within 3 hours after fracture. Basically a fine beam of electrons is scanned across the fractured surface of a specimen. X-ray photons emitted when the beam hits the specimen are collected to provide a signal necessary in producing images with relative depth of field and hence a three dimensional appearance.
SEM studies carried out on the specimens included fractured at room temperature and in liquid nitrogen. The latter is also known as "cryogenic fracture". All the specimens were fractured just prior to SEM examinations. Room temperature fractures were carried out by tensile fracture of a tensile test piece on a J-J Lloyd machine at a crosshead speed of 500 mm/min. For low temperature fracture in liquid nitrogen, to facilitate fracture, a notch was made on two parallel edges of the specimen before freezing. Fracture was then achieved by means of a pliers and the samples were then allowed to warm to room temperature before preparation for SEM scanning. Micrographs of the fractured surfaces were taken at the same degree of magnification so as to enable comparisons to be made.

3.6.11 Transmission Electron Microscopy (TEM)

TEM is another technique that has been used by several researchers to study the micromorphology of heterogeneous polymeric systems [172, 70]. Attempts were made to carry out TEM studies on UA copolymers based on PPG 1, PPG 2 and PPG 4, at 60 and 100 phr of MMA. However, these omitted after unsuccessful attempts made to stain of thin films of microtomed samples with osmium tetraoxide vapour was unsuccessful. The specimens were left in osmium tetroxide vapour for between 6 to 20 hours. However, TEM examination of these samples at time intervals did not show any sign of staining. As osmium tetroxide is known to oxidise rapidly and therefore lost its staining properties, no further attempts to stain the specimens over a longer duration were made.

3.6.12 Solvent Extraction

The percentage extracts of selected UA copolymers and crosslinked-PUs were determined to assess on their relative degree of cross-linking. The test was derived from ASTM D2765-84 method for gel content and swell ratio determination of crosslinked ethylene polymers. The percentage extract is a measure of the amount of polymer that is soluble or is not entrapped in the main gel phase, where:
Percent extract = \( \frac{\text{weight lost during extraction}}{\text{original weight of polymer}} \times 100 \text{ (\%)} \)

This method was chosen in preference to the solvent swelling method as it is more convenient and probably more accurate. In the swelling method, inaccuracy may result from solvent evaporating off during weighing of the swollen sample [142 chap 7, 169].

Toluene was selected as the solvent for this test as its solubility parameter, \( \delta \), lies between that of PMMA and PU [according to reference 197: \( \delta \) for toluene, PMMA and PU are 18.2 (MPa)^{1/2}, 18.2-26.0 (MPa)^{1/2} and 20.5 (MPa)^{1/2} respectively], and its boiling point is at about 110 °C (this is greater than the Tg for commercial PMMA which is at 105 °C). The samples were cut into pieces of about 2 x 4 mm\(^2\) to make up a total average weight of about 1.8g. All the edges of the pieces were smoothed and cleaned with sand paper. The specimens were then weighed accurately before extraction in boiling toluene for 24 hours in a fume cupboard. The extraction apparatus consists of a flat bottom flask fitted with condenser (see ASTM D2765-84). At the end of the reflux, the samples were dried in vacuum oven, set at 100 °C, for 24 hours and cooled to room temperature in a desiccator before weighing.

Antioxidant, as recommended in the ASTM test method, was not added to the extraction mixture, as it was found that this contaminated the samples and in some cases, resulted in the weight of the final dried specimen being greater than its original weight.

Swelling test was also carried out by soaking 1 mm thickness by 10 mm width by 40 mm length of the various test specimen in toluene for 24 hours at room temperature.
Figure 3.2: Synthesis of acrylated-urethane oligomer.
Note: \[\text{polyol chain from urethane component}\]

\[\text{can be another methacrylate chain or polyol chain (i.e. if reaction is with AUO)}\].

I) Formation of UA copolymers through free radical copolymerisation of acrylated-urethane oligomers with monofunctional acrylate monomers (e.g. MMA).

II) Schematic diagram of a UA copolymer network (typical of an ABCP system)

Figure 3.3: Formation of urethane-acrylate copolymers.
Figure 3.4: Typical laboratory apparatus for the preparation of NCO-prepolymers and acrylated-urethane oligomers (taken from reference 16).
Figure 3.5: Mould used for casting UA copolymers.

Figure 3.6: Apparatus set-up (a vibrating needle curometer developed by IPTME) for determination of the curing rate of UA copolymers.
I) Fourier transfer infra red (FTIR) spectroscopy

Figure 3.7: Schematic diagrams showing working principles behind FTIR and ATR (taken from references 199 and 147 respectively).

II) Attenuated total reflectance (ATR)
Figure 3.8: DSC thermogram showing typical thermal process which can occur on heating a polymer (taken from reference 199).

Figure 3.9: Schematic diagram of a DSC cell (cross section view; from brochure taken from TA Instrument).
Figure 3.10: Schematic diagram of a DMTA measuring head assembly.
### Chapter 3

#### Materials: Structural formula and molecular weight

<table>
<thead>
<tr>
<th>Producer / supplier</th>
<th>General descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isocyanates</strong></td>
<td></td>
</tr>
<tr>
<td>Pure monomeric MDI (Desmodur 44 MS)</td>
<td>Bayer</td>
</tr>
<tr>
<td>OCN-CH₂-NH₂</td>
<td>Bayer</td>
</tr>
<tr>
<td>Molecular Weight = 250</td>
<td></td>
</tr>
<tr>
<td>80:20 mixture of 2,4- and 2,6-TDI isomers</td>
<td></td>
</tr>
<tr>
<td>CH₃-NCO</td>
<td></td>
</tr>
<tr>
<td>OCN-CH₂-NCO</td>
<td></td>
</tr>
<tr>
<td>2,4-TDI 2,6-TDI</td>
<td></td>
</tr>
<tr>
<td>Molecular weight = 74</td>
<td></td>
</tr>
<tr>
<td><strong>Polyols</strong></td>
<td></td>
</tr>
<tr>
<td>1000 (for PPG 1)</td>
<td></td>
</tr>
<tr>
<td>2000 (for PPG 2)</td>
<td></td>
</tr>
<tr>
<td>4000 (for PPG 4)</td>
<td></td>
</tr>
<tr>
<td>H-[-OCH₂-CH₂]-n-OH</td>
<td></td>
</tr>
<tr>
<td>Polyethylene glycols of molecular weight:</td>
<td>Lancaster Chemicals Ltd.</td>
</tr>
<tr>
<td>1000 (for PEG 1)</td>
<td>Melting point = 45 °C</td>
</tr>
<tr>
<td>2000 (for PEG 2)</td>
<td>Melting point = 50 °C</td>
</tr>
<tr>
<td>4000 (for PEG 4)</td>
<td>Melting point = 54 °C</td>
</tr>
<tr>
<td>H-[-OCH₂-CH₂]-n-OH</td>
<td></td>
</tr>
<tr>
<td>Hydroxyl propyl methacrylate (HPMA)</td>
<td>ICI</td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
</tr>
<tr>
<td>CH₂=C-C-O-C₃H₆OH</td>
<td></td>
</tr>
<tr>
<td>Molecular weight = 144</td>
<td></td>
</tr>
<tr>
<td>Monomers</td>
<td>ICI</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>Methyl methacrylate (MMA)</td>
<td>Clear, colourless, low viscosity liquid. Boiling point = 100 °C.</td>
</tr>
</tbody>
</table>
| \[
| CH_3 |
| CH_2 = C - C - OCH_3 |
| O |
| Molecular weight = 100 |
| \[
| n-Butyl methacrylate (n-BMA) | Clear, colourless, low viscosity liquid. Boiling point = 163 °C. |
| \[
| CH_3 |
| CH_2 = C - C - OC_4 H_9 |
| O |
| Molecular weight = 142 |
| \[
| Crosslinking Agents | Fisons                                  | Molecular weight = 92 |
| Glycerol          | Clear, colourless, viscous liquid.       |
| \[
| CH_2 - CH - CH_2 |
| OH OH OH |
| Molecular weight = 92 |
| \[
| Dibutyl tin dilaurate (DBTL) | Pale yellowish liquid used as urethane catalyst. |
| \[
| (CH_3CH_2CH_2CH_2) Sn [OCO(CH_2)_{10} CH_3]_2 |
| \[
| Benzoyl peroxide (BPO) | White powder. |
| \[
| N,N-dimethyl-p-toluidene (DMPT) | Pale yellowish liquid. |
| \[
| CH_3 - N - N - (CH_3) _2 |
| Table 3.1: Raw materials details. |
### Synthesis of NCO-prepolymers

<table>
<thead>
<tr>
<th>Codes assigned to NCO-prepolymers</th>
<th>Isocyanate Index</th>
<th>Formulations: amount of reactants at NCO/OH molar ratio of 2:1 and corresponding isocyanate index</th>
<th>Expected NCO content (%)</th>
<th>Codes assigned to the AUOs:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prep 1</td>
<td>105</td>
<td>MDI 262.5 TDI 554.7</td>
<td>5.653</td>
<td>HP 1</td>
</tr>
<tr>
<td>Prep 2 Iso 100</td>
<td>100</td>
<td>MDI 262.5</td>
<td>3.385</td>
<td>HP 2 Iso 100</td>
</tr>
<tr>
<td>Prep 2 Iso 105</td>
<td>105</td>
<td>TDI 250.0</td>
<td>3.106</td>
<td>HP 2</td>
</tr>
<tr>
<td>Prep 2 ISO 110</td>
<td>110</td>
<td>TDI 275.0</td>
<td>3.660</td>
<td>HP 2 Iso 110</td>
</tr>
<tr>
<td>Prep 2 ISO 115</td>
<td>115</td>
<td>TDI 287.5</td>
<td>3.929</td>
<td>HP 2 Iso 115</td>
</tr>
<tr>
<td>S prep 2</td>
<td>105</td>
<td>TDI 720.0</td>
<td>3.385</td>
<td>SHP 2</td>
</tr>
<tr>
<td>TDI-Prep 2</td>
<td>105</td>
<td>TDI 365.4</td>
<td>3.596</td>
<td>TDI-HP 2</td>
</tr>
<tr>
<td>Prep 4</td>
<td>105</td>
<td>MDI 262.5</td>
<td>1.992</td>
<td>HP 4</td>
</tr>
</tbody>
</table>

### Synthesis of corresponding AUO

<table>
<thead>
<tr>
<th>Codes assigned to the AUOs:</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP 1</td>
</tr>
<tr>
<td>HP 2 Iso 100</td>
</tr>
<tr>
<td>HP 2</td>
</tr>
<tr>
<td>HP 2 Iso 110</td>
</tr>
<tr>
<td>HP 2 Iso 115</td>
</tr>
<tr>
<td>SHP 2</td>
</tr>
<tr>
<td>TDI-HP 2</td>
</tr>
<tr>
<td>HP 4</td>
</tr>
</tbody>
</table>

Remarks: Using 10% & 20% excess HPMA respectively.

Table 3.2: Formulations used in synthesis of intermediate products (i.e. NCO-prepolymers and acrylated-urethane oligomers).
Designation of codes

The MDI based NCO-prepolymers were assigned the code "Prep" followed by a number to indicate the molecular weight of PPG used, e.g. "Prep 1" referred to the MDI based NCO-prepolymer based on "PPG 1". Deviations from these such as, for example, variations in isocyanate types or in the isocyanate index used will also be reflected in the code. For examples, "TDI-prep 1" for TDI based NCO-prepolymer made from PPG 1 and "Prep 1 Iso 110" refers to MDI based NCO-prepolymer based on iso index of 110 and made from PPG 1.

"S-Prep 142" refers to NCO-prepolymer based on a blend of PPG 1 and PPG 4 in such proportion as to give an average PPG molecular weight of 2000 (see Section 3.3.1).

The code assignment to the AUO is "HP" followed by a number. The concept adopted in the code assigned followed that for NCO-prepolymer. For example, HP 1 refers to AUO based on PPG 1. Conversion of “S-Prep 142” to AUO is assigned code “S-HP 142”.

The codes assigned to UA copolymers consisted of two terms to indicate the AUO types and the amount of MMA used based on every hundred parts of AUO. For example, "HP2 M80" meant 80g of MMA monomers were used in every 100g of AUO. If equivalent moles of BMA is used, the code will be "HP2 B80".

The codes assigned to the crosslinked PU are simply "X-PU 1" for crosslinked PU based on PPG 1. As in other assigned codes, any deviation from the standard formulations, e.g. TDI is used instead of MDI, will be reflected in the code given where in this case, it will be "TDI-X-PU 1".
### Table 3.3: Prepolymers used in the synthesis of UA copolymers and crosslinked PUs having 2 types of soft segment length.

<table>
<thead>
<tr>
<th>Sample references</th>
<th>Weight ratio of respective components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PPG 1</td>
</tr>
<tr>
<td>I. Oligomers used in synthesis of UA copolymers:</td>
<td></td>
</tr>
<tr>
<td>S-Prep 142</td>
<td></td>
</tr>
<tr>
<td>HP 142</td>
<td></td>
</tr>
<tr>
<td>HP 143</td>
<td></td>
</tr>
<tr>
<td>HP 243</td>
<td></td>
</tr>
<tr>
<td>S-HP 142</td>
<td></td>
</tr>
</tbody>
</table>

Prepared by reacting S-Prep 142 with HPMA.

II. Synthesis of crosslinked PUs

|                    |        |        |      |        |        |        |      |      |      |
| PU 142             |        |        |      | 380.5  | 619.5  |        |      |      |      |
| PU143              |        |        |      | 171.8  | 828.2  |        |      |      |      |
| PU 243             |        |        |      |        |        | 451.5  | 548.5|      |      |
| SPU 142            |        |        |      |        |        |        |      |      |      |

Prepared by reacting S-prep 142 with glycercol.
Codes assigned to represent methacrylate content:

- M indicates MMA monomers used.
- B indicates BMA monomers used.

<table>
<thead>
<tr>
<th>Codes assigned</th>
<th>Methacrylate content (g) based on 100g of AUOs</th>
<th>* BPO content (g) required</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMA ** BMA</td>
<td>HP 1</td>
</tr>
<tr>
<td>M60 or B60</td>
<td>60 85.2</td>
<td>3.048  3.076  3.144</td>
</tr>
<tr>
<td>M70 or B70</td>
<td>70 99.4</td>
<td>3.448  3.476  3.544</td>
</tr>
<tr>
<td>M80 or B80</td>
<td>80 113.6</td>
<td>3.848  3.876  3.944</td>
</tr>
<tr>
<td>M100 or B100</td>
<td>100 142.0</td>
<td>4.648  4.676  4.744</td>
</tr>
<tr>
<td>M110 or B110</td>
<td>110 156.2</td>
<td>5.048  5.076  5.144</td>
</tr>
<tr>
<td>M120 or B120</td>
<td>120 170.4</td>
<td>5.448  5.476  5.544</td>
</tr>
</tbody>
</table>

Table 3.4: BPO/DMPT requirements for UA copolymers synthesis.

* DMPT required will be half the amount of BPO used.
** Amount of BMA required is derived from equivalent moles of MMA it has to replaced.
### UA copolymers based on MMA/BMA mix.

<table>
<thead>
<tr>
<th>UA copolymers based on MMA/BMA mix.</th>
<th>Methacrylate content (g) per 100g of AUO:</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP2 M100</td>
<td>MMA 100, BMA 0</td>
<td></td>
</tr>
<tr>
<td>HP2 (M80B20)</td>
<td>MMA 80, BMA 28.4</td>
<td>Amount of BPO and DMPT required for these castings were based on HP2 M100 system</td>
</tr>
<tr>
<td>HP2 (M60B20)</td>
<td>MMA 60, BMA 56.8</td>
<td>(i.e. BPO = 4.416g, DMPT = 2.208g, see Table 3.4.)</td>
</tr>
<tr>
<td>HP2 (M40B60)</td>
<td>MMA 40, BMA 85.2</td>
<td></td>
</tr>
<tr>
<td>HP2 B100</td>
<td>MMA 0, BMA 142.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5: Formulations for UA copolymers with varying MMA-BMA ratio.

### NCO-prepolymer types

<table>
<thead>
<tr>
<th>NCO-prepolymer types</th>
<th>Approximate sample sizes used for DBA titration (g)</th>
<th>Estimated reaction completion time (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prep 1</td>
<td>0.5</td>
<td>6 to 7</td>
</tr>
<tr>
<td>Prep 2</td>
<td>1.0</td>
<td>17</td>
</tr>
<tr>
<td>Prep 4</td>
<td>1.2</td>
<td>43 to 45</td>
</tr>
</tbody>
</table>

Table 3.6: Guide-lines for synthesis of NCO-prepolymers.
CHAPTER 4

RESULTS AND DISCUSSION

(Part 1 : Raw Materials and Intermediate Products)
4 Results and Discussion: Part I

This chapter presents results obtained from characterisation of the raw materials, the intermediate products (i.e. the NCO-prepolymers and the acrylated urethane oligomers) as well as from preliminary investigations (as described in Section 3.5.1 and 3.5.6) carried out. Discussion will be made with respect to these findings.

4.1 Results

Results will be presented in one or more of the following forms: Tables, Graphs and/or illustration in Figures.

**OH Measurement**

The hydroxyl values of polyols and their equivalent weights are shown in Table 4.1. The molecular weights of the polyols were calculated from their equivalent weights, assuming the average functionality of the polyols to be 2.

**Karl Fischer Measurement**

Moisture content of HPMA stored under various conditions are shown in Table 4.2. These show that the moisture content of HPMA can easily be reduced to below 0.05 % (i.e. an arbitrary value established by supporting company) by storing the HPMA over a dry molecular sieve for about 3 weeks at ambient temperature.

**DSC Measurement**

Transition temperatures observed from DSC analyses of MDI, polyols, selective intermediate products are listed in Table 4.3. A very low transition temperature at -65 °C was observed for the PPG polyols regardless of their molecular weights while both the MDI and PEG exhibited melting peaks above room temperature. Melting peaks of the crystalline PEG increased with increasing molecular weight. All the
intermediate products were found to exhibit single transition at temperatures dependent on the PPG soft segment length. The DSC thermograms of these can be found in Appendix B: Figure B.9.

**Viscosity Measurement**

The viscosities of NCO-prepolymers and AUOs measured at 40 °C, 60 °C, and 80 °C are given in Table 4.4. Surprisingly, the viscosities of these intermediates products were found to be lower for those based on higher PPG segment length.

An Arrhenius plot of ln η versus T⁻¹, as shown in Graph 4.1, illustrates the effect of temperature on the viscosities of the AUOs of varying PPG molecular weight. The activation energies for viscous flow of the AUOs were calculated from the gradients of the slopes. The graph shows that at high temperature (above approximately 110 °C), the relative viscosities of the AUOs are reversed, i.e. lower viscosities are predicted for AUOs based on lower PPG molecular weight.

**GPC Analysis**

Typical GPC chromatogram for PPG polyols is shown in Figure 4.1. The narrow elution peaks obtained showed that the PPG polyols have a narrow molecular weight distribution.

In Figures 4.2 to 4.9, GPC chromatograms of the intermediate products (i.e. NCO-prepolymers and AUOs) show three overlapping peaks labelled A, B, and C. The estimated molecular weights (based on PS calibration curves) of these peaks are given in Table 4.6 for NCO-prepolymers. These 3 peaks remained at the same elution volume in the corresponding AUOs. However, the intensity of peak C was observed to be much more significant in the AUOs than in the NCO-prepolymers. The effects of synthesis variables or conditions on the nature of the reaction products are illustrated in the GPC chromatograms.
Infrared Analysis

The absorbance frequencies of NH and C=O groups of selective AUO samples analysed are given in Table 4.6. Typical IR spectra of PPG polyols, NCO-tipped prepolymers, HPMA and AUOs are shown in Appendix B: Figures B.1 to B.4. Generally, the NH groups showed single absorption bands at around 3300 cm$^{-1}$ to 3316 cm$^{-1}$. AUOs based on higher PPG molecular weight has a relatively slightly lower NH absorption frequencies. Absorption band at 3500 cm$^{-1}$, attributed to the OH groups, was also present as a slight shoulder in IR spectra of all the NCO-prepolymers. This was observed to be more obvious in NCO-prepolymers based on PPG 1 (i.e. prep 1). Figure 4.13 shows an enlargement of this region. The NH absorbance frequencies of HP 4 and HP 1 that has been heated to about 140 °C prior to being scanned, was observed to have raised.

FTIR enlargements of the carbonyl region of the AUOs are shown in Figures 4.11 and 4.12. Except for HP1 and TDI-HP 2, the carbonyl peaks generally show single absorption band at 1726 cm$^{-1}$ (see Figure 4.11). The C=O absorption frequencies of HP 1 and HP 4 characterising that of a less hydrogen bonded state were recorded when these AUOs were scanned at temperature not less than 100 °C (see Table 4.6). Enlargement of C=O peaks for both heat treated and cooled specimens of HP 1 are as shown in Figure 4.12.
<table>
<thead>
<tr>
<th>Polyol Types</th>
<th>OH Values / No.</th>
<th>Equivalent weight (Eq. Wt.)</th>
<th>Molecular weight (MW)</th>
<th>Molecular weight as quoted by supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG 1</td>
<td>101.13</td>
<td>555</td>
<td>1110</td>
<td>1000</td>
</tr>
<tr>
<td>PPG 2</td>
<td>50.90</td>
<td>1102</td>
<td>2204</td>
<td>2000</td>
</tr>
<tr>
<td>PPG 4</td>
<td>27.28</td>
<td>2056</td>
<td>4112</td>
<td>4000</td>
</tr>
<tr>
<td>PEG 1</td>
<td>111.05</td>
<td>505</td>
<td>1010</td>
<td>1000</td>
</tr>
<tr>
<td>PEG 2</td>
<td>60.65</td>
<td>925</td>
<td>1850</td>
<td>2000</td>
</tr>
<tr>
<td>PEG 4</td>
<td>28.80</td>
<td>1948</td>
<td>3196</td>
<td>4000</td>
</tr>
</tbody>
</table>

Table 4.1: Hydroxyl values and equivalent weights of polyols.

<table>
<thead>
<tr>
<th>HPMA Storage Conditions</th>
<th>Percentage moisture content (by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stored in the absence of molecular sieves</td>
<td>0.130</td>
</tr>
<tr>
<td>Stored with molecular sieves for:</td>
<td></td>
</tr>
<tr>
<td>1 day</td>
<td>0.089</td>
</tr>
<tr>
<td>about 3 weeks</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Table 4.2: Moisture content of HPMA as determined by Karl Fischer method.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Glass transition temperature, T_g (°C)</th>
<th>Melting peak temperature, T_m (°C)</th>
<th>Scanning temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG 1</td>
<td>-64</td>
<td></td>
<td>-120 to 200</td>
</tr>
<tr>
<td>PPG 2</td>
<td>-64</td>
<td></td>
<td>-120 to 150</td>
</tr>
<tr>
<td>PPG 4</td>
<td>-66</td>
<td></td>
<td>-120 to 150</td>
</tr>
<tr>
<td>PEG 1</td>
<td>38</td>
<td></td>
<td>25 to 90</td>
</tr>
<tr>
<td>PEG 2</td>
<td>53</td>
<td></td>
<td>25 to 90</td>
</tr>
<tr>
<td>PEG 4</td>
<td>62</td>
<td></td>
<td>25 to 90</td>
</tr>
<tr>
<td>MDI</td>
<td>43</td>
<td></td>
<td>25 to 90</td>
</tr>
<tr>
<td>Prep 1</td>
<td>-39</td>
<td></td>
<td>-150 to 30</td>
</tr>
<tr>
<td>Prep 2</td>
<td>-54</td>
<td></td>
<td>-150 to 30</td>
</tr>
<tr>
<td>Prep 4</td>
<td>-61</td>
<td></td>
<td>-150 to 30</td>
</tr>
<tr>
<td>HP 1</td>
<td>-16</td>
<td></td>
<td>-130 to 150</td>
</tr>
<tr>
<td>HP 2</td>
<td>-39</td>
<td></td>
<td>-130 to 150</td>
</tr>
<tr>
<td>HP 4</td>
<td>-53</td>
<td></td>
<td>-130 to 150</td>
</tr>
</tbody>
</table>

Table 4.3: Transition temperatures as analysed from DSC thermograms.
### Table 4.4I: Viscosities of intermediate products (produced at various synthesis conditions) measured at 40°C, 60°C, and 80°C.

<table>
<thead>
<tr>
<th>Intermediate products</th>
<th>Variables introduced:</th>
<th>Viscosities (poise) at 136 (sec⁻¹) and temperatures at:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>40 °C</td>
</tr>
<tr>
<td>Prep 1</td>
<td>Synthesis temperature:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>55 °C</td>
<td>119.4</td>
</tr>
<tr>
<td></td>
<td>78 °C</td>
<td>179.1</td>
</tr>
<tr>
<td>S-Prep 142</td>
<td>Using polyol blends</td>
<td>59.7</td>
</tr>
<tr>
<td>TDI-Prep 2</td>
<td>Isocyanate types</td>
<td></td>
</tr>
<tr>
<td>TDI-Prep 1</td>
<td>i.e. TDI is used instead of MDI</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.6</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>94.2</td>
<td>39.6</td>
</tr>
<tr>
<td>HP 1</td>
<td>Variation in polyol soft segment length</td>
<td>&gt;scale reading</td>
</tr>
<tr>
<td></td>
<td></td>
<td>349.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>161.5</td>
</tr>
<tr>
<td>HP 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP1 10% excess HPMA</td>
<td>Using excess HPMA</td>
<td>&gt;scale reading</td>
</tr>
<tr>
<td>HP1 20% excess HPMA</td>
<td></td>
<td>&gt;scale reading</td>
</tr>
<tr>
<td>S-HP2B</td>
<td>Obtained by converting S-Prep 142 to AUO (i.e. a different method of producing AUO blends)</td>
<td>34.24</td>
</tr>
<tr>
<td>Acrylated urethane oligomers</td>
<td>Gradient of slope, E/R</td>
<td>Activation energies, E (kJ K(^{-1}) mol(^{-1}))</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>HP 1</td>
<td>5017</td>
<td>41.7</td>
</tr>
<tr>
<td>HP 2</td>
<td>5773</td>
<td>48.0</td>
</tr>
<tr>
<td>HP 4</td>
<td>7582</td>
<td>63.0</td>
</tr>
</tbody>
</table>

Table 4.4.II: Activation energies for viscous flow of the AUOs (see Graph 4.1, Appendix A.7).
<table>
<thead>
<tr>
<th>Sample references</th>
<th>Approximate elution volume (ml)</th>
<th>Corresponding estimated molecular weight (Mw)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBA</td>
<td>9.54</td>
<td>115</td>
</tr>
<tr>
<td>DBA-MDI-DBA</td>
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<tr>
<td>Peak C</td>
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<td>22387</td>
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Table 4.5: Relative molecular weight of NCO-prepolymers and their individual components as determined from GPC analysis (see Figures 4.1 to 4.9).

* based on PS calibration curve.
Table 4.6:  NH and carbonyl absorbance frequencies of various intermediate products as obtained from IR spectra.
Graph 4.1: Arrhenius plot of $\ln \eta$ versus $T^{-1}$.

- HP1: $y = -12.87 + 7582x$
- HP2: $y = -8.182 + 5773x$
- HP4: $y = -6.318 + 5017x$
Figure 4.1: GPC chromatograms of polyols.

Figure 4.2: GPC chromatograms of TDI based NCO-prepolymers.
Figure 4.3: GPC chromatograms of MDI based NCO-prepolymers.

Figure 4.4: GPC chromatograms of acrylated-urethane oligomers (AUOs).
I. Prep 2

Iso 100
(% NCO = 3.10%)

Corresponds to signal
from refractometer

1k 10k 100k

A

B

C

Figure 4.5: GPC chromatograms of NCO-prepolymers and its corresponding acrylated-urethane oligomers at varying isocyanate index.

II. HP 2

Iso 105
(% NCO = 3.35%)

Corresponds to signal
from refractometer

1k 10k 100k

A

B

C

Iso 110
(% NCO = 3.49%)

Corresponds to signal
from refractometer

1k 10k 100k

A

B

C
Figure 4.5 (cont'd)
Figure 4.6: GPC chromatograms of acrylated-urethane oligomers (AUO) with varying percentage excess of HPMA.
Figure 4.7: GPC chromatograms of NCO-prepolymers synthesised using 0.0004 % DBTL catalyst.
Figure 4.7 (cont'd)
I. % NCO = 1.96%

Figure 4.8: GPC chromatograms of NCO-prepolymers at varying extent of reaction (without using catalyst).

II. % NCO = 1.80%

Figure 4.8: GPC chromatograms of NCO-prepolymers at varying extent of reaction (without using catalyst).
After 4 hrs.
NCO content = 5.133 %

After 24 hrs.
NCO content = 4.444 %

Figure 4.9 :  GPC chromatograms of NCO-prepolymer (based on PPG 1) at synthesis temperature of 78 °C.

In vacuum

In nitrogen atmosphere

Figure 4.10 :  GPC chromatograms of NCO-prepolymers synthesised in different environment.
Figure 4.11: FTIR enlargement of carbonyl peaks of acrylated-urethane oligomers
Figure 4.12: Carbonyl absorption bands of HP 1 (AUO) scanned at various temperature.

Figure 4.13: Enlargement of NH absorption band of NCO-prepolymers (Prep 1).
4.2 Discussion

4.2.1 Synthesis of NCO-prepolymers: GPC study.

In the synthesis of PU prepolymers, all possible measures were taken to reduce possible side reactions (such as secondary reactions in urea or biuret formations), and to maintain a constant NCO/OH ratio so that the desired isocyanate tipped urethane prepolymers (i.e. MDI-PPG-MDI) could be obtained. These measures included:

I) keeping the reaction temperature low (between 55 °C to 60 °C),

II) using fresh lots of MDI, and

III) drying the reactants prior to reaction.

It is therefore logical to assume that the side reactions were kept to a minimum if not totally prevented. Theoretically, reaction product of 2 moles of MDI to 1 mole of PPG is an MDI-tipped PU prepolymers, on the condition that there is no side reactions involved. Hence, one can expect the NCO-prepolymers produced to consist mainly of the NCO end-tipped prepolymers and some unreacted MDI. However, the presence of three peaks assigned A, B and C, found in all the GPC chromatograms of the intermediate products, showed that other reaction products were also involved. Peak A is identified to be due to the excess MDI, which may or may not be in dimerised form as MDI are capable of dimerisation at room temperature. Peaks B and C are of about the same intensities and none of these peaks correspond to the elution volume of its respective PPG component. Hence, these peaks are likely to belong to the intermediate products of different length. Although it may still be possible for urea formation to occur through reaction with moisture since isocyanates are generally very reactive, it is unlikely that the GPC is able to detect small changes in the hydrodynamic volume of the polymer due to such a small change in its polymer structure. The molecular weight corresponding to peak C was found to be nearly twice that of peak B. It is believed that the reaction products probably consisted of chain extended products as well.
The reaction products that could result from the reaction between MDI and PPG are:

i) MDI-PPG-MDI

ii) MDI-PPG-MDI-PPG-MDI (i.e. from MDI-PPG-MDI + PPG-MDI)

iii) MDI-PPG-MDI-PPG (i.e. from MDI-PPG-MDI + PPG)

iv) PPG-MDI-PPG (i.e. from 2 x PPG + MDI)

v) PPG-MDI (i.e. PPG + MDI)

Assuming that the molecular weight of the individual components are additive, an estimation of the GPC molecular weight of the above products, tipped with DBA, are as shown in Table 4.7 (Note: DBA was used to react with all active MDI prior to GPC analysis, see Section 3.6.4). These were obtained by adding up the molecular weight corresponding to the elution volumes of its constituents. Comparing the molecular weights corresponding to GPC peaks B and C (see Table 4.6) with the predicted molecular weights (see Table 4.7) indicated that these 2 peaks are likely to be attributed to products (i) and (ii) for NCO-prepolymers based on PPG2 and above. For NCO-prepolymers based on PPG 1, the major reaction products are likely to be that of (ii) and (iv). This is probably due to higher reactivity of PPG 1 and hence allowing it to cap the MDI monomers readily. It is believed, however, that all the above reaction products will exist but in varying proportions. These explained for the presence of a slight OH peak in the I.R. spectra of the NCO-prepolymers (see Figure 4.13). It also explained why the NCO content of NCO-prepolymers did not stabilise at a steady value despite prolonged reaction time (see Section 3.4.1). Instead, a more viscous NCO-prepolymers was obtained when the reaction mass was allowed to continue to react. In this study, discussion will be made with respect to the major peaks, i.e. peak B and C.
Chapter 4

<table>
<thead>
<tr>
<th>Sample reference</th>
<th>Molecular weight as obtained from GPC analysis</th>
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<tr>
<td>DBA-MDI-DBA</td>
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</tr>
<tr>
<td>DBA</td>
<td>115</td>
</tr>
<tr>
<td>PPG 1</td>
<td>1778</td>
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<tr>
<td>PPG 2</td>
<td>3631</td>
</tr>
<tr>
<td>PPG 4</td>
<td>9333</td>
</tr>
</tbody>
</table>

Predicted GPC molecular weight for MDI is \((955 - 2 \times 115) = 725\)

<table>
<thead>
<tr>
<th>Predicted GPC molecular weight for NCO prepolymers based on:</th>
<th>PPG 1</th>
<th>PPG 2</th>
<th>PPG 4</th>
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<td>(i) DBA-MDI-PPG-MDI-DBA</td>
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<td>5311</td>
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<td>(ii) DBA-MDI-PPG-MDI-PPG MDI-DBA</td>
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<td>(iii) DBA-MDI-PPG-MDI-PPG</td>
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<td>20231</td>
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<td>(iv) PPG-MDI-PPG</td>
<td>4281</td>
<td>7987</td>
<td>19391</td>
</tr>
<tr>
<td>(v) PPG-MDI-DBA</td>
<td>2618</td>
<td>4471</td>
<td>10173</td>
</tr>
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</table>

Table 4.7: Molecular weight of the intermediate product as estimated from addition of its individual constituent’s molecular weight.

Although it is not accurate to relate the intensities of the various peaks to the exact ratio of the different components present within a system, (since each of these components may have different refractive indexes, especially in the case of MDI as compared to the prepolymers), the two nearly equally intense peaks have more or less indicated the significance of the chain extended products. It was observed, from the significance of peak C as compared to peak B in the various system studied, that the chain extended products were more significant in NCO-prepolymers based on PPG of lower molecular weight (e.g. as in Prep 1 as compared to Prep 4, see Figure 4.3). This implied that in a system, reaction preferences for lower molecular weight species (i.e. for PPG-MDI formed to react with MDI) became less significant when the molecular weight of the chain extended reaction products is high, as in the case of Prep 4. In Prep 1, the molecular weight of the chain extended reaction products was probably not
high enough (and therefore is still of comparable reactivity as the other reactants present) to cause a reaction preference for the PPG-MDI species to react with the low molecular weight MDI or PPG instead of with MDI-PPG-MDI.

From the above GPC studies, it is surprising to find that even at such low synthesis temperature and in the presence of excess MDI, chain extension is still taking place. In attempts to gain some understanding of the influence of synthesis conditions on this chain extension reaction and hopefully, to find ways of minimising it, a series of PU prepolymeres were made under different synthesis conditions. GPC results with respect to these will be discussed in the next section.

4.2.2 Effect of Synthesis Variables on Molecular Structure of the Intermediates.

Initially, it was thought that the chain extension reaction has occurred probably because of MDI shortage as a result of dimerisation. This could probably happened, especially when long reaction time was involved. For this reason, the catalyst DBTL was used in an attempt to promote the NCO-OH reaction as well as to reduce the reaction time required (see Section 3.5.1). However, GPC chromatograms of these intermediates did not show a reduction in peak C (see Figures 4.7I to 4.7III). Instead, the increasing peak height of peak C in all three different PPG molecular weight NCO-prepolymers showed that the use of catalyst had, instead, encouraged the chain extension reaction. The reaction had also proved difficult to control even with catalyst concentration being as low as 0.001%. The reaction mass became extremely sensitive towards atmospheric moisture, turning translucent white upon short exposure (less than 5 minutes) to the atmosphere. In order to keep the reaction within manageable range for this study, catalyst concentration of as low as 0.0004% was used. Nevertheless, the reaction took 2 hours to complete.

The above experiment showed that it was not feasible to use catalyst for syntheses of the MDI based NCO-Prepolymers. As mentioned in Section 4.3.1, in an uncatalysed system, the NCO content continued to decrease passed its expected value with time,
instead of slowing down to a stable value. In the catalysed system, the NCO groups, having becoming extremely sensitive now to both moisture and polyols were observed to continue to decrease even more rapidly. This made it difficult to obtain an accurate assessment of the NCO content of the NCO-prepolymers, particularly when the NCO measurements method required at least 1/2 hour to accomplish. GPC chromatograms of these over-reacted NCO-prepolymers (see Figure 4.7) showed increased chain extended products, with NCO content reduced to lower than its expected NCO values in less than 2 hours. A much slower reaction was seen when MDI was replaced by TDI. At catalyst concentration of 0.01%, the reaction for TDI took about 24 hours to complete. This is thought to be most likely related to the reactivities of the NCO groups [16].

An alternative to reducing the reaction time is to increase the synthesis temperature. In the study on effect of synthesis temperature on the NCO-prepolymer (Prep1), GPC chromatographs showed that using higher reaction temperature also resulted in a more significant peak C, i.e. the chain extended products (in Figure 4.9). Here again, it was observed that continued reaction only resulted in increased chain extended products.

From the above studies, it can therefore be concluded that any means to increase the reactivities of the reactants will promote the chain extension reaction. This is probably because in such situation, the reactivities of all the species in the system are raised. Hence, reaction preference arising from the inherently more reactive, lower molecular species no longer dominate the reactions. It explained for the increased significance in peak C in the corresponding AUOs as catalyst were used in these synthesis (see Figure 4.4).

In an attempt to control the amount of chain extended products, excess MDI and HPMA were used. However, it was found that although the use of excess MDI and HPMA may reduce the amount of chain extended products, the percentage used may have to be large in order to be effective (see Figures 4.5 and 4.6). Hence, this is not an
effective way of controlling the chain extended products. Figure 4.7 IV illustrated the
effect of using an isocyanate index of 125 for Prep 4 in a catalysed system. It showed
that despite having used a large amount of excess isocyanate, the chain extended
products still grew. The continued fall in NCO content at prolong reaction time
indicated the presence of OH groups available for reaction with MDI.

In order to assess on a suitable synthesis environment, GPC chromatograms of NCO-
prepolymer synthesised under vacuum and under a blanket of nitrogen were obtained
(see Figure 4.10). These showed a relatively lower MDI content for prepolymer
synthesised under vacuum (a lower MDI peak height was noted). This could be due to
loss of volatile MDI monomers under vacuum suction. Hence, to avoid any loss of
volatile component during synthesis process, (specially for synthesis that required long
time) and for safety reason, all intermediate products synthesis were carried out under
a blanket of nitrogen.

4.2.3 Hydrogen Bonding : IR Study

In IR study on AUOs, C=O absorption peaks were found to occur mainly at
1725 cm\(^{-1}\), except for HP 1 and TDI based AUO (see Figure 4.11). Researchers
working on thermoplastic polyurethanes (TPUs) [78, 80] have reported that carbonyl
band occurring in the range 1730 cm\(^{-1}\) to -1740 cm\(^{-1}\) is due to free C=O groups (i.e.
C=O in a non-hydrogen bonded state), whereas that between 1700 to 1725 cm\(^{-1}\) is
caused by hydrogen bonded C=O. Hence, IR study has proved the existence of
hydrogen bonding in the intermediate products.

It had also been reported that the exact absorption frequency of the C=O (or NH)
groups is dependent on the average hydrogen bond strength of the system, while the
breadth of the absorption band reflects the presence of hydrogen bonding of various
strength. In the IR Spectroscopic Atlas of PU Systems [198], variation in absorption
frequencies of hydrogen bonded NH and C=O groups in different PU systems are
indicated. Researchers studying hydrogen bonding in TPUs have found different
orders of hydrogen bonding, dependent on the level of molecular order in the system. It is affected by factors such as temperature, chain packing and conformation, etc. [84, 68, 83, 86]. Generally, the C=O absorption frequencies in TPU s are reported to be lower than 1725 cm\(^{-1}\). This indicated that the AUOs synthesised in this work are likely to have a lower hydrogen bond strength than the TPU s in general. This could be due to a lack of hard segment aggregation in the AUOs. Single transitions seen in DSC thermograms of the AUOs have also indicated a one-phase system. In TPU s, aggregation of the hard segments, (which are made up of a series of NH and C=O groups), will enable more intensive hydrogen bonding between the chains to occur.

In HP 1, the carbonyl absorption band was found to consist of overlapping peaks. The presence of this broad and split C=O band into peaks at 1725 cm\(^{-1}\) and 1713 cm\(^{-1}\) indicated the presence of at least two different levels or types of hydrogen bonding, with 1713 cm\(^{-1}\) corresponding to a stronger hydrogen bond strength. This could be due to:

I. relatively more NH and C=O groups available in HP 1, for more intensive hydrogen bonding.

II. shorter PPG chains, thereby allowing closer chain interactions.

Shoulder peak at 1736 cm\(^{-1}\) was also present (Note: this was not found in HP 2 and HP 4). This is probably due to:

I. the bulkiness of HPMA / MDI structures interfering with chain alignment.
   In allowing for closer chain interactions, (that were responsible for C=O absorption at 1713 cm\(^{-1}\)), some other C=O groups might have been 'forced' out of the chain alignment, resulting in 'free' C=O peak at 1736 cm\(^{-1}\).

II increased presence of C=O groups.

Introducing HPMA component will increase C=O groups to NH groups ratio (Note: C=O groups also come from the ester groups). However, not all of these
C=O groups will participate in hydrogen bonding. This will be more significant in AUOs based on PPGs of lower molecular weight, for example, such as in HP 1.

It was found that with AUOs of higher molecular weight, the C=O peaks became narrower, showing lesser variation in the hydrogen bonding strength. This could be due to increased chain flexibility as the AUO's molecular weight increased, thereby allowing better chain alignment and fitting. The slight decrease in NH absorption frequency for AUOs of higher molecular weight reflected this. In fact, the NH absorption frequency for the HP 4 oligomers, at 3300 cm⁻¹, was found to be very close to that associated with hydrogen bonding between -NH groups and the ether oxygen, at 3295 cm⁻¹ [83]. This indicated the possibility that at higher AUO molecular weight, there were more NH to ether group interactions. Tanaka et al. [90] conducted a study on this aspect and reported that the presence of abundant ether groups will encourage hydrogen bonding between NH and ether groups. It is believed that the very slight shoulder observed at about 1736 cm⁻¹ was attributed to increased free C=O groups resulting from this NH to ether groups interactions.

In HP1 that has been heated to 140 °C, only a single C=O peak was observed at 1725 cm⁻¹. Again, this could be due to increase in chain mobility, thereby allowing for a better and flexible chain fitting. The lack of C=O absorption frequencies at 1736 cm⁻¹ and 1713 cm⁻¹ in the cooled sample showed that the ‘closer’ chain alignment, (that result in more intense level of hydrogen bonding) was time-dependent. For HP1 produced from using excess amount of HPMA, the observed broad absorption band (having peak at 1725 cm⁻¹) indicated that introducing excess amount of HPMA had interrupted the chain alignment and destroyed this higher ‘level’ of hydrogen bonding. This broad absorption band was believed to encompass absorption frequency caused by a corresponding increased amount of C=O in the unbonded state. The very slight shoulder at around 1713 cm⁻¹ could be due to the ‘extra’ OH groups, generated from the excess unreacted HPMA, participating in hydrogen bonding with the C=O or -O- groups.
FTIR enlargement of the C=O peaks of HP 2 at isocyanate index 115 (see Figure 4.11) revealed near identical C=O absorption band as that at isocyanate index of 105. However, the NH absorption frequency was slightly decreased. This could be due to:

I. the use of excess MDI may have influence the level of hydrogen bond strength in the system,

II. more NH groups available for the NH/ether interactions.

For TDI-HP 2, C=O absorption at 1736 cm⁻¹ was believed to be due to 2,4 TDI structure reducing the chain symmetry. This also explained the slightly lower NH absorption frequency, if it resulted in more NH/ether interactions. Another contributing factor could be due to the increased amount of free C=O groups available in the system as a result of adding excess HPMA (approximately 10 % to 12 %) during synthesis of TDI-based AUO (see Section 3.3.1).

4.2.4 Factors Influencing the Viscosity of the Intermediates

In a coating formulation, the viscosity of the base resin is important as it has a major influence on the application technique. Generally, for a low molecular weight polymer, the viscosity of the polymer increases as its molecular weight is increased [173]. However, in this work, the viscosities of the base resins (i.e. the NCO-prepolymers and the AUOs) were found to be higher when these were made from lower molecular weight PPG. At first, it was suspected that the higher reactivity of these lower molecular weight PPG might have resulted in more chain extended products. These products may consist of a few PPG units in an AUO chain. This resultant increase in molecular weight and urethane groups may be responsible for the increased viscosity. However, earlier GPC analysis work had shown that majority of the chain extended products had molecular weight nearly twice that of the ideal products, regardless of the molecular weight of PPG used. Besides, the molecular weight of the chain extended products of, for example, HP 1 (or Prep 1), was observed to be still lower than, for example, HP2 (or Prep 2). Significant amount of chain extended products was also
found in the intermediates based on higher PPGs molecular weight. Hence, it appeared that other factors were also responsible for the higher viscosities at room temperature.

**Chain-end effect**

As can be seen from Table 4.41, the AUOs were observed to have much higher viscosities than the corresponding NCO-prepolymers. Although the viscosities of the PPGs were not measured, the increased viscosities observed when NCO-prepolymers were converted to AUOs were obviously much more than when PPGs were reacted to form NCO-prepolymers. This could probably be due to HPMA groups being able to create greater chain stiffness in the polyol chains than MDI.

It is deduced that the higher HPMA to PPG weight ratio in the intermediates based on lower molecular weight PPGs may be responsible for the higher viscosity than those based on higher PPG molecular weight, as a result of increased chain restrictions. Greater increase in viscosities (measured at 60 °C) seen in HP 1 as compared to S-HP 2, upon conversion from its corresponding NCO-prepolymers, supported this analysis. The restriction of PPG chain mobility by the urethane and the HPMA groups was also reflected in an increased in Tg values after conversion into its corresponding intermediate products (see Table 4.3). Tgs of the PPGs were at about -65 °C regardless of their molecular weights. Upon conversion into intermediates products, higher Tg values were observed with intermediates based on PPGs of lower molecular weight. This showed that the chain-end effects produced in PPG chains of lower molecular weight were greater.

**Effect of hydrogen bonding**

It is believed that the viscosities of the intermediate products are also influenced by the amount of hydrogen bonding existing in the system. Room temperature IR studies on AUOs have shown that the absorption frequencies of both NH and C=O groups belonged to that of a hydrogen bonded state. When IR scanning was carried out on
AUOs (i.e. HP 4 and HP 1) that were heated to about 140 °C, the increase in NH absorbance frequencies illustrated a reduction in the hydrogen bond strength of the heated AUO. This showed that at room temperature, the viscosities of these resins were strongly influenced by the hydrogen bonding forces present in the system. In this case, it is the hydrogen bonding between the NH groups and the C=O / –O– groups. The higher percentage of these groups present in resins of lower PPG molecular weight will naturally contribute to give more hydrogen bonding forces in the system. This resulted in greater chain restrictions, and hence higher viscosities, as compared to those based on higher PPG molecular weight, particularly so at lower temperature. An Arrhenius plot of ln \( \eta \) versus temperature for the AUOs has supported this. From Graph 4.1, the viscosities of the resins at above 100 °C were predicted to be in the order HP 4 > HP 2 > HP 1. Detailed discussion on the IR studies will be given in Section 4.3.4.

**Effect of synthesis temperature**

The viscosities of the intermediate products were observed to be influenced by the synthesis temperature and the percentage of excess HPMA used (see Table 4.4). GPC studies showed that increased synthesis temperature encouraged chain extension. This has probably accounted for the increased viscosity. GPC has also indicated that the use of a large excess of HPMA can reduce the amount of chain extended products, while IR studies showed a reduction in hydrogen bonding strength within such a system (see Figure 4.11). These could have been responsible for the decrease in viscosity observed when excess amount of HPMA was used. The excess HPMA, if unreacted, can also help to lubricate and dilute the AUOs.
CHAPTER 5

RESULTS AND DISCUSSION

(Part 2 : Final Products)
5 Results and Discussion: Part II

In this chapter, results obtained from the characterisation and mechanical testing of the final products, i.e. UA copolymers, crosslinked PUs and the methacrylate homopolymers, are presented. Discussion is made with respect to these results on the structure - property relationships and morphologies of the UA copolymers. Findings obtained from tests that have been carried out on crosslinked PU and UA copolymer cast sheets in determining suitable casting conditions for these polymers, are also included.

5.1 Results

The various test results are presented as tables, graphs and/or figures.

Curing Rate of UA copolymers

The curing curves obtained for the various UA copolymer types are shown in Graphs 5.1 to 5.4. Graph 5.1 shows the effect of using varying PPG molecular weight and MMA content on the curing curves while Graphs 5.2 and 5.3 show the effect of varying isocyanate structure and methacrylate types respectively. The effect of varying BMA content on BMA based UA copolymers is shown in Graph 5.4.

Solvent Extraction

Percentage extracts obtainable from the various UA copolymers tested, are shown in Table 5.1. Solvent extraction tests carried out on crosslinked PUs were not very successful as the swollen samples resembled very weak and sticky gels that disintegrated readily. Their percentage extracts are thus not known, but extensive swelling of the polymers had suggested a very low degree of crosslinking.

Selective UA copolymers had also been subjected to swelling tests. No significant variation in the relative degree of swelling was observed. The swollen samples were
estimated to be 1.5 times bigger than their original forms. Dimensions of the swollen samples were not taken as these broke easily (usually at the edge) when handled. This could be due to stress induced in the sample during sample preparation (i.e. at the cutting stage).

**IR Analysis**

The carbonyl and NH absorbance frequencies of UA copolymers, crosslinked PU, and PMMA are listed in Table 5.2. NH absorbance frequencies of the MMA based UA copolymers are observed to occur between 3352 cm\(^{-1}\) to 3358 cm\(^{-1}\). Typical IR spectra of UA copolymers and PMMA are shown in Figures B.6 to B.7 (in Appendix B). Figures 5.1 and 5.2 show typical C=O absorption bands observed with the MMA based UA copolymers. These consist of at least 2 overlapping peaks, at 1726 cm\(^{-1}\) and 1736 cm\(^{-1}\). In Figure 5.4, similar carbonyl absorption band was also seen with the PMMA.

Typical carbonyl peaks for BMA based UA copolymers and crosslinked PUs also show overlapping of peaks at 1726 cm\(^{-1}\) and 1712 cm\(^{-1}\). These are shown in Figures 5.3 and 5.5 respectively.

**Mechanical Properties**

Tensile properties of UA copolymers and crosslinked PUs produced during preliminary investigations (e.g. different synthesis and casting temperature, see Section 3.5) are shown in Tables 5.3 and 5.4 respectively. The influence of compositional variables (namely PPG soft segment length, polyol blends, methacrylate types and content, isocyanate type, and amount of excess HPMA and MDI) on the mechanical properties of the copolymers are illustrated in Graphs 5.5 to 5.12. The tensile strength, yield strength, elongation at yield and at break, modulus at 5% elongation of these various copolymers types are given in Tables 5.5 to 5.8. Tensile curves typical of UA copolymers at a PPG molecular weights of 1000, 2000, and 4000 (i.e. from using AUOs: HP 1, HP 2 and HP 4) are shown in Figures 5.6 to 5.10. These show the UA
copolymers to be capable of undergoing strain hardening. Unlike the MMA based copolymers, tensile curves of BMA based UA copolymers do not show significant yield strength (see Figure 5.9).

The tensile properties of the reference materials (i.e. crosslinked PUs, PMMA, PBMA) are also shown in Table 5.8. Tensile curves typical of PMMA, PBMA and crosslinked PUs at an average polyol molecular weight of 1000, 2000 and 3000 are shown in Figures 5.11 and 5.12.

**Differential Scanning Calorimetry (DSC)**

Typical DSC thermograms (for both conditioned and unconditioned samples) of the MMA based UA copolymers are shown in Figures 5.13 to 5.16 while those of the BMA based UA copolymers are shown in Figures 5.20 and 5.21. More DSC thermograms of selective UA copolymers, for examples, at various isocyanate index, MMA content, etc. can be found in Figure B.10 (in appendix B). These are not presented here as they do not provide much further information. Generally, several minor transitions are seen in these thermograms. These are as summarised in Table 5.9. Typical DSC thermograms of the crosslinked PUs, PMMA and PBMA are shown in Figures 5.17, 5.18 and 5.19 respectively. These show single transitions as listed in Table 5.9.

All the samples tested did not show any signs of degradation (eg. becoming yellowish-brown) after the tests.

**Dynamic Mechanical Thermal Analysis (DMTA)**

The tan δ plots of the crosslinked PUs and the acrylic homopolymers are shown in Figures 5.22 and 5.23 respectively, while Figures 5.24 to 5.33 show typical tan δ and loss modulus, E", curves for UA copolymers produced from different compositional variables. The tan δ and the loss modulus peak temperatures of the various samples
tested are listed in Table 5.10. This includes values obtained for the conditioned samples of HP 1 M100 and HP 4 M100 (see Section 3.6.8). Typical storage modulus, $E'$, curves of the UA copolymers are shown in Figures B.11 to B.12 (in Appendix B).

Figure 5.32 shows the progressive change in the symmetries of the tan $\delta$ curves and reduction in the tan $\delta$ peak temperatures of MMA/BMA-based UA copolymers, at a PPG molecular weight of 2000 (i.e. HP 2 M100), as the MMA to BMA molar ratio was decreased.

Electron Microscopy (Scanning Electron microscopy)

As mentioned in Section 3.6.11, due to unsuccessful attempts in staining the samples, no TEM micrographs were taken.

SEM micrographs of UA copolymers and the various reference materials, fractured at room temperature, are shown in Figures 5.34 to 5.38. Samples that were fractured at sub-ambient temperature are shown in Figures 5.39 to 5.41. The micrographs were taken at same degree of magnification for each set of study so as to allow direct comparison to be made. However, that of UA copolymers based on HP 4, fractured at room temperature, was taken at a lower degree of magnification due to relatively much lesser cracks found.
<table>
<thead>
<tr>
<th>UA copolymer based on AUOs:</th>
<th>Percentage extracts at MMA content of:</th>
<th>60 phr</th>
<th>80 phr</th>
<th>100 phr</th>
<th>120 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP 1</td>
<td></td>
<td>2.84</td>
<td>2.62</td>
<td>2.06</td>
<td>0.11</td>
</tr>
<tr>
<td>HP 2</td>
<td></td>
<td>4.81</td>
<td>4.36</td>
<td>4.42</td>
<td>5.08</td>
</tr>
<tr>
<td>HP 2 Iso 115</td>
<td></td>
<td>3.82</td>
<td>3.63</td>
<td>5.23</td>
<td>2.99</td>
</tr>
<tr>
<td>HP 142</td>
<td></td>
<td>6.52</td>
<td>5.64</td>
<td>5.73</td>
<td>5.07</td>
</tr>
<tr>
<td>S-HP 142</td>
<td></td>
<td>4.93</td>
<td>4.46</td>
<td>4.64</td>
<td>3.81</td>
</tr>
<tr>
<td>TDI-HP 2</td>
<td></td>
<td>3.97</td>
<td>2.48</td>
<td>2.32</td>
<td>3.68</td>
</tr>
<tr>
<td>HP 143</td>
<td></td>
<td>6.82</td>
<td>5.90</td>
<td>5.82</td>
<td>5.23</td>
</tr>
<tr>
<td>HP 243</td>
<td></td>
<td>5.12</td>
<td>4.76</td>
<td>3.08</td>
<td>2.05</td>
</tr>
<tr>
<td>HP 4</td>
<td></td>
<td>8.04</td>
<td>7.38</td>
<td>6.91</td>
<td>-----</td>
</tr>
</tbody>
</table>

Table 5.1: Percentage extract obtained from MMA based urethane-acrylate copolymers.
<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>NH</th>
<th>C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP1 B60 and HP2 B60</td>
<td>not recorded</td>
<td>1726, 1712 (shoulder)</td>
</tr>
<tr>
<td>HP1 M60 and HP1 M120</td>
<td>3352-3354</td>
<td>1726, 1736 (shoulder)</td>
</tr>
<tr>
<td>HP2 M120 Iso 105</td>
<td>3358</td>
<td>1726, 1736 (shoulder)</td>
</tr>
<tr>
<td>HP2 M120 Iso 115</td>
<td>3352</td>
<td>not recorded</td>
</tr>
<tr>
<td>HP4 M60 and HP4 M120</td>
<td>3358</td>
<td>1726, 1736 (band split into two)</td>
</tr>
<tr>
<td>X-PU 1</td>
<td>3304</td>
<td>1712 (shoulder), 1726</td>
</tr>
<tr>
<td>X-PU 2</td>
<td>3304</td>
<td>1712 (shoulder), 1726</td>
</tr>
<tr>
<td>X-PU 142</td>
<td>3304</td>
<td>1712 (shoulder), 1726</td>
</tr>
<tr>
<td>PMMA</td>
<td></td>
<td>1726, 1736 (stronger)</td>
</tr>
</tbody>
</table>

Table 5.2: NH and carbonyl absorbance frequencies of various intermediate products as obtained from IR spectra (see Figures 5.1 to 5.5).
<table>
<thead>
<tr>
<th>Variables</th>
<th>Samples</th>
<th>Tensile properties</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Casting temperature :</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) Ref. : Room temperature</td>
<td>HP 1 M80</td>
<td>30.38</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>( = 25 °C)</td>
<td>HP 1 M100</td>
<td>29.97</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>b) at approximately 40 °C</td>
<td>HP 1 M80</td>
<td>27.58</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 1 M100</td>
<td>21.84</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td><strong>Storage / conditioning period :</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) 48 hrs.</td>
<td>HP 2 M60</td>
<td>15.72</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M70</td>
<td>17.46</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M80</td>
<td>18.08</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M90</td>
<td>19.99</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M100</td>
<td>21.49</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M110</td>
<td>21.25</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M120</td>
<td>21.86</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>b) 2 weeks</td>
<td>Refer to Table 5.4</td>
<td>Refer to Table 5.4</td>
<td>Refer to Table 5.4</td>
<td>Refer to Table 5.4</td>
</tr>
<tr>
<td>c) 6 weeks</td>
<td>HP 2 M60</td>
<td>15.58</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M70</td>
<td>17.44</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M80</td>
<td>18.36</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M90</td>
<td>19.48</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M100</td>
<td>21.36</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M110</td>
<td>20.21</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 2 M120</td>
<td>20.54</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td><strong>Over reaction</strong></td>
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<td></td>
<td></td>
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<tr>
<td>(of NCO-prepolymers) :</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prep 4 at isocyanate index of 105.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCO content = 1.8%</td>
<td>HP 4 M60</td>
<td>10.67</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 4 M80</td>
<td>12.14</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 4 M100</td>
<td>14.50</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HP 4 M120</td>
<td>16.42</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td><strong>Lot to lot variations :</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCO = 3.37 %</td>
<td>HP 2 M100</td>
<td>21.03</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>NCO = 3.33 %</td>
<td>HP 2 M100</td>
<td>20.68</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>NCO = 3.30 %</td>
<td>HP 2 M100</td>
<td>20.48</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>NCO = 3.22 %</td>
<td>HP 2 M100</td>
<td>21.56</td>
<td>180</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3: Preliminary investigations on synthesis and casting conditions for urethane-acrylate copolymers: tensile properties
<table>
<thead>
<tr>
<th>Variations in:</th>
<th>Curing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Room temperature (= 25°C)</td>
</tr>
<tr>
<td></td>
<td>50°C (48 hrs.)</td>
</tr>
<tr>
<td></td>
<td>65°C (72 hrs.)</td>
</tr>
<tr>
<td></td>
<td>80°C (48 hrs.)</td>
</tr>
<tr>
<td></td>
<td>115°C (4 hrs.)</td>
</tr>
<tr>
<td></td>
<td>65°C (68 hrs.)</td>
</tr>
<tr>
<td></td>
<td>115°C (4 hrs.)</td>
</tr>
<tr>
<td>Section A:</td>
<td></td>
</tr>
<tr>
<td>Catalyst Concentrations</td>
<td></td>
</tr>
<tr>
<td>X-PU</td>
<td></td>
</tr>
<tr>
<td>0.00005</td>
<td></td>
</tr>
<tr>
<td>0.00010</td>
<td></td>
</tr>
<tr>
<td>0.00015</td>
<td></td>
</tr>
<tr>
<td>X-PU</td>
<td></td>
</tr>
<tr>
<td>0.00010</td>
<td></td>
</tr>
<tr>
<td>0.00020</td>
<td></td>
</tr>
<tr>
<td>0.00030</td>
<td></td>
</tr>
<tr>
<td>Section B:</td>
<td></td>
</tr>
<tr>
<td>Casting Temperature (DBTL = 0.00035%)</td>
<td></td>
</tr>
<tr>
<td>X-PU 1</td>
<td></td>
</tr>
<tr>
<td>X-PU 2</td>
<td></td>
</tr>
<tr>
<td>Section C:</td>
<td></td>
</tr>
<tr>
<td>NCO-prepolymer Synthesis Temperature (Prep 1)</td>
<td></td>
</tr>
<tr>
<td>temperature = 55°C</td>
<td></td>
</tr>
<tr>
<td>temperature = 78°C</td>
<td></td>
</tr>
</tbody>
</table>

Note: T refers to tensile strength (MPa). E refers to elongation at break (%).

Table 5.4: Preliminary experiments - tensile properties of crosslinked polyurethanes.
### Table 5.5: Tensile strength and elongation at break of urethane-acrylate copolymers (see Figures 5.6 to 5.9, Graphs 5.5 to 5.10).

<table>
<thead>
<tr>
<th>MMA content (phr of base resin)</th>
<th>HP 1 Iso 105</th>
<th>HP 2</th>
<th>HP 4</th>
<th>UA copolymers with 2 types of soft segment length</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% excess HPMA</td>
<td>10% excess HPMA</td>
<td>20% excess HPMA</td>
<td>HP1 based on BMA (instead of MMA)</td>
<td>Iso 100</td>
</tr>
<tr>
<td>60</td>
<td>27.14 (40)</td>
<td>28.37 (60)</td>
<td>31.38 (20)</td>
<td>14.72 (110)</td>
</tr>
<tr>
<td>70</td>
<td>30.43 (30)</td>
<td>35.04 (10)</td>
<td>36.76 (30)</td>
<td>14.72 (130)</td>
</tr>
<tr>
<td>80</td>
<td>30.38 (30)</td>
<td>45.04 (10)</td>
<td>43.02 (10)</td>
<td>14.66 (130)</td>
</tr>
<tr>
<td>90</td>
<td>28.77 (30)</td>
<td>45.04 (10)</td>
<td>44.02 (10)</td>
<td>14.66 (130)</td>
</tr>
<tr>
<td>100</td>
<td>29.97 (20)</td>
<td>45.04 (10)</td>
<td>44.02 (10)</td>
<td>14.66 (130)</td>
</tr>
<tr>
<td>110</td>
<td>34.78 (10)</td>
<td>54.38 (10)</td>
<td>59.58 (10)</td>
<td>14.95 (140)</td>
</tr>
</tbody>
</table>

Note: Elongation at break values are given in brackets.
<table>
<thead>
<tr>
<th>MMA content (phr of base resin)</th>
<th>Yield Strength (MPa) and Elongation at Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>10%</td>
</tr>
<tr>
<td>Iso 100</td>
<td>Iso 105</td>
</tr>
<tr>
<td>60</td>
<td>35.8</td>
</tr>
<tr>
<td>70</td>
<td>42.3</td>
</tr>
<tr>
<td>80</td>
<td>42.0</td>
</tr>
<tr>
<td>90</td>
<td>39.4</td>
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<td>100</td>
<td>40.9</td>
</tr>
<tr>
<td>110</td>
<td>47.1</td>
</tr>
<tr>
<td>120</td>
<td>55.1</td>
</tr>
</tbody>
</table>

Note: The elongation at yield values are given in brackets.

Table 5.6: Yield strength and elongation at yield of urethane-acrylate copolymers.
<table>
<thead>
<tr>
<th>MMA content (phr of base resin)</th>
<th>HP 1 Iso 105</th>
<th>0% excess HPMA</th>
<th>10% excess HPMA</th>
<th>20% excess HPMA</th>
<th>HP1 based on BMA (instead of MMA)</th>
<th>HP 2</th>
<th>HP 2 based on BMA (instead of MMA)</th>
<th>HP 4</th>
<th>UA copolymers with 2 types of soft segment length</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>716</td>
<td>792</td>
<td>840</td>
<td>134</td>
<td>120</td>
<td>193</td>
<td>167</td>
<td>215</td>
<td>6</td>
</tr>
<tr>
<td>70</td>
<td>802</td>
<td></td>
<td></td>
<td></td>
<td>203</td>
<td>285</td>
<td>281</td>
<td>379</td>
<td>11.5</td>
</tr>
<tr>
<td>80</td>
<td>840</td>
<td>950</td>
<td>1008</td>
<td>131</td>
<td>192</td>
<td>323</td>
<td>364</td>
<td>454</td>
<td>11.2</td>
</tr>
<tr>
<td>90</td>
<td>778</td>
<td></td>
<td></td>
<td></td>
<td>324</td>
<td>404</td>
<td>304</td>
<td>498</td>
<td>15.1</td>
</tr>
<tr>
<td>100</td>
<td>814</td>
<td>1010</td>
<td>1052</td>
<td>145</td>
<td>380</td>
<td>444</td>
<td>450</td>
<td>566</td>
<td>17.2</td>
</tr>
<tr>
<td>110</td>
<td>914</td>
<td></td>
<td></td>
<td></td>
<td>363</td>
<td>450</td>
<td>486</td>
<td>606</td>
<td>13.6</td>
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<tr>
<td>120</td>
<td>1085</td>
<td>1074</td>
<td>1200</td>
<td>155</td>
<td>1</td>
<td>193</td>
<td>167</td>
<td>215</td>
<td>6</td>
</tr>
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</table>

Table 5.7: Urethane-acrylate copolymers: modulus at 5% elongation.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Yield strength (MPa)</th>
<th>Elongation at yield (%)</th>
<th>Modulus at 5% elongation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA copolymers based on MMA/BMA mixtures:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP2 M100</td>
<td>20.70</td>
<td>150</td>
<td>20.20</td>
<td>7</td>
<td>404</td>
</tr>
<tr>
<td>HP2 M80B20</td>
<td>16.74</td>
<td>150</td>
<td>11.88</td>
<td>8</td>
<td>236</td>
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<tr>
<td>HP2 M60B40</td>
<td>14.04</td>
<td>170</td>
<td>6.73</td>
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<td>127</td>
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<td>HP2 M40B60</td>
<td>13.13</td>
<td>180</td>
<td>3.40</td>
<td>9</td>
<td>63</td>
</tr>
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<td>HP2 M20B80</td>
<td>9.68</td>
<td>190</td>
<td>1.40</td>
<td>7</td>
<td>25</td>
</tr>
<tr>
<td>HP2 B100</td>
<td>8.65</td>
<td>200</td>
<td>1.04</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>Reference Materials:</td>
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<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>13.35</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>2604</td>
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<tr>
<td>PBMA</td>
<td>4.69</td>
<td>220</td>
<td>4.10</td>
<td>19</td>
<td>89</td>
</tr>
<tr>
<td>X-PU 1</td>
<td>9.44</td>
<td>230</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>X-PU2 Iso 100</td>
<td>1.65</td>
<td>300</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Iso 100</td>
<td>2.22</td>
<td>300</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Iso 105</td>
<td>2.36</td>
<td>260</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Iso 110</td>
<td>2.45</td>
<td>250</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>Iso 115</td>
<td>1.26</td>
<td>310</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>X-PU 142</td>
<td>1.77</td>
<td>330</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>X-PU 142</td>
<td>1.23</td>
<td>530</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>X-PU 143</td>
<td>1.71</td>
<td>580</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>0.69</td>
<td>670</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>X-PU 4</td>
<td>1.70</td>
<td>200</td>
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<td>TDI-X-PU 2</td>
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</tbody>
</table>

Table 5.8: Tensile properties of reference materials and urethane-acrylate copolymers based on MMA/BMA mixture (see Figures 5.10 to 5.12, Graph 5.12).
### Table 5.9: Summary of DSC results for urethane-acrylate copolymers, crosslinked polyurethanes, methacrylate homopolymers (see Figures 5.13 to 5.21).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Transitions observed (°C)</th>
<th>Scanning temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T₁</td>
<td>T₂</td>
</tr>
<tr>
<td><strong>MMA based UA copolymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP 1 M100</td>
<td>-10</td>
<td>50 (o-s)</td>
</tr>
<tr>
<td>1st run</td>
<td>3</td>
<td>55</td>
</tr>
<tr>
<td>2nd run</td>
<td></td>
<td></td>
</tr>
<tr>
<td>conditioned sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP 2 M100</td>
<td>-41</td>
<td>50 (o-s)</td>
</tr>
<tr>
<td>1st run</td>
<td>-40</td>
<td>50</td>
</tr>
<tr>
<td>2nd run</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP 4 M60</td>
<td>-50</td>
<td>50</td>
</tr>
<tr>
<td>1st run</td>
<td>-51</td>
<td>50 (o-s)</td>
</tr>
<tr>
<td>2nd run</td>
<td>-58</td>
<td>55</td>
</tr>
<tr>
<td>conditioned sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>BMA based UA copolymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP 1 B60</td>
<td>not clear</td>
<td>not clear</td>
</tr>
<tr>
<td>1st run</td>
<td>-50</td>
<td>-10</td>
</tr>
<tr>
<td>conditioned sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP 2 B60</td>
<td>not clear</td>
<td>not clear</td>
</tr>
<tr>
<td>1st run</td>
<td>-50</td>
<td>not clear</td>
</tr>
<tr>
<td>conditioned sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HP 2 B100</td>
<td>-52</td>
<td>-10</td>
</tr>
<tr>
<td><strong>Reference Materials</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-PU 1</td>
<td>-8</td>
<td>65</td>
</tr>
<tr>
<td>X-PU 2</td>
<td>-42</td>
<td>65</td>
</tr>
<tr>
<td>X-PU 142</td>
<td>-51</td>
<td>67</td>
</tr>
<tr>
<td>PMMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st run</td>
<td>50 (o-s)</td>
<td>62 (p)</td>
</tr>
<tr>
<td>repeat scan</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>conditioned sample</td>
<td>50 (o-s)</td>
<td>60 (p)</td>
</tr>
<tr>
<td>PBMA</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- 'o-s' denotes on set value
- 'p' denotes peak value

Chapter 5
### Table 5.10: Effects of structural variables on DMTA results (see Figures 5.24 to 5.31).

<table>
<thead>
<tr>
<th>Variables</th>
<th>UA copolymers based on:</th>
<th>MMA content = 60 phr.</th>
<th>MMA content = 100 phr.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature at E&lt;sup&gt;max&lt;/sup&gt; (°C)</td>
<td>Temperature at tan δ&lt;sup&gt;max&lt;/sup&gt; (°C)</td>
</tr>
<tr>
<td>Soft segment length in MMA system</td>
<td>HP 1</td>
<td>19</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>HP 2</td>
<td>-19</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>HP 4</td>
<td>-45</td>
<td>67</td>
</tr>
<tr>
<td>Soft segment length in BMA system</td>
<td>HP 1</td>
<td>0.5</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>HP 2</td>
<td>-30</td>
<td>21</td>
</tr>
<tr>
<td>Iso index</td>
<td>HP2 Iso 105</td>
<td>-19</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>HP2 Iso 115</td>
<td>-13</td>
<td>63</td>
</tr>
<tr>
<td>Percentage excess HPMA</td>
<td>HP1</td>
<td>19</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>HP1 with 20% excess HPMA</td>
<td>21</td>
<td>73</td>
</tr>
<tr>
<td>Soft segment length</td>
<td>HP2</td>
<td>-19</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>HP142</td>
<td>-22</td>
<td>70</td>
</tr>
<tr>
<td>distributions</td>
<td>SHP142</td>
<td>-15</td>
<td>66</td>
</tr>
<tr>
<td>(i.e. based on polyol blends)</td>
<td>HP143</td>
<td>-40</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>HP243</td>
<td>-33</td>
<td>64</td>
</tr>
<tr>
<td>Isocyanate types</td>
<td>HP2</td>
<td>-19</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>TDI-HP2</td>
<td>-18</td>
<td>47</td>
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</tbody>
</table>

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### Table 5.11: Effect of sample conditioning on DMTA properties.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Samples</th>
<th>Temperature at $E^\prime$ maximum ($^\circ$ C)</th>
<th>Temperature at tan $\delta$ maximum ($^\circ$ C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconditioned</td>
<td>HP1 M100</td>
<td>37</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>HP4 M100</td>
<td>-20</td>
<td>89</td>
</tr>
<tr>
<td>Slow cooled</td>
<td>HP1 M100</td>
<td>37</td>
<td>95</td>
</tr>
<tr>
<td>(at = 1 °C/min. from 95 °C)</td>
<td>HP4 M100</td>
<td>-20</td>
<td>92</td>
</tr>
<tr>
<td>Quench cooled</td>
<td>HP4 M100</td>
<td>-20</td>
<td>86</td>
</tr>
<tr>
<td>(at = 10 °C/min. from 95 °C)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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Figure 5.1: Carbonyl peaks of UA copolymers based on HP 1, at 60 and 100 phr MMA content.

Figure 5.2: Carbonyl peaks of UA copolymers based on HP 4, at 60 and 100 phr MMA content.
Figure 5.3: Carbonyl peaks as seen in BMA based urethane-acrylated copolymers (HP 1 B60 and HP 2 B60).

Figure 5.4: Carbonyl peak of PMMA.
Figure 5.5: Carbonyl peaks as seen in crosslinked polyurethanes. (X-PU 1, X-PU 2 and X-PU 142)
Figure 5.6: Tensile curves of MMA based UA copolymers at a PPG molecular weight of 1000.

Figure 5.7: Tensile curves of MMA based UA copolymers at a PPG molecular weight of 2000.
Figure 5.8: Tensile curves of MMA based UA copolymers at a PPG molecular weight of 4000.

Figure 5.9: Tensile curves of BMA based UA copolymers at a PPG molecular weight of 2000.
Figure 5.10: Tensile curves of UA copolymers based on MMA/BMA mix and PPG molecular weight of 2000.

Figure 5.11: Tensile curves of PBMA and PMMA.
Figure 5.12: Tensile curves of crosslinked polyurethanes.
Figure 5.13: DSC thermograms of HP 1 M100 (conditioned and unconditioned samples).
Figure 5.14: DSC thermograms of HP 2 M100 (unconditioned sample).
Figure 5.15: DSC thermograms of HP 4 M100 (conditioned and unconditioned samples).
Figure 5.16: DSC thermograms of HP 4 M60 (unconditioned sample).

Figure 5.17: DSC thermograms for both conditioned and unconditioned PMMA.
Figure 5.18: DSC thermograms for crosslinked polyurethanes.
Figure 5.19: DSC thermograms of PBMA (unconditioned sample).

Figure 5.20: DSC thermograms of unconditioned samples of BMA-based UA copolymers.
Figure 5.21: DSC thermograms of conditioned samples of BMA-based UA copolymers.
Figure 5.22: Tan δ plots of crosslinked polyurethanes.
Figure 5.23: Tan δ and loss modulus (E'') plots of PMMA and PBMA.

Figure 5.24: Tan δ and loss modulus (E'') plots of MMA based UA copolymers at a PPG molecular weight of 1000.
Figure 5.25: Tan δ and loss modulus ($E''$) plots of MMA based UA copolymers at a PPG molecular weight of 2000.

Figure 5.26: Tan δ and loss modulus ($E''$) plots of MMA based UA copolymers at a PPG molecular weight of 4000.
Figure 5.27: Tan δ and loss modulus (E") plots of MMA based UA copolymers at an average polyol molecular weight of 2000 and 100 phr MMA content.
Figure 5.28: Tan δ and loss modulus (E") plots of UA copolymers at an average polyol molecular weight of 3000 and 100 phr MMA content.
Figure 5.29:  Tan δ and loss modulus (E'') plots of HP 2 M100 at various isocyanate index.

Figure 5.30:  Tan δ and loss modulus (E'') plots of HP 1 M100 with and without excess HPMA.
Figure 5.31: Tan δ and loss modulus (E'') plots of HP 2 M100 at different isocyanate structures.

Figure 5.32: Tan δ curves of UA copolymers based on MMA/BMA mixture, at a PPG molecular weight of 2000.
Figure 5.33: Tan δ and loss modulus (E") plots of BMA based UA copolymers.
Figure 5.34: SEM micrographs of MMA based UA copolymers at various average polyl molecular weight; fractured at room temperature.
Figure 5.34 (cont'd)
Figure 5.35: SEM micrographs of UA copolymers fractured at room temperature - (i) with 10% excess HPMA, (ii) at isocyanate index 115 and (iii) using TDI.
Figure 5.36: SEM micrographs of UA copolymers based on MMA/BMA mix; fractured at room temperature.

Figure 5.37: SEM micrographs of BMA based UA copolymers; fractured at room temperature.

Figure 5.38: SEM micrographs of PMMA and PBMA; fractured at room temperature.
Figure 5.39: SEM micrographs of BMA based UA copolymers; fractured at subambient temperature.

Figure 5.40: SEM micrographs of PMMA, PBMA and X-PU 2; fractured at subambient temperature.
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Figure 5.41: SEM micrographs of MMA based UA copolymers; fractured at subambient temperature.
Graph 5.1: Curing curves for UA copolymers of varying PPG molecular weight and MMA content.
Graph 5.2: Curing curves for UA copolymers of varying PPG molecular weight and at 100 phr MMA content.

Graph 5.3: Curing curves for UA copolymers based on MMA/BMA mixture and at a PPG molecular weight of 2000.
Graph 5.4: Curing curves for BMA based UA copolymers at a PPG molecular weight of 2000.
Graph 5.5: Tensile properties of MMA based UA copolymers of varying polyol segment length.
Graph 5.6: Tensile properties of MMA based UA copolymers at a PPG molecular weight of 1000- with and without excess HPMA.
Graph 5.7: Tensile properties of MMA based UA copolymers at various isocyanate index -- I.
Graph 5.7: Tensile properties of MMA based UA copolymers at various isocyanate index -- II.
Graph 5.8: Tensile properties of MMA based UA copolymers at a PPG molecular weight of 2000 but of a different isocyanate structure.
Graph 5.9: Tensile properties of MMA based UA copolymers at an average polyol segment length of 2000 PPG molecular weight.
Graph 5.10: Tensile properties of MMA based UA copolymers at an average polyol segment length of 3000 PPG molecular weight.
Graph 5.11: Tensile properties of BMA based UA copolymers.
Graph 5.12: Tensile properties of UA copolymers based on a MMA/BMA mixture and at a PPG molecular weight of 2000.
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5.2 Discussion

5.2.1 Preliminary Investigation: Selection of casting conditions

As described in Section 3.5, experimental trials were conducted to determine suitable casting conditions for crosslinked PUs and UA copolymers produced in this project. The effect of synthesis conditions on the tensile properties of the cast sheets were taken as a guide-line when making the selections.

Crosslinked PUs:

It was found that lower tensile strength and elongation at break were generally observed for crosslinked PUs cast at higher temperatures than those cast at lower temperature (see Table 5.4: Sections A and B). Since GPC studies had shown that increasing the reactivities of the reactants tend to result in more chain extended products (see Section 4.3.2 and Graph 4.9), it is likely that crosslinked PUs cast at higher temperature would probably have fewer crosslink sites than those cast at lower temperature. This, coupled with the possibility of imperfect cross-link reaction between glycerol and the NCO groups in the later curing stage (i.e. glycerol OH units may not be linked to all the NCO groups), might have resulted in lower tensile properties observed. The tensile strength of the crosslinked PUs made from NCO-prepolymer synthesised at 78 °C also showed lower tensile properties, and hence support this argument (see Table 5.4, Section C). As PU cast at room temperature took a long time to gel and cure, it was decided to cast all the crosslinked PUs used in the main part of the experimental work, at 65 °C for 72 hours. This was also thought to help to reduce the possibility of glycerol separating out from the mixture prior to gelation.

In order to speed up the gel time, PUs were also cast using varying amounts of catalyst concentration. Much longer cure times were observed when DBTL content was reduced to 0.00005%, while it was difficult to produce bubble-free cast sheet when catalyst concentration was increased above 0.0004%. It was also observed that
increasing catalyst content had a tendency to cause a reduction in the tensile strengths of the crosslinked PUs, (see Table 5.4, Section A). This is in agreement with the above analysis, i.e. increasing reactants reactivities tended to lead to lower tensile strength products. However, the effect of catalyst was rather slight, probably due to the very low amount of catalyst content studied. Based on these observations, it was decided to prepare the crosslinked PUs at a catalyst concentration of 0.0003% to 0.0004% (refer to Section 3.4.4).

UA copolymers:

In preparing UA copolymer cast sheets, it was observed that the tensile properties of the cast sheets made from the same batches of AUOs and methacrylate monomers, could vary. Experimental work (as described in Section 3.5.3) carried out on this aspect showed that this was attributed to the temperature of the casting solution, (see Table 5.3). Therefore, to reduce this variable, free radical initiator (BPO) and accelerator (DMPT) were added into the solution (i.e. of acrylated-urethane oligomer and methacrylate monomer) only after it has been cooled to room temperature.

The effect of lot-to-lot variations (that may have resulted from, for example, different extent of NCO-prepolymer reactions) in the AUOs on the tensile properties of the final UA copolymers was also assessed. As shown in Table 5.3, variations in the tensile properties of UA copolymers, casted from different lots were observed to be insignificant. In fact, the tensile properties of UA copolymers prepared from NCO-prepolymer with a PPG molecular weight of 4000 (i.e. Prep 4), and had been reacted to a NCO content of 1.8 %, was found to show little difference from that synthesised from Prep 4 having NCO content of 2.0% (see Table 5.3).

The tensile properties of UA copolymers were found to reach an optimum after 48 hours (see Table 5.3).
5.2.2 Curing Behaviour of Acrylated Urethane Oligomers and Methacrylate Mixtures

The curing curves for the UA copolymers were observed to adopt an ‘S’ profile as shown in the diagram below.

![Diagram showing curing curve with induction period, setting rate, and fully cured phases.]

Figure 5.42: Typical curing curve as observed with UA copolymers.

From the curing curves obtained for the various AUO and methacrylate mixtures (see Graphs 5.1 to 5.4), it was found that the total curing time of the UA copolymers was taken up mainly by the induction period rather than the setting (or gelling) rate that followed after it. The induction period refers to the time lapsed, starting from the time of adding the initiating system to the time when the reactants start to show a change in viscosity. This change in viscosity signified the start of the gel process (see Figure 5.42). This delay in the curing process is due to the inhibition effect of atmosphere oxygen, which is typical of all free radical curing systems [95-99]. As the experiment was carried out under similar test condition, such effect on the curing process, it can be assumed to be the same for all the samples analysed. Hence, differences in the curing
behaviour of the various UA copolymers seen were influenced namely by the type reactants used rather than to varying amount of oxygen inhibition.

It was observed that any influences exerted by the reactants or the methacrylate content, were focussed on the induction period rather than the setting rate (i.e. the rate of gelation or solidification). Increase in induction period was observed under the following situations:

I) when the PPG soft segment length (i.e. molecular weight) of the AUOs was increased (see Graph 5.1), or

II) when TDI was used instead of MDI (see Graph 5.2), or

III) when BMA was used (see Graph 5.3).

These showed that the induction periods were dependent on the reactivities of the reactants used (i.e. the AUOs, isocyanate structure, or type of methacrylate). The influence of methacrylate content was found to be of little significance except when the reactivities of the reactants used were low. For examples, when AUO based on PPG 4 or when BMA was used (instead of MMA), an average of about 5 to 6 minutes increase in the induction period was observed upon increasing the methacrylate content from 60 phr to 120 phr (see Graphs 5.1 and 5.4). Compared to using a AUO based on PPG 1, the difference in induction period when 120 phr of MMA was used instead of 60 phr, was only about 2 minutes.

The rate of gelation, as reflected by the gradients of the rising slopes of the curves immediately after the induction period, was generally found to be not significantly influenced by varying isocyanate types, PPG chain length, methacrylate content or type (see Graph 5.1). As can be seen from the steepness of the rising slopes of various curing curves, the setting rate was very fast once the induction period was over. Nevertheless, in relative terms, the reactivities of the reactants still had more influence on the rate of gelation than the methacrylate content. For example, the gradient of the slope became less steep when AUO based on higher PPG molecular weight or TDI-
based AUO or BMA was used (see Graphs 5.2, 5.3 and 5.4). These changes were hard to notice when variation was made with respect to methacrylate content.

Difficulties were encountered in trying to produce a homopolymer of the methacrylates and in curing the AUOs on its own (i.e. without diluting it with methacrylate monomers). Polymerisation of the catalysed MMA or BMA monomers took more than 12 hours. This curing process was found to be inhibited by oxygen, unless covered by a layer of (PET) sheet at the coating-air interface. The very low viscosity of the monomers (i.e. water-like) had probably encouraged oxygen diffusion, causing total inhibition to the curing process. Even with the problem overcome, the curing process was observed to be very slow, with monomers taking about 16 hours (i.e. overnight) to be converted to polymer.

Attempts made to cure the AUOs were only successful when the AUOs were diluted with at least 40-50 phr of MMA. This could be due to the relatively high AUOs viscosities preventing the free radicals from carrying out chain propagation (and hence the resin from setting into a solid cast sheet). The lack of C=C bond in such systems (i.e. without methacrylate dilution) may have also played a role in this. Hence, it can be said that curing both the AUO and the acrylate components together, produced a synergistic effect on the curing process by reducing the overall curing time of the system.

5.2.3 Factors Influencing the Relative Degree of Crosslinking in UA Copolymers.

In the solvent extraction tests of UA copolymers, the percentage of extractable components can be affected by homopolymerisation of the methacrylate components and/or the presence of other low molecular species not participating in the crosslink network. Despite of the latter possibility, the test may be used to check whether extensive homopolymerisation of MMA had occurred in the synthesis of UA copolymers. In this work, copolymerisation of the AUOs with MMA can be
considered to be rather efficient as solvent extraction tests of selected UA copolymers showed a generally low percentage of extractable components. This low value also indicated that other species (other than the ideal products of 1 PPG unit tipped by 2 isocyanate units as discussed in GPC study, see Section 4.3.1) that were formed during synthesis of NCO-prepolymers and AUOs were mostly used up in the curing reaction.

From the results of the solvent extraction test, the percentage extracts obtainable from the UA copolymers appeared to be dependent more on the urethane soft segment length than on the acrylic content. This implies that the crosslink density of the UA copolymer was determined by the soft segment length. The test results showed that copolymers based on higher polyl molecular weight generally gave a higher percentage of extracts. This is easily understood. From the method of producing the UA copolymers (see Section 3.1), the network structure developed in the copolymers would resemble that of an ABCP system as illustrated in Figure 3.3, (also refer to Literature Survey, Section 2.3.2). In this case, the crosslink points therefore come from the chain end double bonds in the AUO units as the other reactant, being the monofunctional methacrylates, will not provide extra crosslinking sites. The major molecular chains between any two crosslink points will be either the methacrylate chain or the polyl chain linked to each other through the urethane unit (see Figure 3.2). Accordingly, in AUO based on higher PPG chain length, the number of such double bonds available for crosslinking is reduced and far apart. Hence, the chances of some species not able to form part of the crosslink network was high, (as compared to those based on lower PPG soft segment length), resulting in an expected increase in the percentage extracts. It was possible that under such condition, together with the relatively higher MMA to AUO molar ratio and lower viscosity (of AUO based on higher PPG molecular weight), homopolymerisation of MMA was encouraged. This was reflected in SEM study on UA copolymers based on higher PPG molecular weight, i.e. HP 4 M60 and HP 4 M100, which shows wedges attributed to the MMA component in samples fractured at sub-ambient temperature (see Section 5.4 on SEM). More wedges were noted in samples with higher MMA content, i.e. in HP 4 M100. Table 5.12 shows the molar ratio of the MMA units to a AUO unit in the various UA copolymers. Sample calculation for these can be found in Appendix A.6.
Although the soft segment length had more influence on the percentage extracts than the MMA content, slightly lower percentage extract was recorded at higher MMA content for a specific AUO type (i.e. HP 1 or HP 2, etc). This could be due to more methacrylate monomers being available to find these crosslinking sites.

<table>
<thead>
<tr>
<th>AUO types</th>
<th>No. of moles of methyl (or butyl) methacrylate to 1 mole of AUO unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP 1</td>
<td>M60 (B60)</td>
</tr>
<tr>
<td>HP 2, HP 142</td>
<td>11.7*¹</td>
</tr>
<tr>
<td>HP 143, HP 243</td>
<td>18.2</td>
</tr>
<tr>
<td>HP 4</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>29.7</td>
</tr>
</tbody>
</table>

Table 5.12: Composition of UA copolymers expressed in moles ratio.

*¹ Interpretation of table, for example:
11.7 refers to 11.7 moles of MMA or BMA to 1 mole of AUO unit in UA copolymer HP 1 M60 (or HP 1 B60).

UA copolymers based on blends:

The amount of extract was observed to increase in the order of (for UA copolymer based on) HP 1 < HP 2, S-HP 142, < HP 243 < HP143, HP142 < HP 4, reflecting a decreasing amount of crosslink density in these UA copolymers. From these, it was observed that for UA copolymers using mixed AUOs to produce a specific average PPG segment length, a higher percentage extract was obtained when PPG molecular weight of 1000 was involved. As mentioned in Section 3.3.2, the ratio of mixed AUOs used in these copolymers (i.e. having more than one type of PPG molecular weight) was determined, such as to give the same average PPG chain length as that using AUO
based on a single PPG molecular weight type (i.e. ‘monodisperse’ PPG segment length; see Table 3.3). Theoretically, this would mean the same average number of crosslink points in the resulting polymers regardless of whether single or mixed AUOs were used, as the total number of moles of AUO units were be the same in both cases. This is illustrated in Table 5.13 which shows the AUOs used (see Table 3.3) in molar quantity.

<table>
<thead>
<tr>
<th>Sample references</th>
<th>Weight of AUO used (g)*1</th>
<th>Estimated no. of moles of AUO unit present</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP 1</td>
<td>1000</td>
<td>0.51</td>
</tr>
<tr>
<td>HP 2</td>
<td>1000</td>
<td>0.33</td>
</tr>
<tr>
<td>HP142 consists of:</td>
<td>1000 (total)</td>
<td>0.21</td>
</tr>
<tr>
<td>HP1</td>
<td>407</td>
<td>0.12</td>
</tr>
<tr>
<td>HP 4</td>
<td>593</td>
<td></td>
</tr>
<tr>
<td>HP 143 consists of:</td>
<td>1000 (total)</td>
<td>0.10</td>
</tr>
<tr>
<td>HP 1</td>
<td>188</td>
<td>0.16</td>
</tr>
<tr>
<td>HP 4</td>
<td>812</td>
<td></td>
</tr>
<tr>
<td>HP 243 consists of:</td>
<td>1000 (total)</td>
<td>0.15</td>
</tr>
<tr>
<td>HP 2</td>
<td>462</td>
<td>0.11</td>
</tr>
<tr>
<td>HP 4</td>
<td>538</td>
<td></td>
</tr>
<tr>
<td>HP 4</td>
<td>1000</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 5.13: Conversion table for AUOs from weight to molar number.

*1 This included excess MDI and HPMA used in the synthesis of the intermediate products.

For example, in comparing 1 kg of oligomer HP 142 with 1 kg of oligomer HP 2, the number of moles of the respective AUO units used in HP 142 should add up to equal to the number of moles of AUO units in HP 2. Similarly, the number of crosslink...
points in HP 2 were expected to be higher than that in HP 143 or HP 243. However, the test results showed that both HP 142 and HP 143 had a higher percentage extracts than HP 2 and HP 243. It is deduced that this could be due to a lesser amount of double bonds available for crosslinking as a result of more chain extended products in oligomers mixture having HP 1 (e.g. HP 142, HP 143). Unlike systems based solely on HP 1, there was a possibility that in a system based on two PPG soft segment lengths, the MMA monomers had a preference to react with the relatively more active AUOs of shorter PPG chains (i.e. the chain extended HP 1 was still preferred over AUO based on higher molecular weight PPG). When this happened, the chances of AUOs of longer PPG chains participating in the crosslinking was reduced, leading to a even fewer crosslinked network. This probably also explained why when UA copolymer was made from AUO, converted from NCO-prepolymers based on PPG blends, e.g. in S-Prep 142, the percentage of extract was not as high as that obtained from using AUO blends of, e.g. HP 1 with HP 4. In this case, differences in AUOs reactivities resulting from varying PPG molecular weight would have been reduced after conversion into NCO-prepolymer, prior to reaction with the methacrylate component.

GPC chromatograms of UA copolymers based on TDI (e.g. TDI-HP 2 M100) and those having 15% excess of MDI (e.g. HP 2 M100 Iso 115) have shown a lesser amount of chain extended products than the normal corresponding type (e.g. HP 2 M100). Based on the above same reasoning, the lower percentage extract obtained from these copolymers (i.e. the TDI based UA copolymers and those having 15% MDI) could therefore be due to more crosslink sites available in the systems.

5.2.4 Infrared Analysis

A comparison of the NH absorbance frequencies of UA copolymers with that of the AUOs (which showed NH absorbance between 3300 cm\(^{-1}\) to 3316 cm\(^{-1}\), see Table 4.6) showed a shift in the NH absorbance frequencies of the UA copolymers to a higher range (i.e. 3350 cm\(^{-1}\) to 3356 cm\(^{-1}\), see Table 5.2). Although these absorbance frequencies still signified NH in hydrogen bonded state, they reflected a reduction in
the hydrogen bond strength. This indicated that the crosslink network in the UA copolymers had separated the distance between the hydrogen bonding species, namely the NH groups and the C=O groups, and it probably implied a lack of chain aggregation [84-86].

In FTIR enlargements of C=O absorption bands of the UA copolymers, absorption peaks at 1736 cm\(^{-1}\) became more obvious when MMA content was increased (see Figures 5.1 to 5.3). This indicated that the C=O absorption at 1736 cm\(^{-1}\) may have resulted from the increasing presence of C=O groups from the acrylic component. This further supported earlier analysis work on AUOs based on PPG 1, whereby the presence of absorbance frequency at 1736 cm\(^{-1}\) was deduced to have resulted partially from the introduction of more C=O groups through HPMA addition, (see Section 4.3.4).

For BMA based UA copolymers as well as crosslinked PUs, C=O absorption bands occurred at a lower frequency (at 1726 cm\(^{-1}\) with shoulders at 1712 cm\(^{-1}\), see Figure 5.3 and 5.5), indicating a stronger hydrogen bonded system. This could be due probably to relatively better chain flexibility (than the MMA based UA copolymers), thereby allowing better chain interaction. Absorption at 1712 cm\(^{-1}\) became more obvious for PU based on PPG 1000. Here, likewise with AOU based on PPG 1, the increase in hydrogen bonding species and closer distance between the interacting species, were probably accountable for it.

5.2.5 Mechanical Properties Studies.

Tensile measurements taken on the crosslinked PUs showed that their mechanical strengths were dependent on the polyol's molecular weight used (see Table 5.8, Figure 5.12). This indicated that the mechanical properties of the crosslinked PUs were related to the crosslink density and flexibility of the systems. Increasing crosslink densities (i.e. in the case of a lower PPG molecular weight and therefore a less flexible system), in the order X-PU 4 < X-PU 2 < X-PU 1, produced a corresponding increase
in the tensile strength but also a lower elongation at break. As the molecular weight of the polyol increased, the polymers produced were observed to become more sticky and elastic. With methacrylate homopolymers, PMMA showed a brittle failure while PBMA was observed to have good elongational properties but rather low in strength (see Figure 5.11).

The tensile curves of the various UA copolymers showed that tough polymers (as assessed from area under the curves) were obtained for systems based on longer polyol chain length, i.e. at PPG molecular weight of 2000 and above. The results obtained from the mechanical properties studies of the UA copolymers can be summarised as follows (see Tables 5.5 to 5.8, Graphs 5.5 to 5.12):

I. The tensile properties of the various copolymers were very much dictated by the polyol component although they were also influenced by other compositional variables such as methacrylate content. Generally, increased polymer strength (while elongation at break and at yield remained relatively unchanged), was observed with higher content of MMA, or excess of HPMA or MDI.

II. The influence of isocyanate index on the tensile properties (including the elongation at break) was observed to be significant only when this was increased to 115.

III. At polyol molecular weight of less than 3000, the elongation at yield of the various copolymers were found not to be influenced by the acrylic content.

IV. TDI based UA copolymers were found to exhibit lower polymer strength than the MDI based UA copolymers.

V. The modulus and tensile strength of the BMA based copolymers were much lower than the MMA based UA copolymers. Increasing BMA content produced an increase in the elongation at break but had little effect on tensile strength or modulus (see Graph 5.11).
VI. Replacing MMA with BMA showed a reduction in the polymer strength but with improved elongation at break.

Since the UA copolymers are AB crosslinked systems, the mechanical strengths of the copolymers could be influenced by:

i) the reinforcing effects of the harder methacrylate components in the softer and flexible polyol matrix.

ii) the degree of crosslinking contributed by the double bonds of the AUOs.

Likewise with the crosslinked PUs, the strong dependence of the mechanical properties of UA copolymers (see Tables 5.5 to 5.7) on the polyol soft segment length showed that these properties were associated with the relative crosslink density of the system and to the flexibility (i.e. length) of the polyol chains. In comparison to the corresponding crosslinked PUs, UA copolymers showed greater tensile strength. This indicated that the methacrylate components (i.e. MMA or BMA) were responsible for the improved strength, perhaps by acting as a reinforcement in the soft polyol matrix or through stiffening of the polyol chains with these rigid crosslink branches. As expected, increasing methacrylate content (particularly with the MMA) produced an increase in the copolymer strength. In comparison, the lack of significant variation in the mechanical properties of the copolymers, with respect to the methacrylate content variations, was probably due to the methacrylate chain length not being sufficiently long to produce significant effect on the polymer strength. Table 5.12 shows the theoretical number of monomers unit per mole of AUOs that can be formed at various levels of MMA monomer content.

The substantial increase in the tensile strength of the MMA based UA copolymers, as compared to the BMA series at the same methacrylate content, showed the effectiveness of having a rigid hard segment acting as a reinforcing agent. Hence, toughness of UA copolymers can be increased by a combination of long AUO molecular weight with a hard reinforcer such as MMA (see Figures 5.6 to 5.8).
BMA series

As BMA tends to homopolymersise to form softer materials than MMA, increasing BMA content in a copolymer was not likely to provide the same amount of reinforcing effect as MMA. This explained the lower strength of these copolymers. However, increasing BMA content was found to be more effective in introducing flexibility to the polymer, and hence the extensibility of the system, as reflected from the increase in elongation at break, (see Graph 5.11 and tensile curves in Figure 5.9). This was probably related to better chain flexibility and separation between the two crosslink points.

Graph 5.12 shows the effects of replacing MMA with BMA. According to the above discussion, the tensile results of these MMA/BMA based UA copolymers were therefore as expected (i.e. reduction in tensile strength with corresponding increase in elongation at break as BMA content was increased; see Figure 5.10 for tensile curves of MMA/BMA based UA copolymers).

Using excess isocyanate (MDI)

In study made on UA copolymers with varying levels of excess MDI, the increase in polymer strength was minor until the isocyanate index was increased to and above 115 (see Graph 5.7). The elongational properties of the copolymers also appeared to be affected only when the isocyanate index was 115 or greater. In earlier discussion (on GPC study of NCO-prepolymers of varying isocyanate index), it was found that chain extended products were reduced only when the amount of excess MDI used was sufficiently high. A reduction in chain extended products would also mean an increase in the amount of double bonds available in the corresponding AUOs for crosslinking. Hence, the significant changes in the tensile properties of UA copolymers at isocyanate index of 115 were deduced to have resulted from an increase in the crosslink density, as well as from the system being more rigid due to the presence of more relatively shorter AUOs units and hydrogen bonding forces. Accordingly when the percentage of excess MDI is less than 15% (i.e. at isocyanate index lower than 115), there is
probably little change in the crosslink density of the system and the effect of excess MDI on the polymer properties becomes relatively less significant, (GPC peak attributed to the chain extended products did not show noticeable decrease in the peak height of peak C).

**Using excess HPMA**

GPC study has indirectly indicated that the addition of excess HPMA did not affect the crosslink density. Hence, as in the case of using MMA instead of BMA, the increase in strength and modulus seen in UA copolymers having excess HPMA were probably associated with increased rigidity of the system. This happened when the HPMA copolymerised with MMA. Such an effect was found to be more significant than that of having excess isocyanate, demonstrating again that HPMA was more effective in acting as a physical crosslinker and reinforcer (i.e. through hydrogen bonding) than the MDI in the polyol matrix (see Section 4.2.3).

**Using polyol blends**

The mechanical properties of UA copolymers based on polyol blends were observed to be dependent not only on the average polyol length in the system but also on the molecular weight of the individual polyols used in the blends. Systems using polyol blends consisting of PPG 1 were found to exhibit a higher modulus and yield strength than those using higher molecular weight PPG in the blends. For example, comparing UA copolymers based on HP 143 and on HP 243, the former showed better yield strength and modulus even at low MMA content (see Graphs 5.10). Similar trend was also observed when comparing UA copolymers based on HP 142 with that based on HP 2 (see Graphs 5.9). In both cases, solvent extraction test showed that UA copolymers based on HP 143 and HP 142 had more extractable components, and therefore indicating a lower crosslinking, than that based on HP 243 and HP 2. This increase in rigidity, (despite a lower crosslink network), was believed to be due to additional reinforcement and chain stiffening arising from the shorter PPG 1 polyol chains present in the system. As seen in the earlier study on the AUOs, which showed
HPMA producing more chain stiffening effect on shorter polyol chains than on longer polyol chains (see Section 4.2.3), it is believed that the shorter polyol chains (i.e. PPG 1) in the UA copolymers will experience more chain stiffening effect than the longer polyol chains at the same MMA content.

Copolymers based on polyol blends were also observed to exhibit wide variation in tensile properties at various MMA content. This was probably due to the presence of more components influencing each other. While the elongational properties of UA copolymers based on single narrow PPG molecular weight were not apparently affected by MMA content, those based on polyol blends were found to be dependent on the MMA content (i.e. elongation at break decreased with increasing MMA content). The tensile strengths of such copolymers had also shown greater variations over the range of MMA contents studied (see Table 5.3). It is believed that variation in flexibility of the individual PPG chains at different MMA content was responsible for such result.

For example, in UA copolymers based on polyol blends having average polyol molecular weight of 2000, the tensile strength was observed to be lower than that based on oligomer HP 2 (i.e. of single polyol molecular weight type) when the MMA content was low (e.g. between HP 1 42 M60 and HP 2 M60). This was probably due to a more flexible network arising from the presence of PPG 4. At low MMA content, due to a lower chain stiffening effect exerted on the polyol chains by the MMA chains attached to it, the longer PPG 4 chain was more mobile in molecule space, exhibiting its flexibility characteristics. As MMA content increased, the chain stiffening effect produced on both PPG 1 and PPG 4 chains became increasingly significant, particularly so with the shorter PPG chains. It is believed that the tensile strength of the UA copolymer (e.g. HP 1 42 M120) was dominated by an effect produced jointly by the shorter polyol chains and the hard segments. Hence, a higher tensile strength was observed as the shorter polyol chains (i.e. PPG 1 in HP 1 42) had enhanced the hard segments' effects at high MMA contents. A similar trend was observed in the tensile properties of UA copolymers based on HP 1 43, compared to that based on HP 220.
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243. Tensile properties of HP 143 were slightly lower than that of HP 243 at low MMA content but the former rapidly overrode the latter as MMA content was raised to 70 phr and above. This is in agreement with the observations made on SEM examinations, which showed the presence of more microcracks in UA copolymers involving PPG 1 in the AUO blends. Both the copolymers containing PPG 1 (i.e. HP 142 and HP 143) exhibited lower elongation at break than UA copolymers not having PPG 1. The crosslink network had resulted in a “forced” compatibility between the hard and the soft segments, producing an interdependency of the mechanical properties on the soft segment and hard segment.

The above trends were not seen in UA copolymer based on SHP 142. Hence, it appeared that the method of producing UA copolymers having more than one PPG molecular weight type would also influence the tensile properties. When the copolymers were produced from NCO-prepolymers, that were already made up of polyol blends, prior to converting into the corresponding AUOs (e.g. S-Prep 142), not much difference in the mechanical properties were observed as compared to those based on single narrow PPG molecular weight; except for a slightly better yield strength. This is believed to be related to less differences in the PPG chain length for AUOs produced by this method and therefore less differences in reaction preference of the varies AUO units with MMA.

Generally, copolymers with same average polyol length will have comparatively lesser differences in their mechanical properties than when comparison is made between copolymers having different average polyol length. Hence, at the same MMA content, the polymer strength was observed to decrease in the order: HP 1 > HP 2, SHP 2, HP 142 > HP 143, HP 243 > HP 4. In TDI HP2, less rigidity resulting from the use of TDI instead of MDI could explain for the lower tensile strength of former, without affecting the elongation at break.
5.2.6 Morphological Studies

From the copolymer perspective, nearly all copolymerisations involved some degree of phase separation resulting from basic chemical incompatibility while synthesis method can greatly control the degree of phase separation such as in graft copolymers, block copolymers and interpenetrating polymer networks (IPN’S) [195]. The positions of the Tgs (obtained from e.g. DSC or DMTA analysis) of the respective components are often used as an indication of the relative degree of phase separation or compatibility in a system. The existence of a single Tg, or close Tg value representative of individual phases (i.e. broad transition behaviour) reflects a compatible or semi-compatible system respectively [154, 185, 187, 195]. However, the ability to detect the transitions of a multi-phase systems is often dependent on the sensitivity of the equipment used (i.e. particularly its sensor system). Hence, a polymer may be found to be incompatible by one method while showing compatibility in another [154, 186]. In this section, the results from the DSC, DMTA and SEM studies are employed to provide a better understanding of the copolymers' morphologies.

5.2.6.1 DSC Study

DSC study on the UA copolymers showed a general lack in thermal response. This made interpretation of the DSC thermograms difficult. Such problems have also been experienced by other workers working on urethane-acrylic systems [121]. Nevertheless, the thermograms did reveal the existence of a few minor transitions, indicating the possibility of a “multi-phase” system.

In DSC thermograms of the MMA based UA copolymers, three transitions (T₁, T₂ and T₃) were observed over the scanning temperature range of -100 °C to 200 °C (see Figures 5.13 to 5.16, Table 5.7). Several repeated analyses of specific UA copolymers had confirmed the existence of a low temperature transition (T₁), an endotherm peak at around 60 °C (T₂, onset at about 50 °C), and an endothermic transition at about 170 °C (T₃). The latter two transitions were obvious only for samples analysed for the first time. With UA copolymers based on HP 1, it was found that the low temperature
transition (at around 0 °C) was very close to that observed at around 50 °C, portraying a broad transition starting from around 0 °C to the endotherm peak (see Figure 5.13). As mentioned earlier, this was indicative of a relatively more compatible system than copolymers having the Tgs wider apart.

The low temperature transition, T₁, was obviously associated with the polyol components as it was found to be dependent on the PPG soft segment length. Melting endotherms at around 60 °C were initially thought to be due to vapourisation of acrylate monomers trapped within the copolymers because:

I) The area of the endotherm peak appeared to increase with the MMA content of the copolymers.

II) On repeat scanning and in thermograms of the conditioned samples (where the scanning temperature ranged from -110 °C to 100 °C), this endotherm peak disappeared.

However, DSC thermograms of PMMA samples that had been conditioned at 100 °C for 1½ hours and 40 °C for 14 hours (see Section 3.6.7) also showed endotherm peaks at about 60 °C (see Figure 5.18). This indicated that methacrylate monomers vapourisation was not the main cause. The endotherm seen was believed to be caused by enthalphic relaxation of the methacrylate chains as a result of closer chain organisation [private communication]. In the immediate rerun trace of the PMMA sample, the endotherm peak was replaced by a transition, showing that the chain organisation took place over a period of time.

With UA copolymers, the immediate rescan sample did not appear to show any sign of transition at that temperature range. However, the conditioned sample showed a transition (Tg) having onset temperature at about 50 °C (see Figure 5.18). If this endotherm was attributed to the methacrylate component, then the absence of this endotherm in these samples could be due to:
a) difficulty in aggregation of the participating species (that were responsible for the endotherm) in the cross-link system. On this note, it should be mentioned that DSC experiment conducted on the UA copolymers was done over a spread of 2 to 3 months after the cast date (due to equipment being heavily booked). The samples were stored in the dark during this period.

b) the PMMA chain being too short to show much thermal response in the absence of aggregation which may have broken up during the first scan.

c) lack of sensitivity of DSC for detecting hard segment especially in a crosslink system.

The much lower Tg (i.e. at around 50 °C) of the PMMA sheet casted in this work as compared to that of the commercially available PMMA (i.e. at 105 °C), had indicated that the PMMA chains formed here were of rather low molecular weight.

The third transition (T₃) occurring at around 160-170 °C was believed to be associated with the hydrogen bonding forces in the system since the samples did not show sign of degradation at the end of the test. It was observed to be more significant in DSC thermograms for UA copolymer based on HP 1. This transition could also be found in crosslinked PUs. In fact, it was more significant in the latter, and hence indicating the existence of a more intensive hydrogen bonding system. This study has confirmed IR results on the existence of hydrogen bonding in the crosslinked UA copolymers.

The presence of transitions corresponding to the soft and hard segments in the UA copolymers had indicated the existence of a two phase system. Comparing DSC thermograms of UA copolymers to that of the crosslinked PUs (see Figures 5.18 on X-PU 1 and X-PU 2), the soft segment Tgs of the UA copolymers were observed to be close to the low temperature Tgs of the corresponding crosslinked PUs. These again were indicative of the possibility of a non-mixed phase in the UA copolymer system.
The thermograms of conditioned samples of HP 4 M100 indicated a shift in the low temperature transition from -51 °C to -58 °C. A similar result was obtained upon repeating the test. This shift was not obvious with the HP 1 samples. In a system that was capable of phase separation but which was incomplete in phase separation, a thermal conditioning would encourage further phase separation. This would be shown by the increasing differences in Tgs of the individual phases [154]. DSC study on the conditioned samples of HP 1 and HP 4 showed that the latter was capable of undergoing further phase separation from the shift in the low temperature Tg to an even lower value. This is probably due to greater chain mobility with lower degree of crosslinking in the HP 4 based UA copolymers. The Tgs of the hard segments showed little change. This could be due to difficulty in detecting small changes, that may have occurred, by DSC.

The transition temperatures of UA copolymers based on BMA were unclear but the transition near 170 °C was obvious (see Figure 5.20). However, DSC traces of the conditioned samples of HP 2 B60, HP 2 B100 and HP 1 B100 (at scanning temperature between -100 °C and 100 °C) showed two transitions at temperatures around -50 °C and -10 °C (see Figure 5.21). These indicated the presence of a two phase system in the BMA based UA copolymers. Transition temperature (i.e. Tg) for PBMA is at around 6 °C. Hence, the shift in this transition to -10 °C in the UA copolymer system indicated that BMA chains were more “compatible” with the polyol soft segment chain than the MMA chains. Comparison of the transition observed at 170 °C with that found in the MMA based UA copolymer had indicated a relatively stronger hydrogen bonding system in the BMA based copolymers. This showed that greater chain flexibility of the latter system had resulted in better chain interaction.

5.2.6.2 DMTA

In the DMTA analysis, tan δ curves are often used in preference to the loss modulus, E", peaks in determining the glass transition temperatures as the area under tan δ curve reflects the true relative proportion of the components (of a system) participating in the transitions [35, 41, 49, 54, 137, 161, 163]. In this study, both the tan and the loss
modulus plots were used for reason to be explained in the next two paragraphs. Storage modulus, $E'$, plots were not used for discussion here as changes in modulus at the transition temperatures were rather difficult to detect (see Figures B.10 and B.11 in Appendix B).

Generally, the tan $\delta$ and loss modulus plots of MMA based UA copolymers were found to exhibit broad transition behaviours (an indication of a semi-compatible system, see Figures 5.23 to 5.31) while those of the crosslinked PUs and PMMA showed narrow transition behaviour, indicated a single phase system (see Figures 5.22 and 5.23 respectively). With the UA copolymers, the tan $\delta$ curves appeared to consist of at least two overlapping curves: the first curve appearing as shoulders on the low temperature side of the tan $\delta$ curves, and the second curve forming the tan $\delta$ peak. As the shoulders of the tan $\delta$ curves were found in the temperature region near the tan $\delta$ peak of the respective crosslinked PU, this indicated that the shoulders were related to the polyol component of the copolymers (e.g. see Figure 5.24). The tan $\delta$ peaks (i.e. of UA copolymers), on the other hand, were found in temperatures near to tan $\delta$ maxima of PMMA and was therefore related to the acrylic components.

In the loss modulus plots, the $E''$ curves were also unsymmetrical and in some cases, the present of shoulders on the high temperature side were noted especially when the acrylic content was increased (e.g. see Figure 5.24). As can be seen, the loss modulus component of the urethane (or polyol) soft segment is more prominent than the acrylic component in the loss modulus plots. This showed that the loss modulus plots of the copolymers were more biased towards its urethane components. As it was difficult to locate the position of the shoulder peaks in tan $\delta$ curves, $E''$ maxima of the UA copolymers were chosen in this study to reflect on the response (ie. transition behaviour) of the urethane component to the synthesis variables.

Not surprisingly, likewise with the DSC results, DMTA data (see Table 5.101) also showed that the polyol chain length had a significant effect on the low temperature properties of the copolymers with $E''$ maxima shifting to a lower temperature as soft
segment length was increased. Increased incompatibility, as indicated by the widening temperature gap between the shoulders and the curve maxima in both tan $\delta$ and loss modulus plots, was observed in systems with longer polyol chain length. However, a corresponding decrease in the tan $\delta$ was also observed, showing that the increased incompatibility was not due to improved phase separation but more likely to be due to greater differences in chain flexibility between the acrylics and the polyol segments. This is because, when a ‘multi-phase’ system undergoes phase separation, the Tgs of the respective phase should approach that of its pure form [54, 154]. That is, in this case, the Tg of the soft segment should approach that of the polyol soft segment, while that of the hard segment towards the Tg of the PMMA homopolymer (which is around 70 °C for tan $\delta$ peak).

Increasing MMA content also did not appear to encourage phase separation. Beside producing a slight increase in the tan $\delta$ maxima temperature, it also caused a corresponding slight increase in the $E''$ maxima temperature (see Table 5.10 I and II). This is believed to be due to increased chain stiffness of the hard segment, probably resulting from increased PMMA chain length between two crosslink points. Since the UA copolymers are crosslinked systems, this increase in hard segment chain stiffness is passed on to the polyol chains attached to it, and therefore causing a corresponding increase in the soft segment Tg. The increase in tan $\delta$ peak temperature was slight because the expected increase in the chain length (from calculation) was also slight (see Table 5.12). This could be the reason why in DSC thermograms, the transition representing the hard segment, observed at around 50 °C, remained unchanged regardless of the MMA content; i.e. DSC is not sensitive enough to detect the slight change in transition temperature of the short PMMA chain. According to this calculated chain length, the tan $\delta$ maxima temperatures of the UA copolymers at the same phr of MMA should be in the order HP 1 < HP 2 < HP 4. However, the data obtained showed the tan $\delta$ temperature of HP 1 to be higher than HP 2 and HP 4. Again, this showed that the Tgs of the hard segment (i.e. namely the MMA chain) were influenced by the flexibility of the soft segment PPG chains (i.e. its surrounding).
The loss modulus plot of MMA based UA copolymers having PPG molecular weight of 1000 showed a nearly symmetrical curve at low methacrylate content (e.g. HP 1 M60, see Figure 5.24). Such curve was indicative of a compatible system in which the hard and soft segments are inter-mixed with each other. However, at high MMA content, as in HP 1 M100, the loss modulus plot revealed the presence of a shoulder curve on the high temperature side (at about 55 °C). Obviously, this extra curve was related to the increasing presence of the hard segment component. Such a finding can have the following implications:

I. The system is a one phase system, capable of undergoing phase separation at high MMA content.

II. The system is a two-phase system. However, in UA copolymer based on PPG 1, the polyl chains being shorter, were also stiffer as a result of the crosslinked network. As such, the methacrylate hard segment was more compatible with the soft segment in term of chain stiffness than with the soft segment of UA copolymer based on higher PPG molecular weight (as in for example, HP 4 M60). Hence, the observed DMTA curves. At higher MMA content, e.g. at 100 phr, increased rigidity of the hard segment had increased the difference in chain stiffness between the hard segment and the soft segment. This was reflected as an extra peak in the loss modulus, $E''$, curve.

DSC results of the conditioned sample of HP 1 M100 did not show any sign of the hard segment Tg shifting to a lower temperature (see Table 5.9) upon quench cooled. This indicated that the second implication was more likely to the case. This was further supported by SEM micrograph of HP 1 M100, fractured at subambient temperature, showing a homogenous fracture surface (see Figure 5.41).

As with increasing MMA content, introducing more HPMA or MDI resulted in increased area of the tan $\delta$ peak and increased significance of the shoulders on the $E''$ curves. Slight increase in tan $\delta$ and $E''$ maxima temperatures were observed when excess of these were used. This indicated that these molecular components were more compatible with the hard segments than with the soft segments (see Figures 4.36 and
4.37). The effects of increasing MDI or HPMA content can be related to their influence on the polyol chain length in terms of relative amounts of chain extended products. In the case of HPMA, hard segments with increased HPMA content also increased chain rigidity which, in turn, produced more restriction on the polyol chain.

Changing isocyanate structure from that of MDI to TDI showed a significant reduction in tan δ maxima temperature of the UA copolymers, indicating that isocyanate structures had a strong influence on the hard segment rigidity (see Table 4.7). Again, the isocyanate component was found to be more compatible with the MMA hard segment. The $E''$ maxima remained relatively unchanged because the less rigid TDI was not producing much chain stiffening effect on the polyol chain.

It was found that for UA copolymers based on polyol blends, at low MMA content, the polyols appeared to exhibit closer compatibility from the single broad $E''$ peak obtained (see Figures 5.27 and 5.28). However, at 100 phr MMA content, several overlapping peaks were observed. These were possibly representative of the respective polyol components. For example, in the more obvious case of HP 143, the $E''$ curve of HP 143 appeared to consist of 2 curves with the first curve having a peak at around -40 °C, and the second curve at around -5 °C (see Figure 5.28). In additional, a shoulder at the extreme end of the $E''$ curve, attributed to the acrylic component, was also observed. This showed that incompatibility, as interpreted from the non-symmetrical curves, could also arise among the soft segments derived from different molecular weight polyols. It is believed that at high MMA content, with more MMA monomeric units being available for chain formation with each AUO units, the AUO chains would be further separated. This had allowed the different AUO chain lengths to be detectable as an individual unit, each experiencing a different degree of chain stiffening by the MMA chains that separated them. The implications are:

1. The urethane components do not have the tendency of aggregating into a common urethane domain having an average $T_g$ of the two soft segments.

2. The crosslinked system did not encourage phase aggregation.
3. DMTA is a sensitive method for detecting the presence of the individual components which may not be in aggregates.

As in earlier discussion, the higher tan δ maxima temperatures observed for polyol blends using lower PPG molecular weights were deduced to have resulted from the additional reinforcement effect produced by the short PPG chains on the hard segment (see Table 5.10I). The DMTA analysis was in agreement with earlier discussion on the mechanical properties of the UA copolymers based on polyol blends (see Section 5.2.5).

In Figure 5.33I and II, the tan δ and E'' curves of the BMA based UA copolymers, being generally more symmetrical and narrower than their corresponding MMA series, were also typical of compatible systems. However, from earlier DSC work, this is believed to be due to proximity of tan δ and E'' maxima values between the hard and the soft segments of the BMA copolymers rather than improved phase mixing. In fact, slight asymmetry of the E'' curves of UA copolymers based on HP 2 series were still noticeable.

In Figure 5.32, it can be seen that replacing MMA with equivalent molar proportion of BMA caused a shift in the tan δ peak to lower temperatures. There was no sign of overlapping of curves or presence of a shoulder at the high temperature end to indicate incompatibility between MMA and BMA, since only one tan δ peak representing the hard segment components was found. It is certain that the BMA and MMA produced compatible homopolymer chains.

In a study made on the thermally conditioned samples of UA copolymers: HP 1 M100 and HP 4 M100, DMTA thermograms of these samples that had been cooled slowly to room temperature showed a slightly higher tan δ peak temperature (see Table 5.11). Since DSC thermogram of HP 4 M100 had also indicated a shift in the low temperature transition from -51 °C to -58 °C, it was deduced that the slight increased in tan δ peak temperature tan was probably due to some slight aggregation /
reinforcement of the hard segment phase. The DSC thermogram for similarly thermal treated HP 1 M100 sample did not show any change in the soft segment Tg. Hence, the increase in tan δ temperature observed in this sample could have probably resulted from improved curing. No changes were observed in E" maxima temperature. This is believed to be associated with the sensitivity of the DMTA equipment. In the quench cooled samples, the lower tan δ maxima temperatures observed were indicative of a less reinforcing MMA phase, which could not be detected in the DSC thermograms, (hard segment transition in the immediate repeated DSC scan was not found).

It has been noted that as Tg determined by DMTA technique is both frequency and heating rate dependent, it will therefore not correspond to Tg determined by static techniques such as DSC or dilatometry [149].

5.2.6.3 Electron Microscopy

SEM studies on samples fractured at room temperature (see Figures 5.34-5.37) revealed little information on the extent of phase separation. In the MMA based UA copolymers, microcracks were seen on the fractured surfaces. The relative amount of these microcrack lines could be related to relative brittleness of the copolymers. More cracks were found at higher MMA content or as the polyol segment length decreased, reflecting a more brittle system. It is believed that other than being caused by an increased in the MMA content, the relative amount of these microcracks formed were also associated with the ability of the urethane components to re-adhere (this is related to the PPG chain mobility, i.e. less microcrack will be formed with better PPG chain flexibility). Accordingly, SEM studies showed that less flexible polyol chains were encountered under the following conditions (see Figure 5.35):

1. UA copolymers involving the use of PPG 1. For example, in UA copolymers based on polyol blends, UA copolymer based on HP 143 had more cracks than that based on HP 243 at the same MMA content.

2. increasing MMA content or the amount of excess isocyanate or HPMA
3. using MDI instead of TDI

4. using higher MMA / BMA ratio (see Figure 5.36)

These copolymers also appeared to have lower adhesion /cohesion strengths. No cracks were observed in UA copolymers based on BMA, indicating a flexible system (see Figure 5.37). These findings were in full agreement with earlier DMTA analysis work.

In SEM micrographs of samples that were fractured at sub-ambient temperatures, interpretations of the micrographs were based on the ability of the individual components to recover when these were brought to room temperature. In Figure 5.40, typical micrograph of the fracture surface of a PMMA sample showed great unevenness, with obvious ripples and wedges. In comparison, the PU samples showed a much smoother, silky-like fracture surface appearance. This was interpreted as the ability of the crosslinked PU to recover after brittle fracture at subambient temperature. A comparison of the micrographs of MMA based UA copolymers (see Figure 5.41) with these micrographs indicated the possibility that the wedges and ripples observed in certain MMA based-UA copolymers (i.e. HP 4 M60 and HP 4 M100) might had arisen from differences in the 'texture' of these regions as compared to its surroundings. It is believed that these regions were more rigid than the rest, and was not able to recover as much as the rest when the samples were brought to room temperature. Hence, these regions were likely to be attributed to the stiffer components of the copolymer, namely the methacrylate components.

The various micrographs taken on the MMA based UA copolymers had revealed that better homogeneity in fracture appearance was observed in UA copolymers based on lower molecular weight polyol soft segment. For example, in UA copolymer based on PPG 1, a 'homogeneous' roughness appearance was observed, indicating a very even mix of the hard segment (namely acrylate) with the soft segment PPG. The higher chain stiffness of these shorter polyol chains probably also had an influence on the fracture appearance. Here, the polyol chain would has lesser ability to recover from
the fracture due to its stiffer chain, as well as to a higher crosslinked network. This produced a fracture appearance close to that produced by the methacrylate component. Homogeneity was still observed in UA copolymer having higher MMA content (i.e. HP 1 M100). This supported DTMA analysis: that is, extra shoulder curve observed in loss modulus plot of HP 1 M100 was not due to better phase separation.

In HP 2 M60 and HP 2 M100, the fracture surfaces were also generally homogenous but less "rough" than UA copolymer based on HP 1. According to the above analysis, the polyol chains (i.e. PPG 2) were able to recover better than that of PPG 1. As can be seen, no phase separation was observed, although there might be some wedges present. This could be due to increased MMA to AUO molar ratio (see Table 5.12). Comparing this with the TDI based sample (Figure 4.68), a more homogeneous fracture appearance was seen with the latter. This agreed well with earlier findings about TDI not being able to produce as much chain stiffening effect as MDI.

In HP 4 M60 and HP 4 M100, the wedges became more obvious. In fact, at 100 phr MMA content, it appeared that there was a possibility of a two-phase system, as deduced from the increasing presence of the wedges. However, it was believed that this could be due to a greater tendency of MMA homopolymerisation to form a longer methacrylate chain, rather than to phase aggregation of the individual segment type. Such effect was expected to be further encouraged by the system being relatively more dilute (i.e. lower viscosity), having lower hydrogen bonding, longer induction period and increased MMA to AUO molar ratio (i.e. more MMA to double bond ratio), as compared to system based on lower PPG molecular weight. Further support also came from the DMTA study, which implied a lack of phase aggregation as seen from the interdependency of the soft and hard segments transition temperatures. IR studies had also indicated that the hydrogen bonding species were further apart in the crosslink system. This had indirectly implied a lack of chain aggregation.

It is believed that phase separation, (if it happened), for the UA copolymers could only occur during the induction period. However, the monomers and the oligomers were
observed to show good miscibility and did not exhibit obvious phase separation even when kept overnight. This also indicated that physical separation prior to setting, which was achieved at a very fast rate, was not likely to occur. In addition, the solvent extraction test had also indicated a successful copolymerisation between the oligomers and the monomers. Clear products were obtained from these copolymers, supporting further the lack of phase aggregation in the systems.

The fracture surfaces of BMA based copolymers were found to be much smoother, probably because PBMA component itself is more flexible than the PMMA. The "ripples" in copolymer based on PPG 2 were also wider apart than those based on PPG 1, probably due to increased polyol chain length and flexibility. It is believed that the polyol segments and the acrylate segments still existed on their own without obvious phase aggregation.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS
Cure-rate Measurements

The influence of the reactants on the total curing time of UA copolymers were dominated by their effect on the induction period rather than on the setting time. In this respect, the reactivities of the AUOs and the methacrylate types, rather than the methacrylate content, were the main influencing factors. The influence of the methacrylate content on the induction period was significant only when the reactivities of the AUO or the methacrylate were relatively much lower. The setting time of the UA copolymer system was very fast and was generally not influenced much by the above factors.

Solvent Extraction

The low percentage of extract obtained for the various copolymers, indicated a successful copolymerisation between MMA (or BMA) monomers and the AUOs. The crosslink densities of the copolymers were determined by the available double bonds contributed by the AUOs. The MMA content had little influence on this.

Mechanical Property Assessment

I. The mechanical properties of copolymers based on single PPG molecular weight type were determined mainly by the average molecular weight of the polyol. Copolymers based on high polyol molecular weight exhibited low strength due to the low crosslink density and reduced hard segment reinforcement effect. However, they gave good flexibility and adhesion properties. Toughening of such copolymer system could be achieved through incorporation of an appropriate hard segment types, methacrylate or isocyanate types.

II. The amount of isocyanate and HPMA used could influence the mechanical properties of the copolymers only when these were in excess of 15% (or greater). The resultant increase in mechanical strength are attributed to reduced chain extended products in the AUOs. This also caused an increased chain stiffening effect exerted on a relatively shorter polyol chain.
III. Dependence on the method of producing UA copolymers involving polyol blends: such copolymers have better mechanical properties than those based on single polyol molecular weight type of equivalent average chain length. The mechanical properties of such systems also showed greater dependence on the MMA content.

Morphology Studies on UA copolymers

Morphology studies based on DSC, DMTA and SEM had indicated the presence of two-phase systems in the UA copolymers. This was due to the soft and hard segments domains being sufficiently large enough to be detected rather than to phase aggregation. The two-phase morphology was relatively easier to detect in UA copolymers based on higher polyol molecular weight. In UA copolymers based on oligomer HP 4, the increasing presence of hard segment concentration as observed from SEM examination, was probably due to a higher tendency for MMA homopolymerisation in a lower viscosity system. Conclusions drawn from the various experiments related to these studies were:

I. DSC and IR Studies

. DSC thermograms of MMA and BMA based systems showed two Tgs, indicating the presence of two phase systems.

. Both IR and DSC indicated the presence of hydrogen bonding. IR analysis indicated that hydrogen bonding was probably stronger in BMA based systems. This had been ascribed to the flexibility of the system enabling closer chain interactions.

II. DMTA Analysis

. The hard segment Tg was very much influenced by the types of isocyanate used.

. Using excess MDI or HPMA increased both the hard and soft segments Tgs. Increasing MMA content increased the hard segment Tg but it also caused a
corresponding increase in the $E''$ peak temperature. These showed that the chain stiffness of these segments were interdependent.

- Increasing differential of Tgs between the soft and hard segments at increasing polyol molecular weight was attributed to increasing differences in chains flexibility between the two segments. DMTA plots showing narrower curves were attributed to better compatibility of the two segments in term of chain stiffness.

- For copolymers based on polyol blends, the Tgs of the various polyols molecular weight type could even be detected when the MMA content was sufficiently high. This had again proved that the system did not exhibit phase aggregation.

- UA copolymers based on higher polyol molecular weight (as in e.g. HP 4 M100) were capable of undergoing limited hard segment phase reinforcement when subjected to appropriate thermal conditioning. The reduction in tan $\delta$ peak temperature in a sample that had been heated and quenched cooled had indicated a less organised state.

### III. SEM

- Polymer samples based on lower molecular weight polyols or increasing MMA content were more brittle, producing more microcracks in the fracture surface.

- MMA based UA copolymers based on shorter polyol chains showed homogenous fracture appearance when fractured at sub-ambient temperature. This was ascribed to a stiffer polyol chain having closer compatibility with the methacrylate chain. It had also illustrated a higher degree of stiffening effect produced by the MMA on shorter polyol chain.

- The presence of wedges in copolymers based on longer polyol chains illustrated a relatively more phase separated system. These wedges reflected a more brittle fracture, probably due to a higher methacrylate concentration.
6.2 Recommendation for Further Work

The project could be extended to include the following work:

I. Solvent extraction test has shown the systems to be capable of high crosslink density with the use of mono-functional monomers, the effect of introducing multi-functional monomers on the crosslink density and mechanical properties of the copolymers is worth examining into. This may lead to a way of increasing the mechanical strength of copolymers based on oligomer HP 4, which has the lowest intermediate viscosity.

II. To explore use of multi-functional polyol or methacrylate components, and the different in the effects produced by these variables on the copolymers produced.

III. To study the effect of using polyol components of different molecular structures, molecular weights and abilities to contribute to hydrogen bonding (such as polyester, polybutadiene, etc.) on the intermediates viscosities and the corresponding UA copolymer properties.

IV. To explore into use of other vinyl monomers (or combination of vinyl monomers to produce the desired hard segment effect) that may be cheaper, readily available, etc.

V. Conditioned sample of HP4 M100 showed possibility of slight phase aggregation. Previous work [10] had shown improved mechanical properties when a similar UA copolymer system (but which contained multi-functional acrylic monomers) were subjected to aging at 85 °C for 7 days. In order to further confirm whether the improvement in mechanical properties was attributed to phase aggregation, (which had been claimed by some other researchers), or was due to improvement in crosslink network, a measurement of the crosslink density of the conditioned sample and its mechanical properties might probably be helpful. Methods aimed to achieve phase separation by probably using methacrylate oligomers could be explored so as provide a study on the effect of phase separation on the final copolymer properties.


References


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157. Operating Manual on DMTA from Polymer Laboratory.

158. Operating Manual on Du Pont 983 DMA.


   - Structure-Property Relationships of Polyurethanes Based on Toluene Diisocyanate by C. S. Paik Sung and N. S. Schneider.
   - Effect of Annealing on the Morphology and Properties of Thermoplastic Polyurethanes by C. H. M. Jacques


SAMPLE CALCULATIONS

1. Quantities of reactants required in synthesis of NCO-prepolymer.

A) Example: synthesis of Prep 4

PPG 4:

\[ \text{OH value} = 27.28, \]
\[ \text{equivalent weight} = \frac{56100}{27.28} \]
\[ = 2057 \]

MDI:

\[ \text{equivalent weight} = \frac{\text{molecular weight} + 2}{2} \]
\[ = \frac{250 + 2}{2} \]
\[ = 125 \]

At NCO/OH molar ratio of 2:1,

Iso index 100:

PPG 4 required = 1 x 2057 g
MDI required = 2 x 125 g
= 250 g

Iso index 105:

Actual amount of MDI used = 1.05 x 250 g
= 262.5 g
B) Example: synthesis of 'S-Prep 142' (i.e. using polyol blends):

Equivalent weight of PPG 1 = 555
Equivalent weight of PPG 4 = 2057

Let X be the number of moles of PPG 1 needed to blend with 1 mole of PPG 4 to give a blend with average PPG soft segment equivalent weight equal to that of pure PPG 2 (i.e. 1102.2).

\[
\frac{X \times 555 + 2057}{X + 1} = 1102
\]

i.e. For 2057 g of PPG 4,

\[
(1.743 \times 555 \text{ g}) = 967 \text{ g of PPG 1 is needed.}
\]

At NCO/OH ratio of 2:1,

MDI required = MDI required by PPG 1 + MDI required by PPG 4
\[
= \frac{2 \times 125 \times 967}{555} \text{ g} + 2 \times 125 \text{ g}
\]

\[
= 686 \text{ g}
\]

Alternatively,

1102 g polyol PPG 2 requires 2 x 125 g MDI,

\[
(2057 + 967) \text{ g of polyols (i.e. PPG1 + PPG 4) requires}
\]

\[
= \frac{2 \times 125 \times (2056.5 + 966.8)}{1102.2} \text{ g}
\]

\[
= 686 \text{ g of MDI}
\]

At iso index 105,

Actual amount of MDI used = 686 g x 1.05
\[
= 720.0 \text{ g}
\]
2. Expected NCO content in NCO-prepolymers.

The amount of free NCO available in every 100 g of a compound or prepolymer is expressed as the % NCO content. Hence,

For MDI:
\[
\text{% NCO content} = \frac{\text{molecular weight of NCO}}{\text{molecular weight of MDI}} \times 100 \%
\]
\[
= \frac{42 \times 2}{250} \times 100 \%
\]
\[
= 33.6 \%
\]

For 'Prep 4' at iso index 100:
\[
\text{% NCO content expected} = \frac{42}{(2 \times 125) + 2056.5} \times 100 \%
\]
\[
= 1.82 \%
\]

When 5% excess of MDI is used, free NCO contributed by this excess amount of MDI will be:
\[
33.6 \% \times \left[ 5 \% \text{ of } (2 \times 125) \right] = 4.2 \text{ g}
\]

Hence, at iso index of 105,
\[
\text{% NCO content expected} = \frac{42 + 4.2}{(2 \times 125) + 2057 + \text{the excess MDI}}
\]
\[
= \frac{46.2}{2307 + 12.5}
\]
\[
= 1.99 \%
\]
3. Relative quantities of respective AUO types used in UA copolymers based on AUO blends.

Example HP 142:

**Step I:** Determination of corresponding AUO weight obtained from 2057g of PPG 4 and 555g of PPG 1, at iso index of 105

For NCO-prepolymer based on PPG 4,

theoretical expected NCO content = 1.992%

weight of NCO-prepolymer obtained from reacting 2057g of PPG with MDI

= \( (2057 + 263) \text{ g} \)

= \( 2319 \text{ g} \) (see above, 1A)

Amount of HPMA required for converting 1 equivalent mole of PPG to AUO:

\[
= \frac{\text{equivalent weight of PPG + MDI}}{42} \times 0.01992 \times 144 \text{ g}
\]

\[
= \frac{(2056.5 + 250 + 12.5) \times 0.01992}{42} \times 144 \text{ g}
\]

= 158.4 g of HPMA

Weight of corresponding AUO (i.e. HP 4)

= \( (2057 + 262.5 + 158.4) \text{ g} \)

= \( 2478 \text{ g} \)

Similarly for 555 g of PPG 1, amount of HP 1 obtainable:

= \( (555 + 420.9) \text{ g} \)

= \( 976 \text{ g} \)
Appendix A

Step II: Determining relative amount of HP 1 and HP 4 required to produce AUO having average PPG soft segment length equivalent to that based on pure PPG 2.

To obtain PPG blends with average equivalent weight of 1102 g, we need 2057 g of PPG 4 to 967 g of PPG 1 (refer to above, 1B).

The corresponding AUO weights obtainable are:

For 2056 g of PPG 4 $\rightarrow$ 2056 g + 420.9 g = 2478 g of HP 4

For 967 g of PPG 1 $\rightarrow$ 967 g + $\frac{420.9 \times 967}{554.7}$ g = 1700 g of HP 1

Hence, ratio of HP 4 to HP 1 required = 2478 : 1700 = 1.46 : 1
4. Curing agent required to react with the free isocyanate in NCO-prepolymers.

Example: 500 g of 'Prep 4' with actual NCO content being 1.94 % instead of the theoretical value of 1.99 %,

amount of isocyanate groups present = 0.0194 x 500 g
= 9.7 g

A) to react with glycerol (in synthesis of crosslinked PU),

\[
\text{equivalent weight of glycerol} = \frac{\text{molecular weight}}{\text{functionality}} = \frac{92}{3} = 30.7
\]

42 g of NCO groups would require 30.7 g of glycerol

\[
\therefore\ 9.7 \text{ g of NCO groups would require } \frac{30.7 \times 9.7}{42} \text{ g}
\]

= 7.1 g of glycerol.

B) to react with HPMA (in synthesis of AUOs),

\[
\text{equivalent weight of HPMA} = 144
\]

\[
\therefore\ \text{for 9.7 g of NCO groups, amount of HPMA required} = \frac{144 \times 9.7}{42}
\]

= 33.3 g
5. **BPO and DMPT required for a copolymer synthesis, eg. HP 4 M100.**

**Step I : Determination of HPMA content in HP 4 oligomers**

Let Y be the weight of prepolymer before reacting with HPMA

If % NCO content of the prepolymer = 1.99 %,
then in 100g of the AUO, the amount of HPMA present is:

\[
100 \text{ g} = Y \text{ g} + \left( \frac{0.0199 \times Y \times 144}{42} \right) \text{ g}
\]

\[
= Y \text{ g} + 0.0682 Y \text{ g}
\]

\[
Y = \frac{100}{1.0682} \text{ g}
\]

\[
= 93.6 \text{ g}
\]

\[
\therefore \text{ HPMA content in the AUO} = (100 - 93.6) \text{ g} = 6.4 \text{ g}
\]

**Step II : Determination of BPO/DMPT requirements in eg. HP 4 M100 based on 100 g of HP 4**

Total methacrylate content contributed by MMA and HPMA

\[
= 100 \text{ g MMA} + 6.4 \text{ g HPMA}
\]

\[
= 106.4 \text{ g}
\]

The amount of BPO required (which is at 4 phr of total methacrylate content)

\[
= 0.04 \times 105.8 \text{ g} = 4.232 \text{ g}
\]

The amount of DMPT required (which is at 2 phr) = 4.232 + 2

\[
= 2.116 \text{ g}
\]
6. Calculation for converting weight ratio to molar ratio

<table>
<thead>
<tr>
<th>Reference for methacrylate content:</th>
<th>Methacrylate content (g):</th>
<th>Corresponding no. of moles of methacrylate:</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>BMA</td>
<td>MMA</td>
</tr>
<tr>
<td>M 60</td>
<td>B60</td>
<td>600</td>
</tr>
<tr>
<td>M 80</td>
<td>B80</td>
<td>800</td>
</tr>
<tr>
<td>M 100</td>
<td>B100</td>
<td>1000</td>
</tr>
<tr>
<td>M 120</td>
<td>B120</td>
<td>1200</td>
</tr>
</tbody>
</table>

Molecular weight of MMA = 100g
60g of MMA = 0.6 mole

For UA copolymer HP 1 M60,
composition consists of 100g of HP 1 to 60 phr of MMA.

100g of HP 1 will contain approximately 100 + 975.6
= 0.0513 mole of HP 1 unit.

Hence, the number of moles of MMA monomers available for 1 mole of HP 1 unit will be:

\[ \frac{0.6 + 0.513}{1} = 11.7 \text{ moles} \]
7. Activation energies of viscous flow for AUOs.

Arrhenius equation:

\[ \eta = \eta_0 \exp \left( \frac{E}{RT} \right) \]

\[ \ln \eta = \ln \eta_0 + \frac{E}{RT} \]

where:

- \( \eta \) = viscosity
- \( E \) = "activation energy of flow"
- \( R \) = molar energy constant (i.e. gas constant = 8.314 J K\(^{-1}\) mol\(^{-1}\))
- \( \eta_0 \) = viscosity at a convenient base temperature, \( T_0 \)

From graph of \( \ln \eta \) versus \( T^{-1} \) (refer graph 4.1), gradient of the slope = \( \frac{E}{R} \)

Example: HP 4 oligomers,

gradient of the slope (taken from equation: \( y = -6.318 + 5017x \)) = 5017

Activation energies, \( E \), for viscous flow = 5017 \( \times \) \( R \)

\[ = 5017 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ = 41.7 \text{ kJ K}^{-1} \text{ mol}^{-1} \]
Figure B.1: Typical I.R. spectrum of PPG polyol.

Figure B.2: Typical I.R. spectrum of NCO-prepolymers.

Figure B.3: Typical I.R. spectrum of acrylated-urethane oligomers (AUOs).
Figure B.4: I.R. spectrum of Hydroxyl propyl methacrylate.

Figure B.5: I.R. spectrum of crosslinked PU (TDI-X-PU 2).
Figure B.6: I.R. spectrum of urethane-acrylic copolymer (HP 1 M60).

Figure B.7: I.R. spectrum of P(MMA).
Figure B.8: Synthesis of AUO\textsubscript{s} (HP2); using I.R. technique to follow reactions.
Figure B.9: Typical DSC thermograms for polyols, isocyanate and acrylated-urethane oligomers used in this project.
I. UA copolymers based on HP 1, at varying MMA content.

II. UA copolymers based on HP 2, at varying MMA content.

Figure B.10: Typical DSC thermograms of MMA based UA copolymers.
III. UA copolymers based on MMA / BMA mixture.

IV. UA copolymers at various isocyanate index.

Figure B.10 (cont’d)
(i) Storage modulus, $E'$

![Graph showing storage modulus, $E'$, for HP 4 M60 and HP 4 M100 across different temperatures.]

(ii) Log $E'$ and Log tan $\delta$

![Graph showing log $E'$ and log tan $\delta$ as functions of temperature for HP 4 M60 and HP 4 M100.]

Figure B.11: DMTA plots of HP 4 M60 and HP 4 M100 -- (i) Storage modulus, $E'$; (ii) Log $E'$; and Log tan $\delta$. 
Figure B.12: Log $E'$ and log $\tan \delta$ curves of TDI-HP 2 M60 and TDI-HP 2 M100.