Polyurethane–polyacrylic hybrid dispersions

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POLYURETHANE-POLYACRYLIC HYBRID DISPERSIONS

Rohah A. Majid

A Doctoral thesis submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy of Loughborough University

Supervisor: Professor D. J. Hourston
Institute of Polymer Technology and Materials Engineering

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Finally, I would like to thank DSM-NeoResins, Universiti Teknologi Malaysia and the Malaysian Government for their financial support and for the opportunity to carry out this fascinating research.
DEDICATION

I would like to dedicate this thesis to my husband, Muhammad Fadzil, my two lovely sons, Aiman and Akmal, my mother, Pn. Menah and my sisters, Talha and Taksiah.
ABSTRACT

Pure polyurethane dispersions (PUDs) have been synthesised via the prepolymer mixing method, with two different systems i.e. solvent free and the solvent containing PUDs. Isophorone diisocyanate (IPDI), polypropylene glycol (PPG 2000) and dimethylolpropionic acid (DMPA) were the basic materials. The prepolymers were neutralised with triethylamine (TEA) prior to dispersion into the mixture of deionised water and chain extender, hydrazine monohydrate (HYD). The same procedures were repeated in the making of the solvent containing PUDs with 20 wt. % of N-methyl-2-pyrrolidone (NMP). The film properties were examined with Fourier transform infra-red (FT-IR) spectroscopy, stress-strain tests, dynamic mechanical thermal analysis (DMTA), modulated temperature differential scanning calorimetry (MTDSC) and transmission electron microscopy (TEM). The latex particle sizes were measured with a Malvern Zetasizer. It was found that the plasticizing effect of NMP caused reduction in the glass transition temperature, T\text{g}, which also affected the performance of the sample, particularly the tensile strength and extensibility. Annealing the solvent based PUDs under certain conditions improved the properties due to the evaporation of the NMP that was trapped in the films. The solvent-free samples showed superior properties to the solvent based ones.

Methyl methacrylate/n-butyl acrylate co-monomers (MMA/n-BA) and styrene/n-butyl acrylate co-monomers (STY/n-BA) at different ratios (30 wt. %, 50 wt. % and 70 wt. %) were employed as diluents in the synthesis of solvent-free PUDs. Later, the monomers underwent emulsion polymerisation, resulting in polyurethane-polyacrylic hybrid dispersions (PUAs). The hybrids are well documented as improving the resistance to external elements such as water, weather and alkali, but also improving toughness and giving high abrasion resistance without loss in flexibility. In addition, latex blends at the equivalent polyacrylic ratio as in the hybrids were prepared. Two types of PUDs i.e. solvent free or NMP containing PUDs were stirred with polyacrylic latex for 1 hour at room temperature. The results showed that the different level of hydrophobicities of PMMA and PS affected the solid state properties of the
samples. The polyacrylic ratio in both the hybrid and the blend systems had to be limited up to 50 wt. % to give comparable results.

The addition mode of acrylic monomer and the synthesis technique were also varied. Two techniques i.e. a single batch and a double batch, were employed at 1:1 PU:polyacrylic ratio. Two methods of addition of acrylic were employed as follows: 20 wt. % of acrylic monomer was added at the prepolymer stage, (designated as diluent), or the monomer was added after the prepolymer was completed, but prior to the dispersion stage, (designated as non-diluent). In the single batch method, a diluent or non-diluent monomer (20 wt. %) was carried out to the second stage, where it was polymerised with the remaining 30 wt. % acrylic monomer. In the double batch method, a diluent or non-diluent monomer was polymerised at the first stage, followed by subsequent polymerisation of the remaining monomer at the second stage. The effect of Tg of the polyacrylic was also investigated. The MMA/n-BA with Tgs of 20°C and 50°C were hybridised with PU via a single batch and a double batch technique at 1:1 PU:polyacrylic ratio. It was found that the addition mode of acrylic monomer and the synthesis technique did not have prominent effects on Tg and the degree of mixing between the soft and the hard components. However, they affected the degree of mixing in the interphase regions. The hybrids with lower acrylic Tg favoured more mixing, resulting in a lower tensile strength and stiffness.

Finally, the PU hard segment was modified with different materials in order to investigate the effects on the sample morphology. Hydrazine (HYD) was replaced by ethylene diamine (EDA) as chain extender, while neopentyl glycol (NPG) was incorporated into the PU hard segments at different ratios i.e. 2 wt. % and 4 wt. %. To assist the TEM analysis, 4 wt. % of dibromoneopentyl glycol (dNPG) was inserted into the PU hard segment. Later, the PUDs were hybridised with acrylic monomer, at 1:1 PU:polyacrylic ratio. The higher polarity of the urea linkages in HYD and the presence of methyl side groups in NPG affected the final morphologies. The incorporation of the brominated polyol enhanced the contrast between the core and the shell structures. However, it also affected the mechanical properties of the samples.
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<td>AFM</td>
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<td>DBTDL</td>
<td>Dibutyl tin dilaurate</td>
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<td>DMPA</td>
<td>Dimethylol propionic acid</td>
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<td>dNPG</td>
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<td>$E''$</td>
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<tr>
<td>$E'$</td>
<td>Storage modulus</td>
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<td>EDA</td>
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<td>SC</td>
<td>Soft component in polyurethane-polyacrylic hybrid dispersion</td>
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<td>HS</td>
<td>Hard segment in polyurethane dispersion</td>
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<td>HYD</td>
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<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<td>PPG</td>
<td>Poly(propylene glycol)</td>
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<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>PUA</td>
<td>Polyurethane-polyacrylic hybrid dispersion</td>
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<td>PUD</td>
<td>Polyurethane dispersion</td>
</tr>
<tr>
<td>STY</td>
<td>Styrene</td>
</tr>
<tr>
<td>Tan δ</td>
<td>Damping factor</td>
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<td>Triethylamine</td>
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CHAPTER 1

INTRODUCTION AND OBJECTIVES
Chapter 1

INTRODUCTION AND OBJECTIVES

1.1 Research background.

Polyurethane-polyacrylic hybrid dispersions (PUAs) are composite systems which combine the advantages of two polymers. Their advantages have been well documented by both academic and industrial research, which has attracted many researchers to study and manipulate their properties. Such hybrids are resistant to external elements such as water, weather and alkali as well as exhibiting excellent elasticity, toughness, elongation, high abrasion and impact resistances at low temperatures. They also provide a good cost-performance balance, due to the cheaper price of the acrylic. These water-borne systems are environmentally friendly as they offer lower volatile organic component (VOC) emittance to the air. However, to control the viscosity of the latex, so as to remain low throughout the synthesis, the use of organic solvents such as N-methyl-2-pyrrolidone (NMP) or acetone cannot be avoided. These solvents, even used in small amounts, contribute to the VOC emittance. Researchers in the coating industries have proposed a 2-in-1 design, by introducing acrylic or vinylic monomers as reactive diluents to control the prepolymer viscosity and as the coalescing aids during film formation. In addition, the monomers can be copolymerised afterwards to form hybrids. The poor mechanical properties offered by the latex blends has led to much attention on the hybrids.

A seeded emulsion polymerisation technique allows the particle morphologies to be tailored to the desired structure. The semi-IPN PUAs were accomplished by introducing crosslinking agents such as ethylene glycol dimethacrylate and triethylene tetramine to form a network. Hybridisation via a mini-emulsion polymerisation has been reported. The use of a redox initiation system in mini-emulsion has accelerated free radical generation, thus enhancing polymerisation rate. 1,4-Butanediol was able to act as the chain extender, but also as a co-stabiliser against Oswald ripening in mini-emulsions of PU and...
The grafting technique is another alternative. Polyurethane prepolymer dispersions were end-capped with a hydroxyl functional acrylic monomer, such as hydroxyethylacrylate (HEA). Later, the latexes were copolymerised via emulsion polymerisation to form grafted copolymers. The introduction of a crosslinking agent into the system has been achieved by reactive blending. An acrylic polymer emulsion containing a keto functional group, such as diacetone acrylamide and a polyurethane dispersion containing hydrazine groups, were physically combined by stirring. Both polymers were covalently bonded at the interfaces of the polymer particles, as water was removed during the drying process.

PUAs are widely used in flooring and concrete coatings, and some in industrial and architectural wood coatings. They are suitable for advanced performance surface coatings with the right cost-performance balance and environmental friendliness.

The morphology-property relations of the polyurethane-acrylic hybrid dispersions are not well studied to date. Many papers in the literature concluded that the hybrid itself is a vastly engineered system that can be manipulated in such a way to suit many applications. Moreover, PU itself, can be tailored, for example, by changing the PU hard and soft segments, the type of chain extender, even the amount of ionic moiety, to different morphologies with different properties. Hence, it is imperative to develop a better understanding of the factors that contribute to the morphology-property development of the PUAs.

This research have been designed to synthesise and characterise polyurethane-polyacrylic hybrid dispersions, by engineering the morphologies of the PUAs to get a better understanding of how these changes influence the final properties. The scope of the research is focused on the incorporation of acrylics by varying the following parameters: type of acrylic, acrylic composition, the sequence of acrylic monomer addition, synthesis order i.e single batch or double batch and the hard segment modification of the PU. The mechanical properties, the morphologies and the thermal properties of the dispersions and cast-films were studied.
1.2 Objectives of the study

The objectives are as follows.

1. To synthesise solvent free PU dispersions (PUDs) and to compare the properties and morphologies with the NMP containing PUDs.

2. To copolymerise the solvent free PUDs with methyl methacrylate/n-butyl acrylate (MMA/n-BA) co-monomers and styrene/n-butyl acrylate (STY/n-BA) co-monomers at three different polyacrylic ratios i.e. 30 wt. %, 50 wt. % and 70 wt. %. Investigation to be made on the effects of varying the type and polyacrylic ratio in terms of the morphology-property relationships.

3. To compare the results in (2) with the NMP containing PU-polyacrylic at 1:1 PU:polyacrylic ratio in order to study the effect of NMP on the morphology-property relationships.

4. To synthesise pure PMMA/PBA and PS/PBA via emulsion polymerisation, in which the latexes will be used in making the latex blend samples.

5. To prepare the PU-polyacrylic latex blend versions at equivalent polyacrylic ratios as in the hybrids. Two types of blend were prepared i.e. solvent-free PU-polyacrylic and NMP-containing PU-polyacrylic. Comparisons were to be made between both systems in terms of the morphologies and mechanical properties.

6. To modify the PU hard segments as follows: a) introducing neopentyl glycol (NPG) at 2 wt. % and 4 wt. %; b) introducing dibromoNPG (dNPG) at 4 wt. %; c) replacing the chain extender, hydrazine monohydrate (HYD) with ethylene diamine (EDA) and d) varying the Tg of the MMA/n-BA from 20°C to 50°C. The morphologies and mechanical properties of these samples were investigated.

7. To study the morphology-property relationships by varying the styrene/n-BA co-monomers sequences during the PUA preparations.

The colloidal properties of each sample will be examined in the following ways.

a) Minimum film formation temperature (MFFT) measurement.

b) Viscosity measurement.

c) Solid content determination.
d) pH determination.
e) Particle sizing.

The solid state properties of each sample will be examined in the following ways.
1. Dynamic mechanical thermal analysis (DMTA).
3. Stress-strain tests.
4. Thermogravimetric analysis (TGA).
5. Fourier transform infra-red spectroscopy (FT-IR).
6. Gel permeation chromatography (GPC).
7. Transmission electron microscopy (TEM).

1.3 Sponsor background

This project was sponsored by DSM-NeoResins, Holland. The company was founded by Stahl Finish in 1955, originally known as Peabody in Massachusetts, USA and later was renamed as Polyvinyl Chemical Industries (PVI). In the beginning, the main production was acrylic resin for leather finishing. In 1965, Stahl and PVI were merged under a new name, the Beatrice Chemical Group. After 20 years, ICI purchased the company, but in 1993, Zeneca Resins was formed as a demerger from ICI. Today, renamed as DSM-NeoResins, the company is one of the world leaders in waterborne technology. It operates at five sites in the USA, Spain and Singapore. The world-wide headquarters is located in Waalwijk, Holland. The strong commitment to waterborne technology has led the company to manufacture varieties of water-based products, using polyurethanes, acrylics and polyurethane-polyacrylic composites for laminating inks, liquid inks, plastics and metal coatings, industrial and architectural wood, flooring and concrete coatings and decorative and joinery paints.
CHAPTER 2

POLYURETHANES IN SURFACE COATINGS
2.1 Chemistry and synthesis

Polyurethanes (PUs) comprise one of the most complete and versatile classes of polymeric materials known today. The term PU is extended to all complex reaction products of isocyanates (R-N=C=O) with di- or polyfunctional compounds containing an active hydrogen such as a hydroxyl group (R-OH) via step growth polymerisation.\textsuperscript{8,18} Thus, a typical PU may contain urethane linkages, aliphatic and aromatic hydrocarbon sequences, esters, ethers, amides, urea and isocyanurate groups etc.\textsuperscript{35} PU chemistry has been on a commercial scale since the 1930s, after the discovery made by Otto Bayer of the fibre-forming PUs.\textsuperscript{15} Originally, PUs were developed for foams and plastics. They have been used in coatings since the 1950s.\textsuperscript{16} Raw materials used to produce polyurethanes are classified in three principal groups: isocyanates; polyols and chain extenders. The synthesis of a PU is always based on the utilisation of at least one component of each principal group. Figure 2.1 showed the basic process of PU synthesis with the final product consisting of a segmented structure.\textsuperscript{35}

![Figure 2.1: The basic process of PU preparation.\textsuperscript{35}](image)
Typical PUs contain soft and hard segments. The soft segments are mainly arising from the polyol components, while the hard segments are contributed by diisocyanates, low molecular weight diols and urethane-urea bond sequences. The polymer chains may be linear or slightly branched as in thermoplastic polyurethanes, or they may have a crosslinked network leading to thermosetting products. A large spectrum of properties that can be tailored by selection of raw materials, formulation and manufacturing processes has led to a broad variety of end products such as flexible, rigid and integral foams, elastomers, fibres, surface coatings, adhesives and sealants. Flexible foams accounted for about 50% of the market, rigid foams for 30% and the remainder is covered by elastomers, adhesives, coatings and sealants.

2.2 Raw materials

Three principal raw materials used in making polyurethanes are isocyanates, polyols and chain extenders.

2.2.1 Isocyanates (diisocyanates and polyisocyanates)

The isocyanates are esters of isocyanic acids and were first synthesised by Wurtz in 1848. They are widely used as building blocks for more complicated molecules such as in pharmaceutical and agricultural products. Their use is mainly prompted by the unique capability of isocyanates to undergo nucleophilic addition reactions as well as their ability to perform reversible reactions with many substrates. The reactivity of the isocyanate group toward nucleophilic reactions is best understood by considering the electronic structure of the isocyanate group and the effect of the substitutents. The charge density is greatest on the oxygen and least on the carbon, and the resonance forms as follows.

\[
R - N = \overset{\bullet}{C} - \overset{\bullet}{O} \leftrightarrow R \overset{\bullet}{N} - \overset{\bullet}{C} = O \leftrightarrow R - N = C = O
\]

The reactions of isocyanates with active hydrogen compounds involve attack by a nucleophile at the electrophilic carbon of the isocyanate. Therefore, any substituent that is
electron withdrawing will increase the positive charge on this carbon and thereby increase the reactivity of the isocyanate group toward nucleophilic attack. The details of isocyanate reactions will be discussed further in section 2.3.

For surface coating applications, the major classes of polyisocyanates can be classified as being either aliphatic or aromatic. There are significant differences in reactivities and performance between them. Aliphatic isocyanates are superior for colour retention and weathering characteristics, due to the absence of the aromatic ring, but they are more expensive than the aromatics. The aromatic isocyanates yellow when subjected to oxidation (form a benzophenone). As quinone has a yellow colour, its formation makes the materials appear more yellow as the oxidation proceeds. Therefore, the aromatic based coatings are usually found in interior linings or underground applications.16

The most important diisocyanates for use in surface coatings include the following.

### 2.2.1.1 Aromatic diisocyanates

Toluene diisocyanate, TDI, with the structure shown in figure 2.2, is the principal diisocyanate currently used. The greatest usage of TDI is in polyurethane foams.36 The type of TDI generally used in the paints field is an 80:20 mixture of two isomers, with the 2,4- isomer predominating.16

![Figure 2.2: Structure of TDI isomers.](image)
Diphenylmethane diisocyanate, MDI, the structure of which is shown in figure 2.3, is normally available as the 4,4'-isomer, although in practice the 2,4- and 2,2- isomers are present in trace amounts (2% in total). The structure of polymeric diphenylmethane diisocyanate, PMDI, is shown in figure 2.4. Pure 4,4'-MDI is separated from PMDI by continuous thin film distillation.

![Figure 2.3: Structure of MDI-4,4'-isomer.](image)

![Figure 2.4: Structure of PMDI.](image)

MDI and PMDI are used in many surface coating fields. Technical grade MDIs are used in resins for electrodeposition, in which they are starting to replace TDI. Principally, they give good surface hardness and good chemical resistance as well as strong colouration to the final product. PMDI and MDI are less toxic than TDI as their vapour pressures are lower at ambient temperature.

### 2.2.1.2 Aliphatic diisocyanates

Hexamethylene diisocyanate, HDI, is a symmetrical aliphatic isocyanate, whose structure is shown in figure 2.5.

\[ \text{O} = \text{C} = \text{N} - (\text{CH}_2)_6 - \text{N} = \text{C} = \text{O} \]

![Figure 2.5: Structure of HDI](image)
A light stable, non-yellowing PU is obtained from HDI and its derivatives due to the absence of aromatic structures. Therefore, it is widely used for PU dispersions and elastomers as well as high-performance coatings. HDI is not normally used to produce foams due to its rigid network structure when crosslinked with polyols.\textsuperscript{26}

Isophorone diisocyanate, IPDI, is normally supplied as a 75:25 mixture of the trans and cis isomers. IPDI is in liquid form at ambient temperatures. The two NCO groups have different reactivities. The group that attached to the cycloaliphatic ring is 1.3 to 2.5-fold less reactive than the secondary groups.\textsuperscript{25} The reactivity can vary depending on the mode of catalysis and steric hindrance around the catalytic centre.\textsuperscript{24} The use of HDI in light-fast products has been largely replaced by the use of IPDI.\textsuperscript{26} The structure is shown in figure 2.6.

\begin{center}
\textbf{Figure 2.6: Structure of IPDI}
\end{center}

4,4’-Dicyclohexylmethane diisocyanate, H\textsubscript{12}MDI, is the most commercially successful aliphatic PU but is a very expensive compound.\textsuperscript{16,35} It is comprised of a mixture of \textit{cis} and \textit{trans} stereoisomers. The \textit{trans,trans} isomer has the greatest influence on the properties due to the formation of very ordered, semi-crystalline hard segments in the final polymer network.\textsuperscript{23,25}

\begin{center}
\textbf{Figure 2.7: Structure of H\textsubscript{12}MDI}
\end{center}
HI₂MDI will react more slowly than HDI and IPDI due to the attachment of both NCO
groups at secondary carbon atoms. It is frequently used in polyurethane dispersions,
where it imparts good mechanical properties, hydrolysis stability and thermal stability.
Its colourless and light stable characters (no yellowing after exterior exposure) makes it
popular as finish coats. The structure is shown in figure 2.7.

Tetramethylxylene diisocyanate, TMXDI, is available as both the para and meta isomers.
The structures of both isomers are shown in figure 2.8. TMXDI has two isocyanate
groups which are not conjugated with the aromatic ring. Therefore, it generates no
yellowing after exterior exposure, since quinonic structures cannot be formed. The
reactivity of the isocyanate group is rather weak as it is severely sterically hindered by the
presence of methyl groups. It has been used in performance coatings, roofing
compositions, flooring, sealants and elastomeric compositions for casting and injection
moulding.

![Figure 2.8: Structures of m- and p-TMXDI.](image)

2.2.2 Polyols

Thousands of different polyurethanes can be made from the array of commercially
available isocyanates and active hydrogen compounds (e.g. polyols). In the production of
CASE materials (coating, adhesives, sealants and elastomers), the main active hydrogen
containing compounds are hydroxy functional compounds with a functionality of two.
In flexible foams, the functionality of the main hydroxyl compounds is likely to be three,
while in rigid foams, a functionality as high as eight has been used. Typical polyols have low molecular weight with $\text{Mn} \approx 500$ to 3000 g/mole.

A wide range of polyols is available as co-reactants for the isocyanates. Through variation of molecular weight, structure and functionality, the polyols are critical for the performance of the final product. The hydroxyl compounds that are available are as follows.

- Polyether polyols.
- Polyester polyols.
- Polycarbonate polyols.

The ether-type systems are considerably less expensive than polyester polyols. The advantages of the ether types are their superior resistance to moist environments, while having low-temperature flexibility. The esters impart the advantages of resistance to oils and high temperatures. Polyester polyols contribute to the high strength of the final PU. This is due to their ability to form hydrogen bonds, for which polyethers are not so well suited.

2.2.2.1 Polyethers

Polyethers are of two basic types: those derived from tetrahydrofuran, THF, such as poly(tetramethylene ether glycol) (PTMEG) and those derived from propylene oxide such as poly(propylene glycol) (PPG). Figure 2.9 showed the molecular structures of PTMEG and PPG.

![Figure 2.9: Structures of PTMEG and PPG.](image-url)
The PTMEGs offer excellent hydrolytic stability, excellent flexibility and impact resistance.\textsuperscript{36} The first polyether used for making flexible polyurethane was a poly(oxytetramethylene glycol) (PTHF).\textsuperscript{26} PTHF gives high strength, high resilience elastomers with good hydrolysis resistance.\textsuperscript{25} Linear polyethers (based on propylene oxide) are less expensive than linear polyesters and can tolerate higher aromatic solvent content.\textsuperscript{16,25,26}

The used of ethylene oxide polymers alone is very limited in polyurethanes because all ethylene oxide polymers are water soluble, have poor hydrolytic stability and are sensitive to UV-induced oxidative degradation. On the other hand, propylene oxide polymers are hydrophobic, yielding polyurethanes with good hydrolysis resistance.\textsuperscript{26,29} Most polyether polyols used in polyurethane manufacture are made from propylene oxide or propylene oxide/ethylene oxide copolymers. They are usually diols or triols with average molecular weights in the range of 1000 – 7000 (average number equivalent weights of 500 – 2000)\textsuperscript{26}. These resins are valued in the lining and protection of concrete against waste waters.

2.2.2.2 Polyesters

Polyester polyols are used to lower extent than polyether polyols. They are more expensive to produce and more viscous than polyethers of comparable chain lengths.\textsuperscript{36} They are less sensitive to photo-oxidation, but are susceptible to hydrolysis.\textsuperscript{37} A symmetrical structure of the ester has a tendency to crystallise melting point, which results in hardening of the polyurethane at room temperature.\textsuperscript{25} In CASE applications, adipate esters and poly(caprolactone diols) (PCL) are commonly used. Figure 2.10 shows the molecular structure of PCL.\textsuperscript{36} PCL diols offer performance benefits over adipates, particularly with regard to hydrolysis resistance\textsuperscript{28} and mechanical properties.\textsuperscript{25}

\[
\text{H} \Big[ \text{O-(CH}_2\text{)}_5 \text{O} \Big]_n \text{O-R-O} \Big[ \text{C-(CH}_2\text{)}_5 \text{O} \Big]_n \text{H}
\]

Figure 2.10: Structure of PCL.
Polymers based on terephthalic acid impart high thermal resistance useful in the case of an insulating varnish or powder coating. The linear polyesters have a waxy appearance with a crystalline structure, and hence are mostly solids at room temperature. The branched polyesters can be liquids at room temperature with their viscosity increasing with increasing degree of branching.

2.2.2.3 Polycarbonate polyols

Polycarbonate-based polyols such as poly(1,6-hexanediol)carbonate offer excellent low temperature properties, excellent hydrolytic and oxidation stability, as well as weatherability, despite of their significantly higher cost. They are used mainly for high quality PU elastomers. Figure 2.11 shows the molecular structure of poly(1,6-hexanediol)carbonate.

![Structure of poly(1,6-hexanediol)carbonate.](image)

2.2.3 Chain extenders/crosslinking agents

Chain extenders and crosslinking agents are low molecular weight hydroxyl-terminated or amine-terminated compounds. Difunctional compounds are considered as chain extenders, while compounds with higher functionality are considered crosslinkers. The chain extenders provide the hard segment to the PU. Hard segment content in the polyurethane-urea backbone controls important mechanical properties such as modulus, ultimate strength and thermal and hydrolytic stability of the finished PU. Hydroxyl-containing chain extenders react slowly with isocyanates and require a catalyst to speed up the reaction. On the contrary, amine-containing chain extenders react more rapidly, and sometimes too fast. They may also impart an odour to the resultant product. Table 2.1 lists some important chain extenders used in PU synthesis.
Table 2.1: Typical chain extenders.\textsuperscript{37}

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Butanediol (1,4-BD)</td>
<td>( \text{HO}-(\text{CH}_2)_4-\text{OH} )</td>
</tr>
<tr>
<td>Ethylene diamine (EDA)</td>
<td>( \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2 )</td>
</tr>
<tr>
<td>Trimethylol propane (TMP)</td>
<td>( \text{CH}_2-\text{OH} )</td>
</tr>
<tr>
<td>Neopentyl glycol (NPG)</td>
<td>( \text{HO}-\text{CH}_2-\text{C}-\text{CH}_2-\text{OH} )</td>
</tr>
</tbody>
</table>

2.3 Basic reactions

The basic reaction of polyurethane chemistry is the reaction between the isocyanate groups with compounds containing active hydrogen groups to form PU linkages.\textsuperscript{16} The active hydrogen, usually from hydroxyl end groups of long polyester or polyether chains, are reacted with di- or polyisocyanates to provide the basic step growth polymerisation, as shown in figure 2.12.

\[
\begin{align*}
\text{O} & \equiv \text{C} \equiv \text{N} - \text{R} - \text{N} & \equiv \text{C} \equiv \text{O} + \text{HO}_\vardot \text{OH} & \rightarrow & \text{O} & \equiv \text{C} \equiv \text{N} - \text{R} - \text{NH} - \text{NH} - \text{O} \\
\text{Polyurethane} & & & & & \\
\end{align*}
\]

Figure 2.12: Step growth polymerisation of PU.

The reaction is exothermic, but with polyols of high equivalent weight it proceeds only slowly at room temperature in the absence of a catalyst.\textsuperscript{24,26} The hard to soft segment ratio and the degree of crosslinking are critical parameters in determining the final properties of the polyurethane.\textsuperscript{28}
2.3.1 Reactivity of isocyanate groups

The reactivity of the isocyanate group is based on the presence of two polarisable double bonds. Two resonance forms exist, as shown in scheme 2.1.37

\[
\begin{align*}
R - \overset{\sim}{N} = \overset{\sim}{C} = O & \Leftrightarrow R - \overset{\sim}{N} = \overset{\sim}{C} - OH \\
& \Leftrightarrow R - \overset{\sim}{N} = \overset{\sim}{C} - \overset{\sim}{O}
\end{align*}
\]

Scheme 2.1

Isocyanates have three reactive centres:
- One electrophilic centre – central carbon atom – which can react with nucleophiles.
- Two nucleophilic centres – the oxygen and nitrogen atoms – which can react with electrophiles.

Possible reactions of isocyanate groups are:
1. nucleophilic additions with active hydrogen-containing compounds, H-X;
2. self-polymerisation;
3. polymerisation or copolymerisation forming a polyurethane.

The first and the third reactions involve the reaction with active hydrogen containing compounds, H-X, such as an alcohol, glycol, amino groups and carboxylic groups.37 The diisocyanates have different reactivities. In some cases, such as IPDI, the \(-\text{NCO}\) groups have different reactivities, depending upon their position.19,25 This can be advantageous if certain structures are required. The reactivity range of diisocyanates is as follows: \(4,4'\)-MDI > \(p\)-TDI > \(o\)-TDI > XDI > HDI > neopentyl NCO of IPDI > \(H_{12}\)MDI > secondary NCO of IPDI.16

The reactions of isocyanate groups with the hydroxyl groups are the most important for surface coating applications.19 Aromatic diisocyanates are more reactive than aliphatic ones under the same the conditions, (e.g. no catalyst, same temperature, same reactants and solvent concentrations).26 The substituent groups which are electron donating reduce the reactivity of the isocyanate groups. In substituted phenyl isocyanates, the reactivities are as follows: \(\text{NO}_2 \gg H > CH_3 > CH_3O\).29 Likewise, the reactivity of nucleophiles
attacking the electrophilic carbon increases as their nucleophilicity increases, i.e. aliphatic amines > aromatic amines > primary alcohols > water > secondary alcohols > tertiary alcohols > phenols > COOH.\(^{15,26}\) Steric factors also influence the reactivity of the isocyanate group, i.e. primary isocyanate groups are more reactive than secondary and tertiary isocyanate groups in aliphatic isocyanates.\(^{24}\)

### 2.3.2 Nucleophilic addition reactions with compounds of the type H-X

This class of reaction is by far the most important for surface coatings. The addition can take place at the C=N bond. The reactions are catalysed by metal organic compounds and by bases, generally tin compounds and tertiary amines.\(^{16}\) Figure 2.13 shows the scheme of the reaction.

\[
\text{R-N=C=O} + \text{X-H} \rightarrow \text{R-NH-C(=O)-X}
\]

**Figure 2.13: Nucleophilic addition.**\(^{37}\)

The reactions can be divided into two groups, namely primary and secondary reactions. The primary reactions occur between the diisocyanates with hydroxyls, amines, water or carboxylic groups. The secondary reactions occur between the diisocyanates with urethane and urea groups to produce allophanate and biuret linkages, respectively.\(^{26}\) These reactions are responsible for the introduction of branching and crosslinking of polyurethanes.\(^{25}\)

In table 2.2, the reactions of an isocyanate with nucleophiles of the H-X type are summarised. Reactions a) to d) lead to linear chains, whereas reactions e) to g) result in branched chains. Sometimes, the final product obtained is still capable of reacting with excess isocyanates, which can lead to side-reaction products. This increases the crosslink density of a film.\(^{15}\)
Table 2.2: NCO-nucleophiles reactions.  

| a) | R-NCO + R’OH → R-NH-CO-O-R’ | Alcohol Urethane |
| b) | R-NCO + H₂O → [R-NH-CO-OH] → RNH₂ + CO₂ | Water Carbamic acid: unstable |
| c) | R-NCO + R’-NH₂ → R-NH-CO-NH-R’ | Amine Substituted urea |
| d) | R-NCO + R’-COOH → [R-NHCONR’] + CO₂ | Carboxylic acid Amide group |
| e) | R-NCO + R’-NH-CO-R” → RNHCONR’C’OR” | Amide Acylurea group |
| f) | R-NCO + R’NHCO-OR” → RNHCONR’C’OOR” | Urethane Allophanate |
| e) | R-NCO + R’NHCONHR” → RNHCONR’C’ONHR” | Urea Biuret |

2.3.3 Self-polymerisation

Self-polymerisation, or oligomerisation, is the other reaction mechanism of great importance in surface coatings. It involves the reaction of two or more -NCO groups to form cyclic structures. Two self-polymerisation reactions are commonly used resulting in uretidinediones and isocyanurates, as shown in figures 2.14 a) and b), respectively.

![Figure 2.14](image)

Figure 2.14: a) Uretidinedione preparation and b) formation of the isocyanurate group via trimerisation.  

17
Carbodiimides are formed when isocyanates are heated to between 150°C and 300°C (figure 2.15). The carbodiimides react with carboxylic acids to form stable acyl-urea linked diisocyanates. Aromatic diisocyanate carbodiimides react at room temperature within hours, while aliphatic types react very slowly.

\[
2R-N=C=O \rightarrow R-N=C=N-R + CO_2
\]

Carbodiimide group

Figure 2.15: Formation of the carbodiimide group.

2.4 Morphology of polyurethanes

Polyurethanes are multi-block copolymers of the (A-B)_n type, consisting of alternating sequences of soft and hard segments domains. Such polymers are extensively hydrogen bonded due to the existence of a variety of polar groups and higher electronegative atoms such as N and O. The soft or flexible segments, commonly polyethers and polyesters, which are in a viscous or rubbery state, provide the flexibility characteristics to the polyurethane chains. The hard or rigid segments, which are in a glassy or semi-crystalline state, provide dimensional stability by acting as thermally reversible, multifunctional crosslinks and as reinforcing fillers. They are derived from the diisocyanate and chain extender components. They may contain urea groups if a low molecular weight diamine is used as the chain extender in the synthesis. Research showed that the inter-chain attractive forces are far greater in the hard segments, owing to the high concentration of polar urethane linkages and to extensive hydrogen bonding. The typical macromolecular structure of PU can be divided into three distinctive structures:

- Primary structure which consists of the hard segment and the soft segment, (figure 2.16).
- Secondary structure is characterised by the hydrogen bonds between the urethane groups of the hard segments, (figure 2.17).
- Tertiary structure is characterised by the soft and hard domains, (figure 2.18).
Figure 2.16: The primary structure of typical segmented PU.\(^{36}\)

Figure 2.17: Hydrogen bonding between the hard segments.\(^{37}\)

Figure 2.18: The structure of domains in segmented polyurethanes.\(^{36}\)
Hard segments affect mechanical properties, especially modulus, hardness and tear strength. Figure 2.19 shows the response of the hard and the soft segments under relaxation and elongation states. The presence of urea linkages show a reduction in plasticity in comparison to the homopolyurethane. The adhesion properties of the film depend strongly on the degree of phase separation between hard and soft segments and the inter-connectivity of the hard domains.

Figure 2.19: The response of the hard and the soft segments under the different states.

2.5 Polyurethane dispersions in surface coatings

Polyurethanes are widely used in the coatings industry due to their ability to deliver chemical, water, scratch and abrasion resistance. They also can be designed to have high tensile and impact strengths, along with excellent low temperature flexibility. However, environmental restrictions and legislation pressures on reducing volatile organic compounds (VOCs) in coatings, have driven the industry to accelerate R&D activity on waterborne polyurethanes with sophisticated compositions and architectures which are comparable with their solvent-borne counterparts.
The water-borne polyurethane dispersions (PUDs) evolved in the late 1960s, after the discovery of PU ionomers, which allow them to disperse easily in water without an external dispersant and/or high shear force. PUDs offer many features including low viscosities, very low VOC contents, reduced flammability, less odour and easy application using conventional equipment. In contrast, these systems require high capital cost for upgrading circulation lines and application equipment to stainless steel, while water itself contributes to high conductivity and high surface tension which need pre-treatment of many substrates prior to use. Table 2.3 shows the comparisons between solvent-borne and water-borne systems.

Table 2.3: Comparison of the solvent-borne and water-borne polyurethane dispersions.

<table>
<thead>
<tr>
<th></th>
<th>Solvent-based</th>
<th>Water-based</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical state</td>
<td>Solution</td>
<td>Particles dispersed in water</td>
</tr>
<tr>
<td>Substrate wetting</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Presence of foam</td>
<td>Sometimes</td>
<td>Yes: use of defoaming additives often indispensable</td>
</tr>
<tr>
<td>Film formation</td>
<td>Chemical reaction (with isocyanate, UV, etc.)</td>
<td>Physical drying self-crosslinking</td>
</tr>
<tr>
<td>Film formation temperature</td>
<td>No restriction</td>
<td>MFFT (minimum film formation temperature) controlled</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Affects the viscosity</td>
<td>No effect on viscosity</td>
</tr>
</tbody>
</table>

Unfortunately, requirements for industrial coatings with higher performance, formerly set by solvent-borne coatings, could not be matched by standard water-borne systems. Therefore, extensive research has been done to improve the limitations of the water-borne systems and they are nowadays encountered in many varied applications such as for construction, flooring, furniture, transportation, electronics, textiles, plastics, automotive and adhesives for many polymeric and glassy surfaces.

2.5.1 Morphology of polyurethane dispersions

The essential factors in film formation of a formulated coating, is its ability to form a coherent and defect-free film on a substrate, as well as exhibit good film properties that match
the service need. With a solvent-borne coating, the first factor is readily achieved due to low molecular weight presence in the solvent. By the addition of the crosslinking agent, acceptable mechanical and resistance properties can be achieved in the dry film. On the contrary, water-borne PUs can match the solvent-borne counterpart due to the uniqueness of the synthesis mode, which results in small particle size and swollen internal morphology via plasticization by water molecules, (see figure 2.20).66,68,70

![Figure 2.20: The schematic model of a waterborne PU particle with an open/swollen morphology.]

2.5.2 The components of polyurethane dispersions

Typical components of PUDs are similar to conventional PUs. The components are listed as follows.16

- Soft segment such as a polyether polyols.
- Hard segment of diisocyanate such as IPDI or TDI.
- Chain extender such as a glycol or hydrazine.
- Neutralisation agent such as triethylamine.
- Ionic moiety such as dimethylol propionic acid.
- Catalyst such as dibutyl tin dilaurate.
- Solvent such as acetone or N-methyl-2-pyrrolidone.
The final structure of the polymer is obtained by reacting an excess of isocyanate with a polyol, or a mixture of polyols, to form a prepolymer. Later, the prepolymer is dispersed in water that contains the chain extender to form polyurethane dispersions.

2.5.3 Soft segments

Generally, the soft segments comprise polyols such as polyesters, polyethers or polycarbonates. Polyesters show good external appearance, good abrasion resistance, high temperature resistance and chemical resistance. The use of very high molecular weight polyesters makes it possible to prepare physical drying coatings. Since polycarbonate diols are more expensive than polyesters, compromise systems based on mixed diols have been evaluated. A mixture of polyester/polycarbonate crosslinked with a non-ionic hydrophilically-modified HDI isocyanurate has been reported. It was found that the polycarbonates contribute similar properties to the polyesters with better stability to hydrolysis and to corrosion. Polyethers have good hydrolysis resistance contributed by the ether backbone. PPGs contribute high flexibility, elasticity and storage stability, but impair the external appearance compared to polyesters. The latter gives comparable performances to polyesters or polycarbonates, except for oxidation stability. Polyether diol-based systems are less reactive, compared to polyester diol-based ones. Therefore, they often need a combination of a metal catalyst and an amine catalyst to accelerate the reaction. Polycaprolactone-based polyurethanes with longer soft segments retained their crystallinity even after heating. Hydroxy-functional polyurethane dispersions can also be made by making the dispersion with excess diol. Higher functionality can be achieved by including a trifunctional polyl such as trimethylolpropane (TMP) in the formulation.

2.5.4 Hard segments

Hard segments consist of diisocyanates, ionic moieties, chain extenders and in some cases, urea groups. The segments are held together in discrete domains thorough the action of van der Waals forces and hydrogen bonding interactions.
The common isocyanates used in coatings are aromatics (e.g. TDI and MDI) and aliphatics (e.g. IPDI, H_{12}MDI). The choice depends on the desired properties such as light and colour stability and economic considerations. Aliphatic isocyanates are resistant to UV degradation (no yellowing) and are hydrolysis resistant. On the other hand, aromatic isocyanates contribute hardness and chemical resistance, but poor UV sensitivity (exterior durability and weathering). IR studies indicated that films with aliphatic diisocyanates such as HDI has stronger hydrogen bonding in comparison with aromatic diisocyanates. A statistical study showed that the majority of polyurethane dispersions have been made with aliphatic isocyanates. HDI offers relatively low viscosity products that are more easily dispersed in water, and give higher gloss and more flexible films with good scratch resistance. IPDI generally provides fast drying and harder coatings. H_{12}MDI offers optical clarity and resistance to hydrolysis, due to its low reactivity with water. Binary or ternary diisocyanate mixtures demonstrated different performances. The binary with IPDI/XDI showed higher tensile strength while the ternary, IPDI/XDI/H_{6}XDI, gave the largest ultimate elongation.

2.5.5 The ionic moiety

By definition, waterborne generally defines the broad category of coatings that utilise water as the main volatile liquid component. The dispersions need external emulsifiers and a high shear force to disperse hydrophobic polymers even when their molecular weight is relatively low. Conventional polyurethanes are hydrophobic in nature and they can be easily prepared as solvent-borne coatings. Therefore, the resins are usually modified by increasing their hydrophilic nature prior to taking part into a water-borne coating formulation. The hydrophilic ionic groups are incorporated in the polymer backbone, where they act as an internal ionic stabilisation agent. It is well documented in the literature that by incorporating ionic groups such as 2,2-dimethylol propionic acid (DMPA) or non-ionic hydrophilic ionic groups such as long chain polyethers onto the hydrophobic backbones of polyurethanes, can make the polymers dispersible and self-emulsifiable even under low shear stresses with little or no external emulsifiers. The incorporation can be done via grafting a small portion of the diisocyanates or diols with material that contains water-
solubilizing functional groups onto polyurethane chain. These functional groups are usually non-ionics which incorporate hydrophilic segments and ionics in which the chains contain hydrophilic centres of ionic type i.e. anionic or cationic.

The presence of ionic moieties in ionomers has strong effects on many of their properties. The particle sizes of dispersions increased as the ionic group concentration per unit chain length decreased (less hydrophilic). The ionics groups are located predominantly on the surfaces of the particles and the dispersions in water are stabilized by an electrical double layer. At the interface between a particle and water, a double layer is formed by dissociation of ionic groups. As the particle size is reduced, the number of dispersed particles and viscosity increased. The interactions between ions and their counter-ions are responsible for this effect. However, these polyurethane ionomer dispersions have the disadvantage of increasing the water sensitivity of the product due to the presence of hydrophilic units. The anionic short-chain surfactant can provide additional colloidal stability to the pure polyurethane particles as well as to monomer-swollen particles.

There are three broad classes of stabilising groups of industrial importance.

a) Anionics.

b) Cationics.

c) Non-ionics.

2.5.5.1 Anionics

Polyurethane anionomers, which incorporate built-in sulphonate and carboxylate groups, are pre-dominant. Compounds with sterically hindered COOH groups, such as \( \alpha,\omega \)-dimethylolpropionic acid (DMPA) are introduced into polymer backbones. The hindered carboxylic acid groups on DMPA are unreactive with isocyanates at the temperatures used in preparing polyurethane dispersions, so that the reaction is limited to the hydroxyl groups. Polycarboxylates provide good hydrophobic character, while polysulphonates give dispersions with excellent stability even under unfavourable conditions. Anionics contain carboxylate groups, as shown in figure 2.21.
Polyurethane dispersions with DMPA have been widely used. However, they are subject to hydrolysis, at basic pH, which can lead to breaking the polymer backbone and separation into two phases, especially at elevated temperatures. A study had shown that the method of adding DMPA during the prepolymer reaction affected particle sizes. They found that when DMPA was added in the beginning of reaction (one-shot method), resulted in smaller particles, while the two-shot method (i.e. DMPA was added after 2 hours of a reaction between diol and NCO), produced bigger particles. In the one-shot method, the probability of DMPA units being linked in series was higher than in the latter, in which DMPA units were likely to be separated by the diol units. The tensile strength was increased in the one-shot method due to the stabilising groups which linked in series favoured hard-soft segment separation.

Mequanint et al. found that PUDs with ionic groups located on the hard segment had better hydrolytic stability in aqueous environment than the one located on the soft segment. Hydrophilic groups that attached on polyester segments caused the segments ‘to pack’ at the exterior of particles. Polyester is prone to the hydrolytic attack, thus reducing the dispersion stability. The particle size decreases with the increasing of DMPA concentration, thus increasing the viscosity of the dispersion. The absorption of water into the particles is also increased, owing to the increased hydrophilic properties. Kim et al. reported that increasing the DMPA/PPG ratio augmented the modulus and the tensile strength due to the increase of the hard segment. This also increased the elongation at break, resulting from more phase separation between the soft and the hard segments.

2.5.5.2 Cationics

Cationics contain amine or quaternary ammonium groups as shown in figure 2.22. They are stable at acid pH values and are normally based upon alkylated or protonated tertiary
amines.\textsuperscript{16} N,N-diethylamino-1,2-propanediol can be quaternised with iodomethane to various extents to yield polyurethanes with varying block incompatibility in a controlled manner without changing the overall molecular weight of the polymer.\textsuperscript{60} The ionic types are less stable to addition of electrolytes in comparison with the non-ionic types.\textsuperscript{17}

\begin{equation}
\text{Figure 2.22: Representation of a cationic PUD}
\end{equation}

2.5.5.3 Non-ionics

Non-ionics have no polarity (non-ionisable) such as diols or polyisocyanates with side chains from poly(alkylene glycol monoethers).\textsuperscript{16} They are stable over a very wide pH range.\textsuperscript{68} A representation is given in figure 2.23.

\begin{equation}
\text{Figure 2.23: Representation of a non-ionic PUD.}
\end{equation}

2.5.6 Neutralisation

The carboxylic acids groups of the ionic moiety are neutralised by the addition of a neutralising agent to improve the hydrophilicity of the polymer.\textsuperscript{65} The common agents used are ones that contain ammonium cations such as triethylamine (TEA), trimethylamine and
ammonium hydroxide (NH₄OH) or the agents containing metal cations such as sodium hydroxide (NaOH), lithium hydroxide (LiOH) or potassium hydroxide (KOH).

The stage of neutralisation is important in controlling the colloidal properties of the polyurethane dispersion. Hourston et al.⁴⁷ found that in pre-neutralisation (i.e. TEA is added to the molten pre-polymers before dispersion in water), all unreacted carboxylic acid groups had been ionised completely because of easy access of TEA. This resulted in effective and homogeneous dispersion. Stable colloids with carboxylate anions produced a smaller particle size dispersion. This finding was supported by other workers.⁴⁸,⁵⁸ The pre-neutralisation also gave higher tensile strength and hardness, but lower elongation at break due to the higher degree of segregation between the hard and soft domains.⁴⁸ On the other hand, post-neutralisation (i.e. the molten pre-polymer is added to water that contains TEA and chain extender) caused poor chain extension due to the competition between chain extender and neutralising agent to neutralise carboxylate anions.⁴⁷ Therefore, less chain extender was available for extension. It also facilitated domain mixing and resulted in a decrease in the cohesion in hard domains.

Kim et al.⁶⁰ investigated the effect of using a neutralising agent that contained ammonium cations and metal cations. They found that the former neutralising agent gave higher tensile strength, modulus and thermal stability to the film. The latter gave higher conductivity and stronger anti-bacterial properties. The neutralising agents that contain metal cations always result in smaller particle size than those containing ammonia cations.⁶⁰

The effect of increasing the degree of neutralisation was found to reduce the particle size, and, hence, to increase the viscosity.⁴⁷,⁵⁸ The stable dispersion which resulted from the increasing dissociation of carboxylate anions was able to stabilise a greater total particle surface area. The stabilisation was contributed by the increment of zeta potential from a few dissolvable carboxyl groups, which, hence, increased the surface charge density and made the carboxyl groups dissociated.⁵⁸ The tensile strength of films was found to be increased due to the ionic sites which augment the inter-chain interactions between ionic centres and counterions that mainly occur at the hard domains.⁴⁷,⁴⁸
2.5.7 Chain extenders

In conventional linear polyurethanes, the low molecular weight of polyols (600-3000) and low molecular weight of the polyurethane was extended with chain extension agents to produce higher molecular weight polymers. The amount of chain extender used for chain extension must be equimolar with the concentration of residual NCO groups from the diisocyanates. Jhon et al.\textsuperscript{108} investigated the effect of using 1,6-hexanediamine as chain extender with the residual NCO groups and total surface area of the polyurethane particles. They found that imbalances of excess chain extenders might cause poor chain extension efficiency and subsequent deterioration of mechanical properties of the polyurethane dispersion. The excess amount of chain extender acted like an impurity and consequently had a bad effect on the adhesive strength. They concluded that the chain extension reactions were more favourable with residual NCO groups on the particle surface rather than those in inside particles. The addition of chain extender into the dispersion can be done into several ways. Simultaneously, (chain extender was added to the water prior to dispersion) or post-extension in which the chain extender was added after the dispersion of the prepolymer. In the case of ethylene glycol as chain extender, the extension reaction was carried out before the water dispersion to avoid the competition between the hydroxyl groups of extender and the water.\textsuperscript{31} Later, the water was added to the molten prepolymer. The previous researchers\textsuperscript{47} found that the simultaneous method produced a smaller particle size than post-extension. Hence, the resulting film exhibited higher initial modulus, tensile strength and elongation at break. This was due to an increased number of inter-chain interactions and higher separation of hard and soft segments.

Coutinho et al.\textsuperscript{31} investigated the effects of using different types of chain extenders i.e. ethylene diamine (EDA), hydrazine (HYD) and ethylene glycol (EG). EDA and HYD led to the formation of poly(urethane-ureas) while EG resulted in the formation of polyurethanes. The EDA and HYD films were less flexible than those from EG because of the presence of urea groups which caused an increase in the crystallinity of the materials and consequently, in their rigidity and brittleness. They also verified that the thermal stability was influenced by chain extender type. Thermal stability was higher when a diamine chain extender was used,
in comparison with the diol, due to the stronger hydrogen bonding of the urea groups. Hydrazine was found to impart the highest thermal stability due to the higher polarity of the resultant hard segment.

2.5.8 Catalysts

Catalysts are commonly used to increase the reaction rate of polyurethane systems. The type of catalyst that is most suitable depends on the system. Tin-based catalysts such as dibutyl tin dilaurate (DBD TL) is mostly used in systems to catalyse the OH and NCO reaction.\textsuperscript{30} Tin (IV) catalysts have been shown to be effective in improving the rate of reaction of H\textsubscript{12}MDI with polyols to assist in prepolymer synthesis.\textsuperscript{23} Bismuth-based catalysts can be used to reduce water and NCO reaction effects. However, by using bismuth-based catalysts, the reactivity of NCO, such as in IPDI, was reduced, resulting in a broader molecular weight dispersion and higher viscosity.\textsuperscript{30} Amine catalysts are specially used in foam formulations to catalyze the foaming. In the case of a polyether, a combination of amine and metal (tin) catalysts can be used to optimise cell structure. Other catalysts that are commonly used are organic acids such as oleic and adipic acids and heat-activated catalysts such as 1,4-diazobicyclo[2,2,2]-octane (DABCO).\textsuperscript{21} It has been reported for IPDI systems that in the presence of DBTDL, the reaction of secondary isocyanate groups was favoured, while in the presence of DABCO, the primary isocyanate group was preferred.\textsuperscript{24}

2.5.9 Solvents

The function of solvent depends on the coating system it works with. In the solvent-borne system, it is used to dissolve the resin and thus reduce its viscosity.\textsuperscript{69} In the water-borne system, solvent is used as a film-forming aid by plasticizing the polymer particles temporarily, thus reducing the minimum film forming temperature (MFFT), to form continuous film.\textsuperscript{69} It is also used to regulate the viscosity of the prepolymer that has to be sufficiently low to facilitate the dispersion. This can be achieved by using a solvent such as acetone, dimethyl formamide (DMF) or N-methyl-2-pyrrolidone (NMP) or using elevated
temperatures to maintain the prepolymers in the molten state. NMP is often the preferred co-solvent because it acts as a process aid (viscosity control) and also as a coalescing aid (low volatility) in film formation. Typical NMP levels are 10 wt. % to 15 wt. % for PUDs and 3 wt. % to 8 wt. % for hybrids. NMP is needed in some polyurethane systems especially when the diisocyanate or the polyol exist as a solid or high viscosity liquid at room temperature. The NMP is required to dissolve the DMPA, which is insoluble in the polyol-diisocyanate mixture during the prepolymers stage.

The presence of acetone in the dispersion caused a decrease in the modulus, and tensile strength, but an increase in particle size and elongation at break, particularly for the samples which have the longest soft segments. This was thought to be because the trapped acetone among the polymer chains acted as an internal plasticizer, lowering the chain interactions. In addition, it is probably adsorbed by the hydrophobic part of PU chain, resulting in the swelling of particles. Previous workers have conducted the solvent free polyurethane dispersions by using TMXDI as the isocyanate component. The resulting polymer can be dispersed at high temperatures (90°C – 120°C), due to the low reactivity of the tertiary NCO groups. However, the higher temperatures were needed to reduce the viscosity of the prepolymers due to the absence of solvent.

2.6 Microphase-property relationships

Different terms have been used to describe the cause of microphase or microdomain separation between the soft and the hard segments: self-association of hard segments, thermodynamic incompatibility of both segments, and chemical immiscibility between the hard and soft segments, are all primarily related to inter-urethane and urea hydrogen bonding between two segments. Research showed that many factors could influence the degree of microphase separation: the length of the soft segment, the length of hard segment, polarity of both segments, the molecular weight and the types of polyol, crystallisation of both the hard and soft segments, and isomerism and the types of isocyanates. A study had shown that sample with 2,4-TDI and polypropylene oxide
displayed more segmental mixing than the one with 2,6-TDI. The symmetric structure of the latter was thought to be responsible for the different morphological behaviour of those samples. Microphase separation has a profound influence on the mechanical properties of films. Films with higher degrees of microphase separation possessed a high value of tensile strength and initial modulus and good solvent resistance, while retaining the elasticity of the film.20

In poly(ether-urethanes), the –NH groups of the urethane and urea linkages in the hard segment are the donors, while the ether oxygens, -O-, in the soft segment and carbonyl group, -C=O, in the hard segments are hydrogen-bonded acceptors. If the –NH groups are hydrogen-bonded with -O- in the soft segments, segmental mixing or partial segmental mixing is favoured. If they are hydrogen-bonded with carbonyl groups in the hard segments, microphase separation is observed.27 Thus, the degree of segmental mixing or de-mixing via hydrogen bonding can yield specific film properties.66 The type and the molecular weight of the polyols used have a significant effect on phase separation.27,42 The DMTA data revealed that the segmental mixing of hard-soft segments was more favourable when PPG was used rather than PTHF, at the same molecular weight.42 This was thought to be because of the methyl groups in PPG hinder the polymer chains aligning for hydrogen-bond formation.

A study42 had shown that Tg of the soft segment, Tg values, for different isocyanates increased in the order of IPDI < IPDI/HDI blend < H12MDI < TMXDI. The symmetrical structure and the 4,4'-isomer of H12MDI led to more separated domains and hard phase crystallisation.34 However, the presence of other 2,2- and 2,6-isomers reduced the overall strength of the film. The presence of urea linkages and the type of urethane affect the thermal properties.31,34 A thermogravimetric analysis (TGA) study of the degradation profile showed poly(urethane-urea) films were more stable than polyurethane alone due to the presence of urea linkages that give the higher thermal stability to the film.31 It was found that the degradation took place at two stages. The initial degradation occurred in the hard segments, while the second stage occurred in the soft segments. Higher soft segment molecular weight would produce films with higher thermal stability i.e. higher decomposition temperature.
2.7 The synthesis of polyurethane dispersions

The basic way to prepare the PUDs consists of two steps.\textsuperscript{32}

a) Preparation of a low to medium molecular weight isocyanate prepolymer from di- or polyols with di- or polyisocyanates.

b) The prepolymer chain is extended and dispersed in water via different ways by introducing hydrophilic solubilizing groups.

2.7.1 Preparation method

Depending on the starting components, solvents and the process sequence, several preparation methods are common, including most importantly the following.

1. Acetone process
2. Prepolymer mixing process
3. Melt dispersion process
4. Ketamine-ketazine process

2.7.1.1 Acetone process

In the acetone process, the prepolymer is synthesised and chain extended in polar/hydrophilic solvents such as acetone, methyl ethyl ketone (MEK) or THF, in order to avoid high viscosity.\textsuperscript{18,59} The amount of solvent used is generally high (40-60 wt. %), due to the low temperatures of the urethane-forming reactions, which results in higher viscosity of the prepolymer.\textsuperscript{19} The polymer solution, (mixture of prepolymer and solvent), spontaneously forms dispersions when water is added. By removing the solvent via distillation, a purely waterborne dispersion, with smaller particle size and narrower particle size distribution, is formed.\textsuperscript{32,38,59} Depending on the content of the ionic groups and the concentration of the non-ionic hydrophilic groups, the aqueous dispersion is generated either by precipitation of the hydrophobic segments and by phase inversion of an intermediately generated inverse emulsion.\textsuperscript{18} Figure 2.24 shows a schematic diagram of the acetone process.\textsuperscript{18}
Chapter 2

Polyurethanes in surface coatings

The process has the advantages that the polymerisation is completed in acetone before addition of water, thus producing a variation in structure and particle size, high quality end products and reliable reproducibility. There is also no concern about the competition with water during reaction. On the other hand, the processing cost is relatively high as a result of the acetone removal step with its long processing time as a result of foaming during the early stages of distillation. Since the reaction is run at relatively low solids content, it requires greater processing time per unit of solids content to get a high reactor-volume product.

2.7.1.2 Prepolymer mixing process

The most common way to prepare polyurethane dispersions is by the prepolymer mixing process (adding water) or the inverse process (adding into water). The prepolymer mixing process consists of two-stages: preparation of an isocyanate-terminated prepolymer by reacting polyol, diisocyanate and ionic moiety such as DMPA. Later, the prepolymer is
neutralised, dispersed and chain extended in water. Figure 2.25 shows the prepolymer mixing process.

**Figure 2.25: Prepolymer mixing process.**

In comparison with the acetone method, this method uses little or no solvent.\(^{38,59}\) In this procedure, a low molecular-weight prepolymer is prepared by reacting diisocyanates with diols and hydrophilic extender diols such as DMPA. The prepolymer is neutralised with triethylamine and is dispersed by stirring into water. Chain extension is accomplished by adding diamines to the prepolymer dispersion. The NCO groups react preferably with diamines instead of water at lower temperatures.\(^{16}\) It was reported that the reaction rate of -NCO groups with -NH\(_2\) groups, is about a thousand times faster than the NCO with water.\(^{38}\) The reason is that the NCO groups are surrounded and protected by the hydrophilic ionic moieties in the outer part of the droplets causing the reaction to become more selective.\(^{38}\) The dispersion prepared by this method has very good quality with small particle size distribution.
and good storage stability. Drawbacks of this process are the dispersions have higher viscosities and require the use of powerful mixers.

2.7.1.3 Ketamine-ketazine process

In this process, the isocyanate prepolymer is blended with a blocked amine (ketamine) or hydrazine (ketazine). Figures 2.26 shows the ketazine-ketamine process. The mixture of masked diamines or masked hydrazines can be mixed with the NCO prepolymer without a reaction occurring and dispersed in water. The amino function is liberated simultaneously by hydrolysis and chain extension occurs. In contrast to the prepolymer mixing process, the liberated amine is already homogeneously distributed in the
dispersed particles. Therefore, the process is suitable for converting reactive NCO prepolymerm with aromatically bound NCO groups. The stabilizing effect of the carbazide groups increases the resistance to UV and oxidation.

2.7.1.4 Melt dispersion process

In the melt dispersion process, an ionically/non-ionically modified isocyanate-terminated prepolymer in the form of a low viscosity solution is reacted with urea or ammonia to form a capped oligomer with terminal biuret groups. Figure 2.27 shows the melt dispersion process with formaldehyde extension.

\[
\text{Hydrophilic bis-biuret}
\]

\[
\text{Water}
\]  
\[
\text{CH}_2\text{O (formaldehyde)}
\]  
\[
\text{Dispersed poly(urethane-urea)}
\]

Figure 2.27: Melt dispersion process.
The biuret group is subsequently reacted with an alkylation agent, α-chloroacetamide, to become a hydrophilic bis-biuret ionomer. After the self-dispersing step in water, chain extension is accomplished by methylation of the biuret groups with formaldehyde and reduction of pH to initiate polycondensation reactions. This process is simple and easy to control, as solvents are not needed. The system is not sensitive to inexact stoichiometry and gives excellent yield with no problems in production on a large scale. This process is less important for the preparation of the surface coatings raw materials.

2.8 The minimum film formation temperature

The minimum film formation temperature (MFFT) is the lowest temperature at which, a clear uniform film can be formed. For any water-borne system, a MFFT of lower than 5°C is necessary for a good film formation. If the MFFT value is higher than 5°C, an incoherent, brittle and powdery film will be produced. The process of film formation of polyurethane dispersions involves a multi-step process of evaporation of water, coalescence of the particles with the formation of a continuous film and cohesive strength development due to molecular diffusion. The steps may take place simultaneously or in consecutive order. The coalescence and molecular diffusion are a function of the viscosity of the polymer at the application temperature.

The glass transition temperature of a polyurethane dispersion influences the minimum film formation temperature (MFFT) and hence the quantity of the coalescing agent necessary. The higher the T_g of the polymers, the greater the quantity of coalescing agent needed to decrease the MFFT i.e. to achieve sufficient flow and fusion of the particles. Low boiling point solvents and humidity during application, reduce the curing time. Solvents with high boiling points will be present for several days in the film, within which they will perform the function of plasticizers.
POLYACRYLIC DISPERSIONS

It has been stated in many papers that the performances of water-borne PUs are usually inferior to their solvent-based counterparts. Lower molecular weight\textsuperscript{59} and water sensitivity due to the presence of the hydrophilic ionic groups\textsuperscript{9}, are such examples that can affect their system performance. Higher raw material prices, lower outdoor resistance, lower compatibility with pigments and lower adhesion to various substrate are the other factors that needed to be considered. As a consequence, several ideas have been proposed to improve the water-borne coating properties, which can match and in some instances exceed those provided by solvent-borne systems. One popular approach is by introducing other polymers to form multiphase structures in the dispersion through various techniques, such as physical blending or hybridisation e.g. seeded emulsion polymerisation and interpenetrating networks (IPNs).\textsuperscript{59} The most attractive properties are offered by acrylic- and vinyl-based polymers such as poly(methyl methacrylate) (PMMA) and polystyrene (PS). They are easy to copolymerise with their own class of polymers, which can lead to a variety of physical properties such as Tg and solubility characteristics.\textsuperscript{90} It has been reported that the PU dispersions copolymerised with these polymers exhibit high solid contents with relatively low viscosities and their properties are easily adjustable by changing the compositions.\textsuperscript{59} Research showed that by incorporating acrylic polymers that have lower Tg values, such as methyl acrylate (MA) and ethyl acrylate (EA), effectively increased the system hydrophobicity without sacrificing the elasticity of the original polyurethane.\textsuperscript{4} The next section highlights the general background of acrylic polymers plus emulsion polymerisation, as these monomers were selected to be copolymerised with PUDs in this research.

3.1 Acrylic polymers

Acrylic polymers, or polyacrylcs, find use in a variety of paints and coatings that support the automotive, appliance and coil industries. They can have very high molecular
weights and this gives advantages for overall film properties.\textsuperscript{73} The key attributes of acrylic coatings is their high gloss, excellent weatherability, the wide range of glass transition temperature, good chemical resistance, easy thickening, and high compatibility with pigments due to their polarity.\textsuperscript{59,67} They are also relatively cheaper than PU. All the advantages offered by the acrylics can be manipulated to compensate for the deficiencies of the PU dispersion systems.

Solvent borne acrylic technology holds a strong position in the coating of both automotive components and general industrial plastics. The primary advantage of a solvent borne system is adhesion, quick drying, and durability.\textsuperscript{73} However, solvent-borne systems face a pressure from environmental regulation regarding the solvent evaporation. An alternative route is via the waterborne technology, which offers no, or minimal, VOC problems. Here, the acrylic particles are forced together upon water evaporation, leaving a durable film. A drawback is it makes the entanglement step very slow and in some cases, optimal film formation is never achieved because the coalescence aids that keep the polymers mobile, evaporate before the entanglement is completed.\textsuperscript{73} For high Tg and high molecular weight acrylic dispersions, high levels of coalescence aids are required to form a good film.

Acrylic polymers are prepared through the emulsion polymerisation of acrylic monomers, or their corresponding esters, as shown in figure 3.1.

\[
\begin{align*}
R_1 = H, & \quad R_2 = H & \rightarrow \text{Polyacrylate} \\
R_1 = H, & \quad R_2 = \text{CH}_3 & \rightarrow \text{Polymethacrylate} \\
R_1 = \text{CH}_3, & \quad R_2 = \text{CH}_3 & \rightarrow \text{Poly(methyl methacrylate)}
\end{align*}
\]

Figure 3.1: Typical types of acrylic monomer.\textsuperscript{73}
Acrylic polymers used in coatings are classified as being either thermoplastic or thermosetting, depending upon their cure properties.\textsuperscript{26} Thermoplastic acrylic polymers form hardened coatings simply through solvent evaporation. Thermosets form a crosslinked structure by functionalising the acrylic polymer with reactive groups such as carboxyl or hydroxyalkyl, to allow the crosslinking either with itself or with various other resins such as epoxies.\textsuperscript{81} Thermosetting acrylic polymers show improved hardness, toughness and chemical resistance over their thermoplastic counterparts.\textsuperscript{9} Conventional acrylic polymers with low \( T_g \)s normally produce tacky films and lack blocking and dirt pick-up resistance, surface hardness and film cohesion.\textsuperscript{72} Usually the acrylic polymers are combinations of monomers, often with a high content of water insoluble monomers such as methyl methacrylate, butyl acrylate and styrene and a much smaller fraction of water soluble monomers such as acrylic and methacrylic acids. The water soluble monomers give oligomeric acid segments at the latex particle surface which improve the colloidal stability of the formulation and adhesion and curing characteristics of the film.\textsuperscript{82} It is also common to combine a soft phase (low \( T_g \)) and a hard phase (high \( T_g \)) of acrylic polymers in one particle, which has been found to exhibit good film properties such as high blocking resistance, good surface hardness, elasticity, high gloss, weather stability and water resistance.\textsuperscript{82} Properties of acrylate copolymers can be tailor made according to the compositions of acrylate co-monomers.\textsuperscript{83} The alkyl chain on the acrylate influences the hardness of the film and its solubility.\textsuperscript{80} Methacrylates are harder than their corresponding acrylates. For example, methyl methacrylate gives a hard polymer, while methyl acrylate is used as a plasticizing co-monomer.\textsuperscript{80}

### 3.2 Emulsion polymerisation

Acrylic polymers are synthesised via an emulsion polymerisation technique. Emulsion polymerisation is a free radical initiated chain reaction in which a monomer, or a mixture of monomers, is polymerised in the presence of an aqueous solution of a surfactant, to form a latex.\textsuperscript{86} It is used in the production of a wide range of speciality polymers including adhesives, paints, binders for non-woven fabrics, additives for paper, textiles and construction
Emulsion polymerisation encompasses several types of process such as the conventional type, the inverse type and mini-emulsion polymerisations.

The emulsions can be characterised according to the size of the droplets and their colloidal stability i.e. macro-emulsions, mini-emulsions and micro-emulsions. Macro-emulsions do not use co-surfactants and are very unstable. These have droplets with diameters on the order of 1 to 100 microns, whereas mini-emulsions use co-surfactants/hydrophobes to provide stability to sub-micron monomer droplets, thereby reducing the average particle size to 0.1-0.5 microns. The third one is the most stable with droplet size of 10 to 100 nm, owing to a relatively large quantities of emulsifiers used in the process. The choice of a emulsion polymerisation process is justified by the fast polymerisation up to high solid contents, while maintaining a relatively low viscosity. Therefore, high molecular weights can be obtained and the heat of reaction can be removed relatively easily. Since water is used as a dispersant, the process is operated without the use of organic solvents, which is beneficial in applications such as coatings and adhesives with regards to the reduction of VOCs.

3.2.1 Basic components

The typical main ingredients in the emulsion polymerisations are monomer, water, surfactants, initiators and chain transfer agents.

3.2.1.1 Water

Water is needed to maintain a low viscosity and is the medium for heat transfer. It also works as the medium of transfer of the monomer from droplets to particles and the medium of dynamic exchange of surfactant between the phases. It is able to isolate the polymerisation loci and provides the locus for initiator decomposition and oligomer formation.
3.2.1.2 Surfactants

Surfactants play important roles in emulsion polymerisation. They are required for emulsification of the monomers, providing sites/loci for particle nucleation, (i.e. monomer swollen micelles) and colloidal stabilization to the growing particles. In addition, surfactants reduce the surface tension of the resulting dispersion which is required for wetting of a substrate and for film formation. Surfactants are divided into three types: anionic, cationic and non-ionic. However, surfactants are in most cases water soluble and mobile components in the film. They have a tendency to cluster together or migrate either to the film-air interface or the film-substrate interface. The surfactant exudation affects the water sensitivity of the film, as well as the adhesion and gloss characteristics. This creates hydrophilic channels through the film and causes water transport through the film to the substrate.

One possibility to avoid this major drawback is to use reactive stabilisers or macro-monomers that remained attached to the final particle. Such polymeric surfactants have the advantage of low usage level and excellent emulsion stability. They also can improve water resistance, adhesion and water and vapour permeability.

3.2.1.3 Initiators

Water soluble initiators, such as inorganic potassium persulphate, will dissociate into two sulphate radical anions, which can initiate polymerisation. Redox initiators, such as persulphate-bisulphate, are a mixture of an oxidising agent and a reducing agent whose reaction generates radicals. They are used in polymerisation at low temperatures. Non-ionic initiators, such as t-butyl hydrogen peroxide, t-BHPO, which has neutral pH, have been used in the synthesis of poly(urethane-acrylic) copolymers. The initiator was able to maintain the colloid stability of the polyurethane particles during acrylic polymerisation. Oil soluble initiators, such as azo compounds, are used in order to control particle morphology and grafting reactions within particles, and to reduce the residual monomer at the end of reaction.
3.3 Type of process

There are three types of emulsion polymerisation processes: batch, semi-batch and continuous. In the batch process, all ingredients are added at the beginning of the process. The reaction begins as soon as the initiator is added and the temperature is raised, with latex particles forming and growing simultaneously.\textsuperscript{86} The reaction is exothermic due to the heat generated by the polymerisation. Pre-made seed latex, or pre-emulsion, is often used at the start of the polymerisation, in order to control the particle number.\textsuperscript{86} In the semi-batch process, one or more of the ingredients are added continuously or in increments.\textsuperscript{86} The monomers may be added neat or as emulsions. The properties of the composite particles depend on the types of monomer used in the polymerisation process, polymerisation conditions, and the sequence of monomer feed.\textsuperscript{3} Various parameters can be controlled throughout the reaction such as the rate of polymerisation, the rate of generation and removal of heat, the particle number, colloidal stability and coagulum formation, and copolymer composition and particle morphology.\textsuperscript{86} This technique allows the formation of polymers with specific morphology and composition.\textsuperscript{3} The multi-phase structure in each polymer particle provides a broader spectrum of physical properties than emulsions with uniform composition particles. In the continuous process, the ingredients are fed continuously into either one or more stirred reactor tanks that are connected in series. The latex product is simultaneously removed at the same rate. The advantages of the process are high production rates, steady heat removal and the uniform quality of the latexes.\textsuperscript{86}

3.4 The mechanism

Emulsion polymerisation process can be divided into three stages or intervals as shown in figure 3.2.\textsuperscript{86-88} The first stage is the particle formation, or nucleation, stage, (interval I). The nucleation stage is important as it determines the kinetics, particle size distribution and latex properties.\textsuperscript{86} The dispersed mixtures of monomer droplets and monomer swollen surfactant micelles in a continuous aqueous phase are polymerised into monomer swollen polymer particles.\textsuperscript{88} The stage ends when all the micelles have disappeared.
Figure 3.2: A three-stage concept for the emulsion polymerisation process.87

The second stage is the particle growth at the expense of monomer droplets, (interval II). Each particle behaves as a micro-reactor. The particle number and rate of polymerisation are constant throughout the entire interval.86 The third stage is the disappearance of the monomer droplets, (interval III). Polymerisation continues in this interval until all monomer present in the particles, or dissolved in the aqueous phase, is depleted and the polymerisation is completed. However, the particle number is constant and equal to the value reached at the end of interval I.88 The polymerisation rate may show decrease-increase-decrease behaviour depending on the nature of the polymer/monomer and particle size. The rate increase is attributed to a decrease in the termination rate between radicals inside the particles due to the increased internal viscosity.86

3.5 The incorporation of acrylic into PU dispersions

The introduction of acrylics into polyurethanes has combined the beneficial attributes of each polymer. Acrylic emulsions give excellent weather, water and alkali resistances due to the main chain carbon-carbon bonds, while PUDs offer the properties of excellent elasticity, high abrasion resistance and superior low temperature impact resistance.14,77 The specific
interactions between two polymers can be built by introducing crosslinking or grafting reactions via covalent bonding, hydrogen-bonding interactions, anion-cation interactions or ion-dipole interactions.\textsuperscript{9} Latex/direct blends and hybridisation techniques are the popular methods used by many workers.\textsuperscript{59,64,77,78} The performance of both systems is determined by the amount and the degree of compatibility of each polymer in the interphase regions of the mixture.\textsuperscript{6} The hybrids give an excellent tensile performance and in some areas exceed the PU alone. On the contrary, the blended systems have poor mechanical properties and exhibited incoherent film formation.\textsuperscript{59,64,67,92,93} Latex blends have approximately 5-20\% by weight of each polymer in the interphase, while the hybrids give 20-30\% of polyurethane and 35-50\% of acrylic in the interphase.\textsuperscript{77} The hybrids are excellent for coatings and adhesives, as they provide protective, decorative, anti-corrosive properties.\textsuperscript{5} By copolymerising PU with poly(t-butyl acrylate), the thermal and abrasion resistances have been improved.\textsuperscript{59}

3.5.1 Latex blending and the reactive blending

Many workers have reported on the disadvantages of the physical mixing method over the hybrid one when it comes to the performance of the materials. Limited compatibility between PU and polyacrylic becomes the main issue. It is very difficult to obtain an ideal composite system with this approach. A drawback of this system is the distinction between the PU and polyacrylic regions within the wet coating. It would be expected that this region would still partially exist within the coating after film formation.\textsuperscript{9,13,77,78} The combination of PUD and PMMA by direct blending exhibited clearly, two distinct glass transitions for the polymers, as revealed by DSC analysis.\textsuperscript{67}

A reactive blending method which introduces a crosslinking agent into the system has been proposed.\textsuperscript{9,83} Acrylic emulsions and PU dispersions were mixed at the certain stage. Later, the crosslinking agent,\textsuperscript{9} or latent curing agent,\textsuperscript{83} was added into the mixture. An acrylic polymer emulsion containing a keto functional group from diacetone acrylamide and a polyurethane dispersion, containing hydrazine groups were physically combined by physical stirring for 1 hour at ambient temperature.\textsuperscript{9} The keto carbonyl groups react with hydrazine to form hydrazones, which gave high yields even at ambient temperature (figure 3.3).
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Both polymers were covalently bonded at the interfaces of the polymer particles as water was removed during the drying process. The storage stabilities of the systems were improved because water acts as an inhibitor of the crosslinking reaction between the keto group and the hydrazine group under storage conditions.

A similar approach has been taken by Lai et al. in a post-curing reaction. The PUD was reactively blended with acrylate emulsion copolymer (i.e. n-butyl acrylate, acrylic acid and methyl methacrylate) in the presence of a latent curing agent di- and tri-aziridinyl compounds, and produced a stable single component and a self-curable polymer dispersion at higher pH (>8). The polymer carboxyl groups reacts with the aziridinyl groups when its pH value drops below 6 or on air drying. Hence, urethane-acrylic copolymers were formed (figure 3.4).

3.5.2 Hybridisation

Many hybridisation techniques can be used to prepare the hybrids such as grafting, interpenetrating polymer networks (IPNs), seeded emulsion polymerisation and mini-
emulsion polymerisation. Each technique will be discussed in the following sections. The factors reported to control the hybrid behaviour were the synthesis route, the length and type of the soft segments, type of the hard segments and type of acrylic used i.e. functionality and the acrylic properties. Polyurethane particles are able to swell with acrylic monomer and act as a polymeric surfactant to stabilise the monomer swollen particles throughout the reaction. The swelling capacity depends on the nature of polyurethane and its hard and soft segment contents. The PUD prepared from polyols of the higher molecular weight showed a superior swelling capacity with acrylic monomer.

3.5.2.1 Seeded emulsion polymerisation

A typical seeded emulsion polymerisation of PU-polyacrylic hybrid dispersions (PUAs) consists of two steps:

1. Step-growth polymerisation of PU seed, via the acetone process, prepolymer mixing etc.
2. Free-radical emulsion polymerisation, in which the acrylic monomer is polymerised with the polyurethane seed particles.

In general, the seeded emulsion polymerisation is carried out after the seed is swollen by the secondary monomer until swelling equilibrium is attained. This increased the ability of mixing of these two components and allows the formation of polymers with different morphologies such as core-shell, acorn, half-moon, strawberry, raspberry, octopus, mushroom and inverse core-shell types.

The important parameters for the polymerisation are:

a) the phase composition i.e. copolymer composition, \( T_g \) and polarity;
b) the phase ratio;
c) the component compatibility;
d) polymerisation sequence;
e) molecular weights of the polymer phases.
With a fixed composition, the phase ratio or weight ratio of soft to hard components is the most important influence on the particle structure. The final morphology of the structured particles is determined by the interplay of the thermodynamic and kinetic factors. Thermodynamic aspect will push the system towards an equilibrium morphology, to attain the lowest free energy. The reduction of the mobility of polymer chains from the high viscosity or crosslinking in the polymer particle will result in a kinetically controlled morphology. In principle, seeded polymerisation has many advantages in preparation of micron size structured particles and various functional polymer microspheres, while increasing the size of the seed particle with a narrow size distribution. It does not involve the procedure of exchanging the reaction medium and higher solids content can be used.

3.5.2.2 Latex interpenetrating polymer networks (LIPNs)

Another type of seeded emulsion polymerisation of polyurethane-polyacrylic dispersions, is via latex interpenetrating polymer networks. The PUD is copolymerised with an acrylic or vinyl monomer in the presence of a crosslinking agent such as ethylene glycol dimethacrylate (EGDMA), hydroxyethyl acrylate (HEA) or adipic dihyrazide (ADH). Kim et al. reported that by using 1 wt. % EGDMA in PU-polymethacrylate, the particle size increased with polyacrylate ratio. The acrylic monomer polymerised inside the PU particles augmenting the particle mass. Insufficient ionic content made the particles unstable and they coalesced, thus increasing particle size. Shi and co-workers proposed a post-crosslinking technique between the epoxy and the latent curing agent, triethylene tetramine (TETA), to improve the water resistance of a PUA. However, the epoxy content was limited to 20 wt. % to produce a stable latex.

In LIPNs, intimate mixtures of crosslinked polymers are held together by permanent entanglements. Tan δ from the DMTA results showed a single broad peak, implying that the LIPNs samples were highly interpenetrated and interlocked to behave as a single network. The entanglement/interpenetration improved the miscibility and augmented the crosslink
density, thus increasing the tensile strength, elongation at break and the water resistance.\textsuperscript{4,13} Figure 3.5 shows the synthesis of polyurethane-polyacrylic LIPNs.\textsuperscript{13}

![Diagram of synthesis process](image)

**Figure 3.5: Synthesis of polyurethane-polyacrylic LIPNs.\textsuperscript{13}**

### 3.5.2.3 Graft copolymers

The hybridisations of urethane-acrylic composites can also be accomplished by grafting reactions. A urethane prepolymer was co-oligomerised with vinyl monomers, by endcapping the \(-\text{NCO}\) terminated ends of the diurethanes with a hydroxyl functional acrylic monomer, such as hydroxyethylacrylate (HEA) or hydroxymethylmethacrylate (HMMA).\textsuperscript{5,7,78,96} The resulting prepolymer with a terminal double bonds, then was dispersed in the water before undergoing the subsequent emulsion polymerisation with the acrylic to form a graft copolymer. The particle morphology consists of a hard polyacrylic core surrounded by a soft polyurethane shell.\textsuperscript{7} Film coalescence was facilitated by the soft polyurethane shell. Hence, the MFFTs of the copolymers was lower than conventional hard acrylic latexes.\textsuperscript{7}

Kim et al.\textsuperscript{5} investigated the grafting efficiency in such acrylate modifications of a polyurethane. They found that the grafting efficiency increased with increasing hard segment content i.e. DMPA. From FTIR spectroscopy and TLC/FID analysis, it was suggested that the grafting reactions occurred by an abstraction of hydrogen from the \(-\text{NH}\) groups.\textsuperscript{5,154} Figure 3.6 shows the structure of such (urethane-g-acrylic) copolymers.
3.5.2.4 Mini-emulsions

In general, mini-emulsion consist of stable small droplets which are obtained by intense shearing of a system containing an oil phase, (monomer or co-monomer and co-stabiliser), and water phase, (water and surfactant). A distinctive feature of a mini-emulsion from the conventional one, is particle formation is dominated by droplet nucleation mechanism, while the latter adopts micellar nucleation (see section 3.4). Figure 3.7 shows the basic procedure of mini-emulsion polymerisation.
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A co-stabiliser/hydrophobe is a component which retards the Ostwald ripening, (i.e. the mass transfer from small monomer droplets to large droplets, to reduce the total surface energy of system), thus providing stability to monomer droplets.\(^{89,147,170}\) The effectiveness of a co-stabiliser is determined by its very low water solubility, molecular weight and a degree of hydrophobicity.\(^{94,147}\) The more hydrophobic the hydrophobe, the more stable the mini-emulsion is.\(^{148,171}\) Hexadecane and cetyl alcohol are the most often encounter co-stabilisers in reports.\(^{89,93,150,151}\)

Several attempts have been made to synthesise PUAs via the mini-emulsion technique. Wang and co-workers\(^{93,94,173}\) have made extensive studies in this area. They found that 1,4-butanediol (BD) could be used not only as a chain extender, but also as a co-stabiliser, as it was hydrophobic enough to stabilise the monomer droplets against Oswald ripening.\(^{93}\) They also used hexadecane as co-stabiliser and compared the results with the latex blends.\(^{94}\) They found that the hybrid latexes showed better homogeneity than the blends, particularly at 30 wt. % PU content. Further, they compared the results with the PUAs that were synthesised via seeded emulsion polymerisation.\(^{173}\) Both hybrids did not show significant differences in the polymerisation kinetic, but differed in particle size. The latter depended more on the nature and the amount of the emulsifiers used in the recipe.

Barrère and Landfester\(^6\) have shown that polyurethane dispersions can be prepared in a one-step procedure using the mini-emulsion process, (i.e. one-pot method). In this method, the polyaddition and radical polymerisations are conducted in one droplet/particle by controlling the reaction temperature.

A study\(^{149}\) had been conducted by using a redox initiation system in mini-emulsion polymerisation of MDI or IPDI, PPG and n-butyl methacrylate (n-BMA) monomer at 30°C. The NCO-terminated PU and n-BMA monomer were mini-emulsified in the presence of hexadecane as co-stabiliser prior to polymerisation, which resulted in smaller particles. A redox initiation system enhanced the polymerisation rate by generating free radicals quickly at relatively low temperature.\(^{149}\) The nano-sized PUA was obtained prior to chain extension.
3.6 The effect of acrylic diluents on polyurethane-polyacrylic dispersions

It was discussed earlier that acrylic monomers could replace solvents as diluents to control the prepolymer viscosity and as coalescing aids during film formation. Various types of monomers or co-monomers have been used such as MMA, ethyl methacrylate (EMA), ethylene glycol dimethacrylate (EGDMA) and n-butyl methacrylate (n-BMA).\textsuperscript{14} It was found that the acrylic diluent phase is more compatible with the PU hard segments than the soft segments, due mainly to similar polarity and hydrogen bond formation between the urethane and acrylate carboxyls.\textsuperscript{14}

Lee et al.\textsuperscript{14} investigated the effect of varying the ratio of the multifunctional acrylate diluents on the PUA hybrids. Systems that used diluents, such as the monofunctional acylates e.g. MMA, decreased the modulus while increased ductility, whereas by using multifunctional acrylates, such as trimethylolpropane triacrylate (TMPTA), the crosslinked product gave the opposite effect.

Sanderson et al.\textsuperscript{1} outlined the reactivity order of different diluents used in phosphate based urethane-acrylic copolymer dispersions as follows: MMA > EMA > n-BMA > EGDMA. MMA gave the highest reduction in viscosity, followed by EMA. Higher viscosity in n-BMA and EGDMA was related to chain length and the presence of dimethylacrylate groups, respectively.
CHAPTER 4

EXPERIMENTAL
CHAPTER 4

EXPERIMENTAL

This chapter addresses the materials, experimental procedures and characterisation techniques that were employed in this research. The samples were divided into two major groups i.e. polyurethane dispersions and the hybrid polyurethane-polyacrylic dispersions.

4.1 Materials

The materials used in the preparation of polyurethane dispersions (PUDs) and polyurethane-polyacrylic hybrid dispersions (PUAs) are listed in tables 4.1 and 4.2, respectively.

Table 4.1: Materials used in the syntheses of PUDs.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Abbreviation</th>
<th>Supplier</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene glycol 2000</td>
<td>PPG 2000</td>
<td>Sigma-Aldrich</td>
<td>Polyol</td>
</tr>
<tr>
<td>Dimethylol propionic</td>
<td>DMPA</td>
<td>Sigma-Aldrich</td>
<td>Ionic Moiety</td>
</tr>
<tr>
<td>Isophorone diisocyanate</td>
<td>IPDI</td>
<td>Sigma-Aldrich</td>
<td>Diisocyanate</td>
</tr>
<tr>
<td>Neopentyl glycol</td>
<td>NPG</td>
<td>Sigma-Aldrich</td>
<td>Short diol</td>
</tr>
<tr>
<td>Dibromoneopentyl glycol</td>
<td>dNPG</td>
<td>Sigma-Aldrich</td>
<td>Short diol</td>
</tr>
<tr>
<td>Tin (II) octoate</td>
<td>-</td>
<td>Sigma-Aldrich</td>
<td>Catalyst</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>TEA</td>
<td>Sigma-Aldrich</td>
<td>Neutralising agent</td>
</tr>
<tr>
<td>Hydrazine hydrate</td>
<td>HYD</td>
<td>Sigma-Aldrich</td>
<td>Chain extender</td>
</tr>
<tr>
<td>Ethylene diamine</td>
<td>EDA</td>
<td>Sigma-Aldrich</td>
<td>Chain extender</td>
</tr>
<tr>
<td>Deionised water</td>
<td>DI water</td>
<td>-</td>
<td>Dispersion medium</td>
</tr>
<tr>
<td>N-methyl-2-pyrrolidone</td>
<td>NMP</td>
<td>Sigma-Aldrich</td>
<td>Solvent</td>
</tr>
</tbody>
</table>
4.1.1 Selection of the raw materials

The selection of raw materials was partially controlled by the sponsoring body (DSM-NeoResins) of this work. Figure 4.1 shows the chemical structures of the raw materials used in making the polyurethane-polyacrylic hybrid dispersions.

Figure 4.1: Chemical structure of the raw materials.
IPDI was the main choice for this work because it has relatively low vapour pressure, is safe to handle and exists as a liquid at room temperature. Notably, the aim of the research is to synthesise solvent-free PUDs and thereby to reduce, or eliminate the usage, of solvents such as NMP and acetone. Apart from that, different reactivities of its two NCO groups can be used for controlling the PU structure by selective sequential reaction.\textsuperscript{25} Polyether-based polyol, PPG of molecular weight 2000 can be used readily during synthesis as it is also in the liquid form at room temperature. The criteria for the other raw materials have been explained briefly in the introductory section of this thesis.

Table 4.2: Materials used in the syntheses of the PUA.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Abbreviation</th>
<th>Supplier</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane dispersion</td>
<td>PUD</td>
<td>DSM-NeoResins</td>
<td>Seed for emulsion polymerisation</td>
</tr>
<tr>
<td>Methyl methacrylate monomer</td>
<td>MMA</td>
<td>Sigma-Aldrich</td>
<td>Acrylic monomer/diluents</td>
</tr>
<tr>
<td>n-Butyl acrylate monomer</td>
<td>n-BA</td>
<td>Sigma-Aldrich</td>
<td>Acrylic monomer/diluents</td>
</tr>
<tr>
<td>Styrene monomer</td>
<td>STY</td>
<td>Sigma-Aldrich</td>
<td>Acrylic monomer/diluents</td>
</tr>
<tr>
<td>Methacrylic acid monomer</td>
<td>MAA</td>
<td>Sigma-Aldrich</td>
<td>Ionic moiety (stabiliser)</td>
</tr>
<tr>
<td>Butylated hydroxytoluene</td>
<td>Ionol CP</td>
<td>Sigma-Aldrich</td>
<td>Inhibitor</td>
</tr>
<tr>
<td>Iron ethylene diamine tetracetic acid</td>
<td>FeEDTA</td>
<td>Sigma-Aldrich</td>
<td>Catalyst</td>
</tr>
<tr>
<td>t-Butylhydroperoxide</td>
<td>t-BHPO</td>
<td>Sigma-Aldrich</td>
<td>Initiator (redox)</td>
</tr>
<tr>
<td>Iso-ascorbic acid</td>
<td>-</td>
<td>Sigma-Aldrich</td>
<td>Decomposer</td>
</tr>
<tr>
<td>Ammonium persulphate</td>
<td>APS</td>
<td>Sigma-Aldrich</td>
<td>Initiator</td>
</tr>
<tr>
<td>Sodium lauryl sulphate</td>
<td>SLS</td>
<td>Sigma-Aldrich</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Ammonia</td>
<td>-</td>
<td>Sigma-Aldrich</td>
<td>pH adjuster</td>
</tr>
</tbody>
</table>
4.2 Syntheses of polyurethane dispersions (PUDs)

4.2.1 Prepolymer mixing method

Two types of PUDs i.e. solvent free and NMP containing PUDs, were synthesised via the prepolymer mixing method. The method involves two steps, namely, the prepolymer step and the dispersion step (see figure 4.2). All raw materials were used without further purification. PPG 2000 and DMPA were charged into the reaction vessel with the speed of the agitator set at 20 rpm at room temperature. In the case of NMP containing PUDs, 20 wt. % of the solvent was added simultaneously. Later, IPDI was charged and the temperature was increased to 50°C. The reaction was conducted under a nitrogen flow to prevent any side reactions. The reaction temperature was monitored by thermocouple, while the water bath or heating mantle were used as alternates to control the reaction temperature. Later, a catalyst, tin (II) octoate, was added. The temperature was increased to 90°C and the reaction was maintained at this temperature for 2 hours. The prepolymer was allowed to cool at 85°C and the NCO percentage was determined via the di-n-butyl amine (DBA) back titration method\(^{128}\), (refer in Appendix A1). If the NCO percentage had not reached the theoretical value, the reaction was continued at a constant temperature of 85°C. Then, neutralising agent, TEA was added into the prepolymer whilst agitating thoroughly. TEA was used to neutralise the COOH groups of DMPA.

4.2.2 Dispersion steps

The neutralised prepolymer was transferred via a feeding funnel into a reactor containing deionised water. The reactor temperature was set at 20-25°C. During transfer, the prepolymer temperature was maintained at 70°C, with the assistance of an extra heating mantle attached near the prepolymer feeding funnel. Higher temperature was needed to reduce the viscosity of the prepolymer and enable flow through the capillary: the prepolymer was tend to solidify and stick at the funnel walls at room temperature. The total transfer time was set to 75 minutes. Finally, hydrazine monohydrate was charged into the dispersions for the chain extension process i.e. 85 % chain extension. The ‘under-extension’ is purposely
designed to minimise side reaction with water, to maximise molecular weight build up and to avoid any free hydrazine being left in the sample. The dispersion was filtered with a 200 micron wire mesh. Figure 4.3 shows the apparatus used in making the polyurethane dispersions. The solvent free sample was designated as "A" while the NMP containing PUD was "B". The full recipe of the solvent free PUDs is shown in table 4.3, while the basic recipe calculations, such as TEA and hydrazine requirements, are shown in Appendix A1. The dried film B was annealed at 80°C for 16 hours in a vacuum chamber and designated as "BT".

Figure 4.2: Synthesis of PUDs via the prepolymer mixing method.
Figure 4.3: The apparatus used in the synthesis of PUDs.

Table 4.3: Sample descriptions for A, B and BT

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100% solids* without solvent</td>
</tr>
<tr>
<td>B</td>
<td>80% solids* with 20% of N-methyl-2-pyrrolidone (NMP)</td>
</tr>
<tr>
<td>BT</td>
<td>Film B annealed at 80°C for 16 hrs in a vacuum chamber</td>
</tr>
</tbody>
</table>

*The wt % of PPG, DMPA, IPDI and catalyst only.
Table 4.4: The recipe for the solvent-free PUDs.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG 2000</td>
<td>418.0</td>
</tr>
<tr>
<td>DMPA</td>
<td>32.50</td>
</tr>
<tr>
<td>IPDI</td>
<td>199.0</td>
</tr>
<tr>
<td>Tin (II) octoate</td>
<td>0.13</td>
</tr>
<tr>
<td><strong>Total prepolymer solids</strong></td>
<td><strong>650</strong></td>
</tr>
<tr>
<td>TEA</td>
<td>24.50</td>
</tr>
<tr>
<td>HYD (15.2 %)</td>
<td>77.0</td>
</tr>
<tr>
<td>DI water</td>
<td>1164</td>
</tr>
<tr>
<td><strong>Total solids</strong></td>
<td><strong>662</strong></td>
</tr>
<tr>
<td><strong>Total dispersion (35 wt. % solids)</strong></td>
<td><strong>1891</strong></td>
</tr>
</tbody>
</table>

Sample A was observed to be an opaque latex while B showed a clear one. The latter was less viscous than A, due to the presence of NMP that can dissolve DMPA. The environment legislation about VOC, made sample A as an ideal candidate for further hybridisation studies.

4.3 Syntheses of polyurethane-polyacrylic hybrid dispersions (PUAs)

The PUA was made via a free radical polymerisation using a single or a double batch technique. Two types of acrylic monomers i.e. MMA/n-BA co-monomers and styrene/n-BA co-monomers, were copolymerised with the PUD. The samples were designated as "the A series" and "the B series" depending on the type of PUD seeds, (i.e. sample A and sample B). Tg of the polyacrylic was calculated by using the Fox equation and was set at 50°C; (refer to Appendix A1 for detail calculations).

4.3.1. The single batch method

The ratios of polyurethane to polyacrylic were fixed at 70:30, 50:50 and 30:70. Table 4.5 shows the sample descriptions. The reactions were carried out under a nitrogen flow.
Table 4.5: Sample descriptions for the single batch method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>70% PU: 30% PMMA/PBA</td>
</tr>
<tr>
<td>A2</td>
<td>50% PU: 50% PMMA/PBA</td>
</tr>
<tr>
<td>A3</td>
<td>30% PU: 70% PMMA/PBA</td>
</tr>
<tr>
<td>A4</td>
<td>70% PU: 30% PS/PBA</td>
</tr>
<tr>
<td>A5</td>
<td>50% PU: 50% PS/PBA</td>
</tr>
<tr>
<td>A6</td>
<td>30% PU: 70% PS/PBA</td>
</tr>
<tr>
<td>B1</td>
<td>50% PU: 50% PMMA/PBA</td>
</tr>
<tr>
<td>B2</td>
<td>50% PU: 50% PS/PBA</td>
</tr>
<tr>
<td>BT1</td>
<td>Film B1 annealed at 80°C for 16 hrs in a vacuum chamber</td>
</tr>
<tr>
<td>BT2</td>
<td>Film B2 annealed at 80°C for 16 hrs in a vacuum chamber</td>
</tr>
</tbody>
</table>

At first, the PUDs and DI water were charged into a reactor. Then, half amounts of the monomers were charged into the polyurethane dispersion and were left to swell the polyurethane particles for 1 hour at 25°C under slow agitation. The initiator, t-BHPO, and the catalyst, FeEDTA, were added and stirred for 5 minutes. Then, 20% of reducing agent, iso-ascorbic acid, was added and stirred for 15 minutes. The radicals were produced using redox reactions at low temperature i.e. 25°C. The pH of the mixture was set at 8 using ammonia. This was important to obtain a longer storage stability. As the reaction was exothermic, the temperature was kept at 25°C with cooling water.

The other half amount of the monomer was added into the mixtures and stirred for a further 1 hour. Then, four shots of iso-ascorbic acid were charged every 15 minutes until the reaction was completed. The addition of iso-ascorbic acid was divided into five shots to ensure that all the monomers were consumed during the reaction. The dispersions were filtered through a 200 micron wire mesh. The basic characterisation of the latexes, including solids content, MFFT, pH and viscosity, were carried out by DSM-NeoResins, and can be referred to in Appendix A1. Figure 4.4 shows the syntheses process of PUA, while table 4.6 shows the recipe for sample A2. For the B series, the PU:polyacrylic ratio was fixed at 1:1. The samples was synthesised via the same technique as in the A series.
Chapter 4

**Experimental**

**Figure 4.4:** Synthesis of PUA for the A and B series.
Table 4.6: The recipe of PUA for sample A2.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent free PUD (35% solids)</td>
<td>747.20</td>
</tr>
<tr>
<td>DI water</td>
<td>368.0</td>
</tr>
<tr>
<td>MMA (75 %)</td>
<td>196.14</td>
</tr>
<tr>
<td>n-BA (25 %)</td>
<td>65.38</td>
</tr>
<tr>
<td>t-BHPO</td>
<td>8.26</td>
</tr>
<tr>
<td>FeEDTA</td>
<td>1.15</td>
</tr>
<tr>
<td>Iso-ascorbic acid</td>
<td>113.8</td>
</tr>
<tr>
<td>Total solids content</td>
<td>525</td>
</tr>
<tr>
<td>Total dispersion (for 35 wt. % solids content)</td>
<td>1500</td>
</tr>
</tbody>
</table>

The latexes from both series were dried at room temperature for 5 days prior to further drying in a vacuum chamber for 2 days at RT. Some of the B series were annealed at 80°C for 16 hours to study the possibility of NMP retaining in the dried films (designated as BT1 and BT2).

4.3.2. Acrylic monomer as a diluent

Two synthesis methods were employed to prepare PUA s i.e. a single batch and a double batch technique. In this study, the acrylic monomer was used as a diluent at the prepolymer stage or as a non-diluent if the monomer was added after the prepolymer was completed, but prior to the dispersion stage. The PU:polyacrylic ratio was fixed at 1:1 with a polyacrylic Tg of 50°C.

4.3.2.1 The single batch method

In this work, the acrylic monomer addition was divided into two stages. In the first stage, 20 wt. % of the monomer was added as a prepolymer diluent or as a non-diluent. The
addition of inhibitor, butylated hydroxy toluene (IonoLP, CP), was needed to inhibit the polymerisation of acrylic monomer during the prepolymer preparation.

The reactions were carried out in the atmospheric environment as the inhibitor only works in the presence of oxygen. Because of the nature of the reaction, i.e. exothermic, full care has to be taken to ensure that the reaction temperature is not in excess of $80^\circ C$, especially during the neutralisation stage because of TEA's highly flammability. Later, the remaining 30 wt. % of acrylic monomer was added and the all the monomers from both stages (total 50 wt. %) were polymerised. PMMA/PBA-based hybrid was designated as the C series while PS/PBA one was designated as the D series.

4.3.2.2 The double batch method

20 wt. % of the acrylic monomer was added as a diluent or as a non-diluent at the prepolymer stage. Later, the monomer was polymerised to the polyacrylic after the dispersion step. The remaining 30 wt. % monomer was added and polymerised at the second stage. Figure 4.5 shows the synthesis route for the single and the double batch methods.

4.3.2.3 Tg of polyacrylic

Tg of the C series had two values i.e. $20^\circ C$ and $50^\circ C$. They were synthesised via the single and the double batch methods at the fixed 1:1 PU:polyacrylic ratio. The sample descriptions are shown in table 4.7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Double batch technique. Tg of PMMA/PBA is $50^\circ C$</td>
</tr>
<tr>
<td>C2</td>
<td>Single batch technique. Tg of PMMA/PBA is $20^\circ C$</td>
</tr>
<tr>
<td>C3</td>
<td>Double batch technique. Tg of PMMA/PBA is $20^\circ C$</td>
</tr>
</tbody>
</table>
Figure 4.5: Synthesis of PUAs with acrylic monomers as 1) diluent and 2) non-diluent.
4.3.2.4 The addition mode of acrylic monomer

The addition mode of acrylic monomer of the D series (PS/PBA-based hybrid) was changed in such a way to investigate the resulting effect on the morphology-property relationships. Apart from that, the samples were synthesised either via the double or the single batch technique. The mode of monomer addition is shown in table 4.8. The PU:polyacrylic ratio was fixed at 1:1 with a polyacrylic Tg of 50°C.

Table 4.8: Sample descriptions for the D series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis technique</th>
<th>Description</th>
<th>Acrylic monomer addition sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>Double batch</td>
<td>Dilaents.</td>
<td>First stage - (pre-polymer mixing). 20wt % acrylic monomer was added.</td>
</tr>
<tr>
<td>D2</td>
<td>Double batch</td>
<td>Non-dilaents.</td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>Single batch</td>
<td>Non-dilaents.</td>
<td></td>
</tr>
<tr>
<td>D4</td>
<td>Single batch</td>
<td>Dilaents.</td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>Single batch</td>
<td>Only n-BA monomer as diluents.</td>
<td>Only styrene monomer was added. Later, all monomers were polymerised.</td>
</tr>
</tbody>
</table>

4.3.3 Modification of the PU hard segments of the A series

The samples were made based on the DMTA and MTDSC data for the pure PUDs and the hybrids of the A series.

4.3.3.1 Type of chain extender

The hard segment of the solvent-free PUD was modified with three types of chain extender i.e. EDA, NPG and dNPG. The idea was to increase the stiffness of the hard segment and studying the effects using the DMTA and MTDSC. The chain extender that was
used in the A series (i.e. hydrazine) was replaced with EDA. The formation of poly(urethane-urea) was expected as the $-\text{NH}_2$ groups of EDA are able to react with the urethane linkages to form urea groups. The sample was designated as AE.

Meanwhile, a short diol, NPG, was added at two different weight ratios i.e. 2% and 4%. The higher NPG content was expected to produce a stiffer sample, owing to the branch methyl groups of NPG, which could restrict the mobility of PPG, thus reducing the sample flexibility. The samples were labelled as AN1 (2 % NPG) and AN2 (4 % NPG).

The brominated polyol, dNPG was incorporated into the hybrid of the A series at a PU:polyacrylic ratio of 1:1. The aim was to get clear contrast between the core and the shell structures of the hybrid via the TEM technique. A heavy element, bromine, is incorporated in the hard segment, which imparts higher electron density, thus giving a darker shade in the TEM image. The embedding latex technique was employed. A few drops of sample latex was embedded to the secondary single-phase latex that has latex particles bigger than the sample i.e. 150 – 200 nm. Later, the dried resultant film was embedded into an epoxy resin prior to being microtomed. However, the film needed to be stained with RuO$_4$ to prevent, or minimise, electron beam damage. The experiment was performed in a collaboration between DSM-NeoResins and Jeff Stubbs of University of New Hampshire, USA. The sample descriptions before and after the modifications are shown in table 4.9. The reaction route for all samples was the same as for the PUD system (refer to figure 4.2)

Table 4.9: Sample descriptions and their modifications.

<table>
<thead>
<tr>
<th>Modification</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Description</td>
<td>Sample</td>
</tr>
<tr>
<td>A</td>
<td>Solvent free PUD</td>
<td>AE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AN1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AN2</td>
</tr>
<tr>
<td>A2</td>
<td>PU:PMMA/PBA at 50:50 wt. %</td>
<td>A2D</td>
</tr>
<tr>
<td>A5</td>
<td>PU:PS/PBA at 50:50 wt. %</td>
<td>A5D</td>
</tr>
</tbody>
</table>
4.4 Synthesis of polyacrylic latex

The pure polyacrylic latex was synthesised via a free radical polymerisation. The sample was purposely designed to assist the characterisations and evaluation of properties of their hybrid counterparts. It was also used in the preparation of the latex blend samples. Two types of polyacrylic latexes i.e. PMMA/PBA latex (designated as E) and PS/PBA latex (designated as F) were prepared. Both samples were copolymerised in the presence of methacrylic acid (MAA) to ensure the stability of the resultant latexes. Table 4.10 shows the sample descriptions, while table 4.11 shows the raw materials and the recipe for sample E.

Table 4.10: Sample descriptions for pure polyacrylic latexes.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>PMMA/PBA</td>
</tr>
<tr>
<td>F</td>
<td>PS/PBA</td>
</tr>
</tbody>
</table>

Table 4.11: The recipe for PMMA/PBA latex (sample E).

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>847</td>
</tr>
<tr>
<td>SLS</td>
<td>25</td>
</tr>
<tr>
<td>APS</td>
<td>3</td>
</tr>
<tr>
<td>MMA</td>
<td>430</td>
</tr>
<tr>
<td>n-BA</td>
<td>148</td>
</tr>
<tr>
<td>MAA</td>
<td>12</td>
</tr>
<tr>
<td>Iso-ascorbic acid</td>
<td>0.3</td>
</tr>
<tr>
<td>t-BHPO</td>
<td>0.5</td>
</tr>
<tr>
<td>Ammonia</td>
<td>19</td>
</tr>
</tbody>
</table>

The reaction was carried in nitrogen environment. The reaction temperature was monitored by a thermocouple and the reactor temperature was controlled with a water bath and heating mantle. At first, DI water and 32 wt.% of SLS were charged into a reactor. MMA, n-BA and MAA were charged into the monomer feed tank while the remaining SLS, DI water and 65.5 wt. % of APS were stirred together in the initiator tank. Later, 10% of the monomer mixtures
was added to the reactor at 85°C. The temperature was reduced to 75°C before the addition of the remaining APS into the reactor. Then, the temperature was raised back to 85°C. Both monomers and initiator feeds were charged simultaneously into the reactor for 90 minutes. When the feeds were completed, the temperature was decreased to 50°C. Then, 33 wt. % of t-BHPO and iso-ascorbic acid were charged and stirred for 30 minutes. Later, another 33 wt. % of t-BHPO was added after 10 minutes from the first charged and followed by another 33 wt. % of t-BHPO after 20 minutes from the second charge. The temperature was cooled down to 25°C. The pH of the emulsion was adjusted to 8 with ammonia. The emulsions were filtered through a 200 micron wire mesh. The copolymerisation of acrylates and styrene is shown in figures 4.6a) and b), while the synthesis flow diagram is shown in figure 4.7.

Figure 4.6: Copolymerisation of a) MMA/n-BA/MAA and b) STY/BA/MAA.
Figure 4.7: Synthesis of PMMA/PBA via a free radical polymerisation.
4.5 Latex blends

Apart from the hybrid samples, a comparison with the latex blend version could give more information about the morphology and properties of samples. Pure PUD from the A and B series were mixed with the pure polyacrylcs by physical blending at the equivalent ratio to the hybrids. The solvent free PUD was designated as the AP series while the NMP containing PUD was designated as the BP series. The mixture was mixed for 1 hour at room temperature. The latexes were degassed in a vacuum chamber prior to casting onto Teflon plates. The sample descriptions are shown in tables 4.12 and 4.13.

Table 4.12: Sample descriptions for the AP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP1</td>
<td>70 wt.% PU: 30 wt. % PMMA/PBA</td>
</tr>
<tr>
<td>AP2</td>
<td>50 wt.% PU: 50 wt. % PMMA/PBA</td>
</tr>
<tr>
<td>AP3</td>
<td>30 wt.% PU: 70 wt. % PMMA/PBA</td>
</tr>
<tr>
<td>AP4</td>
<td>70 wt.% PU: 30 wt. % PS/PBA</td>
</tr>
<tr>
<td>AP5</td>
<td>50 wt.% PU: 50 wt. % PS/PBA</td>
</tr>
<tr>
<td>AP6</td>
<td>30 wt.% PU: 70 wt. % PS/PBA</td>
</tr>
</tbody>
</table>

Table 4.13: Sample descriptions for the BP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP1</td>
<td>70 wt.% PU: 30 wt. % PMMA/PBA</td>
</tr>
<tr>
<td>BP2</td>
<td>50 wt.% PU: 50 wt. % PMMA/PBA</td>
</tr>
<tr>
<td>BP3</td>
<td>30 wt.% PU: 70 wt. % PMMA/PBA</td>
</tr>
<tr>
<td>BP4</td>
<td>70 wt.% PU: 30 wt. % PS/PBA</td>
</tr>
<tr>
<td>BP5</td>
<td>50 wt.% PU: 50 wt. % PS/PBA</td>
</tr>
<tr>
<td>BP6</td>
<td>30 wt.% PU: 70 wt. % PS/PBA</td>
</tr>
</tbody>
</table>

Finally, a summary of all samples prepared in this work is presented in figure 4.8.
Figure 4.8: The summary of all sample syntheses.
4.6 Characterisation techniques

In this study, several characterisation techniques were employed to investigate the morphology-properties relationships. Dynamic mechanical thermal analysis (DMTA) and modulated temperature differential scanning calorimetry (MTDSC) were used to study the glass transition behaviour and morphology. In addition, the phase morphology was further investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The identification of molecular groups and the degree of grafting between –NH groups and the polyacrylic were studied by the FTIR spectroscopy technique. The average particle size was measured with a Malvern Zetasizer, while the mechanical properties were determined with stress-strain tests. Lastly, wide angle X-ray diffraction (WAXD) was employed to verify the crystallinity of certain samples. The latexes were cast onto Teflon plates and dried at ambient temperature for 5 days. Later, the films were further dried in a vacuum oven at 20 mm Hg at 25°C for 2 days. These films were used for all the characterisations, except for particle sizing.

4.6.1 Fourier transform infra-red spectroscopy (FT-IR)

Infra-red (IR) spectroscopy is one of the most often used spectroscopic tools for the study of polymers. It can be used to provide information on chain conformations, chemical structure, crystallinity and orientation of the polymers.\textsuperscript{25} IR spectroscopy can also be used to estimate the degree of hydrogen bonding.\textsuperscript{25} The IR method is rapid and sensitive with sampling techniques that are easy to use. IR spectroscopy detects transitions in a molecule between rotational and vibration energy levels of the ground (lowest) energy state.\textsuperscript{157} There are two kinds of fundamental vibrations for molecules i.e. stretching and bending.\textsuperscript{157} When infrared light at the same frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased. When the molecule reverts from the excited state to the original ground state, the absorbed energy is released as heat. There are a few types of sampling techniques i.e. the transmission and attenuated total reflection (ATR).\textsuperscript{156} The latter is a widely used technique for the analysis of polymer samples with low transmission.\textsuperscript{118} It involves a crystal with a high refractive index and with low IR absorption in the IR region of
interest. In order for a particular vibration to result in the absorption of infrared energy, that vibration must cause a change in the dipole moment of the molecule. The IR studies on the PUDs were focused on three regions: the \(-\text{NH}\) stretch absorptions \((3500-3200 \text{ cm}^{-1})\), the \(\text{CH}_2\) stretch absorptions \((3000-2700 \text{ cm}^{-1})\) and the carbonyl vibrations \((1750-1650 \text{ cm}^{-1})\).\(^{98}\) Participation in hydrogen bonding decreases the frequency of the \(-\text{NH}\) vibration and increases its intensity, making this absorption useful in the study of hydrogen bond effects.\(^{99}\)

The important absorption peaks in PUD and PUA are summarised in table 4.14.\(^{35,59}\)

Table 4.14: Absorption peaks for PUD and PUA.\(^{59}\)

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500-3200</td>
<td>(-\text{NH}) stretch absorptions</td>
</tr>
<tr>
<td>2949 and 2867</td>
<td>Alkane (-\text{CH}) stretching vibration</td>
</tr>
<tr>
<td>2250 - 2285</td>
<td>Free NCO group</td>
</tr>
<tr>
<td>1732-1680</td>
<td>C=O stretching of urethane or acrylate groups</td>
</tr>
<tr>
<td>1610-1557</td>
<td>Carboxylate ion stretching</td>
</tr>
<tr>
<td>1600-1500</td>
<td>Aromatic ring</td>
</tr>
<tr>
<td>1640-1635 and 1625 - 1620</td>
<td>Unreacted vinyl group of n-BA</td>
</tr>
<tr>
<td>1560-1530</td>
<td>(-\text{NH}) bending of urethane</td>
</tr>
<tr>
<td>1280</td>
<td>Aliphatic amine stretchings</td>
</tr>
<tr>
<td>1150-1070</td>
<td>C-O-C stretching</td>
</tr>
</tbody>
</table>

In this study, the Fourier transform infrared spectroscopy coupled with attenuated total reflectance (FTIR-ATR), consists of the heated cell controller from Specac 20100 Eurotherm and a Unicam FTIR spectrometer. The total reflectance spectra were obtained using a ZnSe internal reflectance element at an incidence angle of \(45^\circ\). Scanning was repeated 200 times before the spectra were recorded at a resolution of 4 cm\(^{-1}\). The polyurethane dispersions and hybrid samples were prepared by casting the dispersion on to a glass plate using a 300 micron K-bar. Each was left to dry for one week and further dried in a vacuum chamber at \(20 \text{ mm Hg}\) at room temperature for 2 days. The dried films were analysed using the ATR mode.
Meanwhile, the acrylic samples were press moulded in the form of KBr pellets and were examined using the transmission mode.

4.6.2 Particle sizing

The colloidal particles size is measured using the laser light scattering technique of photon correlation spectroscopy (PCS). The fluctuations in the intensity of light scattered by colloidal particles are analysed using a digital correlator to determine the diffusion coefficient and size distribution of the particles. The upper limit of the particle size range is mainly determined by the onset of particle sedimentation and depends on both the size and the density of the particles. Meanwhile, the lower limit is determined by scattering intensity. The size measurements are possible over a range of particle diameters from 2 nm to 3 microns with a temperature range of 10°C to 70°C and a scattering angle range of 12° and 190°. Figure 4.9 shows the working diagram of particle size measurement by the instrument.

![Figure 4.9: The measurement units in the Zetasizer.](image)

In this research, the particle sizes of the dispersions were determined using a Malvern Zetasizer 3000HS, with a measurement range of 10 nm to 3 microns. The measurements are made based on the Brownian movement of the particles at 25°C. The Brownian movement is dependent on the viscosity of the dispersant. Approximately, 0.2 ml of sample was diluted...
with distillation water to an approximate concentration of 0.1 % and was measured at 25°C. The test was repeated several times until a constant average particles size was reached.

4.6.3 Thermogravimetric analysis (TGA)

The technique is widely employed to determine the thermal stability of polymers. Apart from that, it also can be used to characterise polymer through loss of a known substances e.g. HCl from PVC or for determining volatilities such as plasticizers or other additives. A continuous measurement of the mass of the sample at the constant heating rate is recorded as a thermogram. Weight loss may arise from the evaporation of residual moisture or solvent, but at higher temperatures it originated from polymer decomposition.

In this work, a TGA 2950 Thermogravimetric Analyzer from TA Instruments, was used for the study. Samples masses of 15 mg to 50 mg were heated at room temperature to 450°C in the atmospheric environment. The heating rate was set at 10°C/min. The test was carried out to calculate the amount of NMP retaining in the dried film for the B series.

4.6.4 Wide-angle X-ray diffraction (WAXD)

This technique was employed to determine the presence of ordered arrangements of atoms and molecules. It identifies crystallinity and orientation in polymers. In addition, phase identification such as size, geometry, type of atoms and their position in the unit cell can be determined. Figure 4.10 shows the principle of X-ray diffraction. The crystalline regions diffract X-rays. The angle of diffraction, θ, can be used to calculate the distance between the parallel planes in the crystallites by using the Bragg's law.

\[ n\lambda = 2d \sin\theta \]

where, \( \lambda \) = wavelength of the radiation.
\( d \) = inter-planar spacing (1/s).
\( n \) = integer
Highly crystalline materials reflect the waves to produce diffraction rings or haloes. In PUD systems, the restriction of chain mobility by the covalent linkages and the presence of strong interactions through hydrogen bonding, decreased the degree of crystallinity.\textsuperscript{46} The soft segment may form crystalline structures due to longer chain lengths and ordered structure.\textsuperscript{98}

In the present study, WAXD was used to verify crystallinity in the PUD modified sample. A Bruker model D8 X-ray generator was operated at 40 kilovolts and 40 milliamperes. A graphite monochromator and copper $k_{\alpha}$ radiation ($\lambda = 0.1542$ nm) were used throughout. The scan speed was 0.24°/min. with the angle from 1° to 25°.

4.6.5 Modulated temperature differential scanning calorimetry (MTDSC)

Differential scanning calorimetry (DSC) is a technique used to study thermal transitions of a polymer, in which the difference in heat flow to a pan containing the sample and a pan filled with N$_2$ (reference) is monitored against temperature, while the temperature of the sample, in a specified atmosphere, is programmed.\textsuperscript{21} Small temperature differences occurring due to the exothermic/endothermic effects in the sample are recorded as a function of the programmed temperature (figure 4.11).\textsuperscript{163}

The DSC is used in polymer research for different types of experiments:
\begin{itemize}
  \item[a)] glass-rubber transition temperature, $T_g$;
  \item[b)] melting/recrystallisation temperature, $T_m/T_c$;
  \item[c)] percentage of crystallinity.
\end{itemize}
The glass transition temperature, \( T_g \), represents the temperature region at which the amorphous phase of a polymer is transformed from a brittle, glassy material into a tough rubber-like state.\(^{119} \) This effect is accompanied by a step-wise increase of the DSC heat flow/temperature of specific heat/temperature curve. This means heat is being absorbed by the sample, thus increasing its heat capacity.\(^{21} \) The glass transition can also respond to the compatibility between two polymers\(^{158} \) and can be related to structure dependent features in amorphous thermoplastics such as the bulky side group, which obstructs the free rotation of the C-C bonds along the main chain in polystyrene.\(^{159} \)

![DSC thermogram depicting several transition types.](image)

Figure 4.11: DSC thermogram depicting several transition types.\(^{143} \)

Recently, a new technique was introduced to provide the same qualitative and quantitative information as conventional DSC, known a modulated temperature DSC (MTDSC). Figure 4.12 shows a schematic diagram of a cross section of a MTDSC cell.\(^{163} \)

![Schematic diagram of a cross-section of a MTDSC cell.](image)

Figure 4.12: Schematic diagram of a cross-section of a MTDSC cell.\(^{163} \)
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Experimental

The basic principle of MTDSC is the linear temperature heating or cooling rate used in the conventional DSC, is modulated with a periodic temperature modulation of a certain amplitude and frequency (or period), as shown in figure 4.13.\(^{132,133}\)

![Figure 4.13: Typical modulated temperature profile versus time. The dashed line shows the underlying heating rate.\(^{163}\)](image)

It introduces two different time scales simultaneously with a single experiment. A long time scale corresponding to the underlying heating rate (i.e. the heating rate is applied to the sample at the required temperature range) and the shorter time scale corresponding to the frequency of the modulation.\(^{132}\) Each modulation starts anew at the end of every period and only those molecular motions with relaxation times of the order of the period will respond to each modulation.\(^{132}\) The total heat flow signal which is equivalent to the conventional DSC, can be separated into two thermal behaviours i.e. the reversing and non-reversing signals.\(^{126,127}\) The reversing signal is related to the molecular motions such as vibrational, rotational and translational motions.\(^{134}\) The step-change in this signal indicates the glass transition temperature.\(^{102}\) The non-reversing signal is resulted from the kinetically hindered events such as chemical reactions, crystallisation and melting.\(^{134,137}\) The total heat flow is shown by equation 1.

\[
\frac{dQ}{dT} = C_p \frac{dT}{dt} + f(T, t) \tag{1}
\]
where $\frac{dQ}{dT}$ is differential heat flow rate (watts), $C_p$ is heat capacity (specific heat x mass), $\frac{dT}{dt}$ is heat rate (${^\circ}C/min$) and $f(T,t)$ is kinetic heat flow (watts). The first term is called as the reversing component signal while the second term is the non-reversing component.\textsuperscript{127}

Figure 4.14 shows the reversing and non-reversing signals that have been separated from the total heat flow.\textsuperscript{163}

![Figure 4.14: The signals obtained from the total heat flow.\textsuperscript{163}](image)

In MTDSC, the programmed temperature that is modulated sinusoidally at any time $t$, is given by

$$T = T_0 + Bt + A \sin \omega t$$

where $T_0$ is the starting temperature, $B$ is the heating rate, $A$ the amplitude of the temperature modulation and $\omega$ the frequency, which is equal to $2\pi/P$, where $P$ is the period of modulation.

The instantaneous heating rate can be expressed as:

$$\frac{dT}{dt} = B + A \omega \cos(\omega t)$$

The resulting heat flow can be expressed as:

$$\frac{dQ}{dt} = C_pB + f'(t,T) + C_pA \omega \cos(\omega t) + C \sin(\omega t)$$

(Underlying signal) (Cyclic signal)
where \( f'(t,T) \) is the average underlying kinetic function and \( C \) is the amplitude of the kinetic response to this modulation. Apart from two signals (i.e. reversing and non-reversing) obtained from a single experiment, MTDSC is capable of determining the extent of mixing of two blended polymers that have \( \Delta T_g \) within less than 15°C, which cannot be measured by DSC.\(^{133}\) By integrating the derivative \( C_p \) against temperature, the \( \Delta C_p \) can be calculated.\(^{77,134,164}\)

\[
\Delta C_p = \int_{T_i}^{T_f} \left[ \frac{dC_p(T)}{dT} \right] dT
\]

where \( T_i \) and \( T_f \) are the initial and final values of the temperature in the glass transition region. For an immiscible polymer blend, the total \( \Delta C_p \) is the linear sum of the \( \Delta C_p \) values of the two constituent polymers as shown in equation 6.

\[
\Delta C_p = w_{10}\Delta C_{p1} + w_{20}\Delta C_{p2}
\]

where \( w_{10} \) and \( w_{20} \) are the weight fractions of polymer 1 and polymer 2. \( \Delta C_{p1} \) and \( \Delta C_{p2} \) are the values of the increments of heat capacity at the corresponding \( T_g \).

For a partially miscible blend, the change of heat capacity of the interface, \( \Delta C_{pi} \), can be added to calculate the \( \Delta C_p \).

\[
\Delta C_p = \Delta C_{p1} + \Delta C_{p2} + \Delta C_{pi}
\]

\[
\Delta C_p = w_1\Delta C_{p10} + w_2\Delta C_{p20} + \Delta C_{pi}
\]

where \( w_1 \) and \( w_2 \) are the weight fractions of polymer 1 and polymer 2. \( \Delta C_{p10} \) and \( \Delta C_{p20} \) are the values of the increments of heat capacity at the corresponding \( T_g \)s before mixing. The weight fractions, \( \delta_1 \) and \( \delta_2 \), in the interfacial regions of polymer 1 and 2 can be calculated as:

\[
\delta_1 = w_{10} - \frac{\Delta C_{p1}}{\Delta C_{p10}}
\]

\[
\delta_2 = w_{20} - \frac{\Delta C_{p2}}{\Delta C_{p20}}
\]

where \( w_{10} \) and \( w_{20} \) are the weight fractions of polymers before mixing.
This approach was employed to determine the amount two or more polymers in the interphase regions of the PU-polyacrylic blend and hybrids,\textsuperscript{77} the degree of mixing for the interpenetrating polymer networks (IPNs)\textsuperscript{107,144,164} and the morphology study of blends of PMMA/PS-acrylonitrile.\textsuperscript{133}

The MTDSC used in the study was a TA 2092 calorimeter. The samples weights are in the range of 10 - 15 mg and were examined from -90°C to 150°C at a heating rate of 3°C/min. The oscillation amplitude was set as 0.8°C with an oscillation period of 60 s.

4.6.6 Stress-strain tests

Stress-strain tests were the principal technique employed for the determination of the mechanical properties of the samples. Information regarding the strength, toughness and elasticity can all be obtained from this technique. Tensile strength is the maximum tensile stress sustained by the test specimen during a tensile test. It can be calculated by dividing the exerted force (F) by the cross-sectional area (A) of the sample.\textsuperscript{21}

\[
\text{Tensile stress} = \frac{F}{A} \text{ (kN/m}^2\text{)} = \text{(MPa)}
\]

Elongation is the deformation that relates to the change in length while under stress. It is calculated by dividing the stretched length (L) by the original length of sample (L\textsubscript{0}), and then multiplied by 100.

\[
\frac{L}{L_0} \times 100 = \% \text{ strain}
\]

A slope of the stress-strain curve represented the modulus.

\[
\text{Modulus, } E = \frac{\sigma}{\varepsilon}
\]
In addition, a stress-strain curve (figure 4.15) can give information about the behaviour of the sample e.g. brittle, tough or elastic. In a typical tensile test, a sample in the form of a dumbbell is clamped between two sets of grips.\textsuperscript{159} The sample is pulled at a constant crosshead speed until it breaks. Crosshead speed depends on the nature of the polymer: fast for extensional materials and slow speed for rigid ones. Figure 4.16 shows a typical dumb-bell shaped sample for a tensile test.

![Stress-strain curve](image)

**Figure 4.15:** Stress-strain behaviour of polymeric materials.\textsuperscript{21}

![Tensile test piece](image)

**Figure 4.16:** A typical tensile test piece.\textsuperscript{21}

For the purpose of this research, a Lloyds 10 000 tensometer equipped with a 500N load cell was used. The crosshead speed was set at 50mm/min at the room temperature, (typically = x to y °C). The latexes were cast onto Teflon plates and dried at ambient temperature for 5 days. Later, the films were further dried in a vacuum chamber at 20 mm Hg at 25°C for 2 days. The
samples were cut into the dumb-bell shapes using a cutting die type S2, which satisfied the DIN 53502 standard for rubbers and elastomers. For each sample, 4 or 5 tests were carried out and the average values are quoted. The information obtained were tensile strength at break, elongation at break and modulus at 5% strain.

4.6.7 Dynamic mechanical thermal analysis (DMTA)

This technique is commonly used to determine transition temperature and phase morphology.\textsuperscript{140} It can detect small changes in the state of a material.\textsuperscript{125} The basic principle of DMTA can be described as the application of an oscillating mechanical force to a sample which induces a sinusoidal strain (see figure 4.17).\textsuperscript{120} The properties such as viscosity from the phase lag and the stiffness (modulus) from the sample recovery, can be calculated. The modulus calculated in this method is not the same as that determined in the stress-strain tests. In DMTA, a complex modulus, $E^*$, a storage modulus, $E'$, and a loss modulus, $E''$, are calculated from the material response to the sine wave, whereas in the classic stress-strain tests, the modulus is normally calculated over a range of stresses-strains, as it is the slope of a line.\textsuperscript{120} The ratio of a loss modulus to a storage modulus is called damping, (i.e. the ability of a material to lose energy through molecular rearrangements and internal friction) or tan $\delta$.\textsuperscript{103} If the material is perfectly elastic, the in-phase response is obtained (no phase lag). If it is purely viscous, the response will be the out-phase one.\textsuperscript{139}

![Figure 4.17: Schematic diagram of material responses (strain) when subjected to an oscillating stress.\textsuperscript{120}](image)

$F_d = \text{Dynamic or oscillatory force.}$

$F_s = \text{Static or clamping force.}$
Polymer falls in between these two responses. The relationship between and the moduli is shown in figure 4.18.

\[ E^* = \text{complex modulus} \]
\[ E' = \text{storage modulus} \]
\[ E'' = \text{loss modulus} \]
\[ \delta = \text{phase angle} \]
\[ \tan \delta = \frac{E''}{E'} \]

Figure 4.18: Relationship between the phase angle, \( \delta \), and the moduli.\textsuperscript{120}

Two types of scanning techniques can be performed i.e. the time-temperature scan and the frequency scan. The former is conducted at constant frequency while increasing the temperature and commonly used to investigate the relaxation processes. The latter is carried out by holding the temperature constant and scanning across the frequency range of interest. However, both scanning techniques can be performed simultaneously to speed up data collection, (i.e. preferred at multi-frequencies), as shown in figure 4.19.

Figure 4.19: Effect of different frequencies on storage modulus and \( \tan \delta \) for poly(ethylene terephthalate).\textsuperscript{139}
The transition temperature is shifted to the higher value with increasing frequency. This can be explained as follows. At the lower frequency, the sample is able to relax and respond, and hence behaves like a liquid or viscous material. At the higher frequency, the sample needs more energy to respond to the shorter time scale stresses imposed. As mentioned earlier, DMTA can be an efficient tools to study the degree of miscibility, as shown in figure 4.20.

![Figure 4.20: Dynamic behaviours of pure components (A and B) and the blend (A + B).](image)

The parent polymers A and B are immiscible, as the resulting blend exhibits two glass-rubber transitions. The intermediate plateau shows where the polymers are partially miscible so that two Tg's are still observed but they are moved towards that of the ideally miscible blend. An IPN polymer exhibits very broad glass transition and have good damping properties such as good shock and sound absorbing materials.

In this work, dynamic mechanical properties were measured with DMA 2980 from TA Instruments. It was a dual cantilever clamping assembly with the bending mode (figure 4.21). Dual cantilever clamps are good for testing weak elastomers and for curing supported resins. The temperature scanning mode was carried out in the temperature range of -90°C to 150°C at 10 Hz. A heating rate was 3°C/min, an amplitude of 20 µm and the static force of 0.01 N were applied. The sample had the dimensions of ca. 1 mm thick, 5 mm wide and 17.5 mm long. The sample was clamped at both ends and the central point was vibrated by a drive shaft.
4.6.8 Transmission electron microscopy (TEM)

An electron microscopy is a powerful technique used to study the morphology at around the nanometre scale. It produces an exceptionally high resolution of detail in the object by use of a beam of electrons. In TEM, the image is formed from electrons which pass through the specimen. The resultant beam will contain some of the original free electrons, which have not been changed in velocity or direction and some electrons which have been changed either way, or both. Since the electron image cannot be viewed directly by the eye, the image is projected onto a fluorescence screen and when ready, is transmitted to a photographic plate or film. The beam of electrons is generated and accelerated using a typical electron gun. Figure 4.22 shows a working diagram of image formation in TEM.

The TEM instrument used in this study was a JEOL JEM 100CX operated at an accelerating voltage of 100 kilovolts. The hard film can be readily cut into ultra-thin sections (90 -150 micron) using a LKA Bromma 8800 Ultratome III ultramicrotome. The soft film needed to be cryogenically-microtomed at Birmingham University prior to analysis. The samples were stained for 20 minutes with ruthenium tetroxide (RuO₄) vapour.
4.6.9. Atomic force microscopy (AFM)

AFM is a type of scanning probe microscopy that allows three dimensional topographical imaging of a surface. A very fine-tipped probe is in contact with the sample surface, as it moves over the sample. In this work, the AFM images were recorded with a Nanoscope IIIa controller from DI Scanning Probe Dimension 3000 Microscope, operating in the tapping mode at ambient temperature. A Nanosensors TESP type single beam cantilevers, with a length of 125 μm were employed, at resonance frequencies of 301 to 350 KHz and spring constant of 35 to 40 N/m. The analysis was carried out at DSM-NeoResins, Holland.

Figure 4.22: The image formation in TEM.\textsuperscript{160}

Figure 4.23: Schematic diagram of an AFM.\textsuperscript{118}
CHAPTER 5

POLYURETHANE DISPERSIONS
CHAPTER 5

POLYURETHANE DISPERSIONS

This chapter addresses the polyurethane dispersions (PUDs) that have been synthesised using the following different formulations.

a. Solvent free PUDs.

b. PUDs with 20 wt. % N-methyl-2-pyrroldione.

In a later investigation, the cast films from b) were annealed at the different temperatures and time scales, in order to study the effect of the residual solvent on the morphology-property relationships. Comparative studies were made of the characteristics exhibited by each sample.

5.1 Solvent free versus the NMP containing polyurethane dispersions

The use of solvents, or co-solvents, cannot be avoided in many PU syntheses. In the solvent-borne system, these are used to dissolve the resin, and thus reduce the viscosity. In the water-borne system, it works synergistically to reduce the minimum film forming temperature to produce a continuous film and at the same time it controls the viscosity of the prepolymer to facilitate its dispersion.\(^{16,17}\) This is crucial for the systems that use solid or higher viscosity diisocyanates or polyols in their formulations. The solvents are also used to dissolve dimethylol propionic acid (DMPA), which is used as the particle stabiliser.\(^{166}\) Solvents such as acetone, dimethyl formamide (DMF) and N-methyl-2-pyrrolidone (NMP) are not unusual. However, the VOC problem originating from solvent evaporation has alerted the authorities to reduce, minimise or eliminate their use. Several approaches were proposed.\(^{14,7,83}\) One promising approach is by using reactive diluents, such as acrylics, to replace the solvent.

This research is designed to utilise NMP as co-solvent in a selected sample and to compare its property with the solvent free system. NMP has been chosen because of its abilities to work
as a processing aid (viscosity control) and as a coalescing aid (low volatility) in film formation. Isophorone diisocyanate (IPDI) exists as a liquid at room temperature and with the choice of a low molecular weight polypropylene glycol (PPG), it is possible to synthesise PUDs without the aid of a solvent. The discussion below addresses the morphology-property relationships of both samples. Later, the NMP containing sample was compared with the unannealed one, in order to investigate the effect of NMP on the final properties. Table 5.1 presents the sample descriptions.

Table 5.1: Sample descriptions for A, B and for BT. Also, see figure 4.8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Solvent-free PUD</td>
</tr>
<tr>
<td>B</td>
<td>PUD with 20% NMP</td>
</tr>
<tr>
<td>BT</td>
<td>Film B annealed at 80°C for 16 hours in a vacuum chamber</td>
</tr>
</tbody>
</table>

1. Films A and B have been dried for 5 days at room temperature prior to further drying in a vacuum chamber for 2 days at room temperature.
2. BT has been cast as a film after 6 months pot life.

The additional standard properties such as pH, MFFT, absorbance, viscosity and hardness are listed in Appendix A1. The data are provided by the industrial sponsor, DSM-NeoResins, Waalwijk, Netherlands.

5.1.1 Fourier transform infrared spectroscopy

FT-IR spectroscopy can be used to provide information on chain conformation, chemical structure, crystallinity and orientation of polymers. The identifying of the chemical structure present in samples A and B is important as both samples will be used as seed in the next hybrid preparation (refer to chapter 6). It is noteworthy that the spectrum of A was acquired in the ATR mode, while sample B was by the transmission mode. Figure 5.1 shows the FTIR spectra of the dried films of A and B. Hydrogen bonding in the sample can be determined from the −NH bonded absorption peaks that are located at 3310 cm⁻¹ for A and 3327 cm⁻¹ for B, respectively. It have been demonstrated in the literature that the frequency of the hydrogen bonding between the hard-hard segments (responsible for the phase
separation) is in the region of 3100-3300 cm\(^{-1}\), while for the hard-soft segments (induces mixing) is at 3300-3450 cm\(^{-1}\).

![FT-IR spectra of the dried films of A and B.]

The results showed that the frequency of \(-\text{NH}\) bonded peak of B was shifted towards the hard-soft segment stretching band, indicating more mixing. The diisocyanate was completely consumed in the reaction, as no absorption peak of free NCO (2250-2285 cm\(^{-1}\)) was detected.\(^{59}\) The formation of the urethane linkages have been observed as the \(-\text{NH}\) bending and the \(-\text{C}=\text{O}\) bonded stretching bands are detected in the region of 1533-1535 cm\(^{-1}\) and 1703 cm\(^{-1}\), respectively.\(^{96,98}\) The \(-\text{CH}_2\) stretching was in the range of 2884-2891 cm\(^{-1}\), while the band representing the C-O-C structure from PPG was located at 1096-1105 cm\(^{-1}\).\(^{78}\) These spectra confirmed the formation of a polyurethane structure for both samples.

**5.1.2 Particle sizing and the average molecular weight distribution**

Particle sizing gives quantitative information about the particle diameter. The particle size distributions are shown in figure 5.2.
Both samples exhibited unimodal distributions. The addition of NMP caused a larger particle size and a broader distribution. Sample A showed a narrow distribution, meaning a more uniform particle size. Table 5.2 shows the average particle size and the average molecular weight for each sample, respectively. The average molecular weights for both samples were determined by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the eluent. The column was calibrated using polystyrene standards.

Table 5.2: Particle sizes and the molecular weight distributions for both samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57 (± 0.3)</td>
<td>87 850</td>
<td>191 500</td>
<td>2.2 (± 0.1)</td>
</tr>
<tr>
<td></td>
<td>(± 10677)</td>
<td>(± 2192)</td>
<td>(± 65800)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>125 (± 2.0)</td>
<td>141 000</td>
<td>663 500</td>
<td>4.8 (± 0.7)</td>
</tr>
<tr>
<td></td>
<td>(± 3400)</td>
<td>(± 65800)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.2: Particle size distributions for A and B.
The particle diameter of sample B increased about two fold in comparison with A. Higher concentrations of carboxyl groups per unit chain length would lead to a smaller particle size. Any factor that perturbs the ionic association, such as the length of the spacer group between the polymer backbone and the ionic group, could affect the particle size. However, in this work, the molecular weight of polyol and the degree of the neutralisation remained constant. The amount of DMPA was fixed and water was the only dispersion medium that was used. The difference was only that sample B contains NMP. It was thought that NMP plasticizes the polymer chains, thus increasing the free volume of the particles.

Questions arise about the role of the ionic surfactant in the presence of NMP. Owing to the polarity of NMP, it was thought that NMP was capable of developing some interactions with the carboxylate anionic groups that surrounding the PU particles, which perturbed the particle stability in the dispersion. Other workers suggested that higher NMP contents might decrease the dispersant efficiency and the solvent might partition differently at higher solid contents. The same trend was found when acetone and ethyl acetate were used as solvents. It was suggested that the retained solvent in the film has been adsorbed by the hydrophobic part of PU chain via molecular interactions such as hydrogen bonding, thus resulting in the swelling of the particles. However, a systematic study was needed to investigate the effect of NMP on the concentration of the carboxylate anionic groups.

The average molecular weights, both Mn and Mw, were higher for B. The higher polydispersity index indicated that a higher heterogeneity exist in B. There is no straightforward relationship between the size of the particle and the average molecular weight. However, these results showed that both properties were augmented in the presence of NMP.

5.1.3 Thermogravimetric analysis

The TGA test was carried out to determine the possibility of NMP retention in the film that was dried at ambient temperature. Studies have shown that solvents such as DMF and acetone do not evaporate completely during film formation. Solvent retention, such as for acetone, in the dried films could decrease the modulus and tensile strength, but increase the
elangation at break, particularly for samples that have long soft segments.\textsuperscript{31,53} Table 5.3 summarizes the calculated amount of NMP evaporated from the TGA test, while figure 5.3 depicts the behaviour of the samples that have been annealed under various conditions.

![Figure 5.3: Weight loss of NMP from B under various conditions.](image)

**Table 5.3: Amount of NMP evaporated from the annealed sample.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing condition</th>
<th>Sample weight (mg)</th>
<th>Amount of NMP evaporated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>wt.% loss</td>
</tr>
<tr>
<td>B</td>
<td>Room temperature</td>
<td>47.3</td>
<td>4.00</td>
</tr>
<tr>
<td>BT</td>
<td>80(^{\circ})C for 16 hrs</td>
<td>22.2</td>
<td>2.20</td>
</tr>
<tr>
<td>BT(_{48})</td>
<td>80(^{\circ})C for 48 hrs</td>
<td>23.6</td>
<td>1.90</td>
</tr>
<tr>
<td>BT(_{200})</td>
<td>200(^{\circ})C for 2.5 hrs</td>
<td>15.7</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The percentage weight loss obtained at 200\(^{\circ}\)C can be associated with the amount of NMP evaporated from the samples. The temperature point is in compliance with NMP boiling point of 202\(^{\circ}\)C. About 4 wt.% of NMP was obtained from the film that was dried at ambient...
temperature. As expected, the amount of NMP was down to 1.8 wt.% when the same sample was treated at 200°C for 2.5 hours. Detailed calculations are shown in Appendix A2.

Figure 5.4 compares the behaviours of A and B, in which both films were dried at room temperature. Sample B showed a steeper gradient of weight loss and degraded at a lower temperature than A. Earlier analysis (IR spectroscopy) postulated that segmental mixing was higher in B. Studies have shown that the hard-soft segment interactions e.g. hydrogen bonding, create more mixing.\textsuperscript{42,49} However, the bonding is weaker in comparison with the one that involving the hard-hard segment interactions.\textsuperscript{49} As a consequence, the weaker interactions that exist in B were thought responsible for lowering the degradation temperature.

![Graph showing weight loss of NMP for A and B that were treated at room temperature.](image)

**Figure 5.4:** Weight loss of NMP for A and B that were treated at room temperature.

Figures 5.5 a) - c) present the optical images of the samples that have been annealed under various conditions. Obviously, sample A did not show any changes when treated at 80°C for 2 days. In contrast, small bubbles appear in B when treated under the same conditions. The bubbles were linked with the evaporated NMP that was retained in the cast film. When the temperature was increased to 200°C, the bubbles became bigger within the short experimental
time scale. This could be explained as the temperature was set near to the NMP boiling point, which led to more rapid and complete NMP evaporation. All of these observations supported the arguments arising from the TGA results.

Figure 5.5: The annealed films. a) Sample A at 85°C for 48 hours. b) Sample B at 80°C for 48 hours. c) Sample B at 200°C for 2.5 hours.

5.1.4 Stress-strain tests

The stress-strain tests were carried out for a comparative study on the three basic mechanical properties i.e. modulus, tensile strength and elongation at break. The modulus was calculated at a low strain value i.e. 5%. Figure 5.6 shows the common behaviour of elastomeric materials exhibited by A. The soft segment of PPG was responsible for the flexibility of the sample. Table 5.4 shows the mechanical properties of A and B.

The first of the two rows in the table show that sample A was harder than B. The reason lies in the plasticizing effect caused by the NMP that remained in the film. It reduced the dipole-dipole interactions between the carboxylate group\textsuperscript{42,97} and decreased the hydrogen bonding interaction in the hard segments.\textsuperscript{98} This led to more mixing between the soft and the hard
segments, thus lowering the modulus and tensile strength. As discussed in the previous results, the average molecular weight of B was higher than A. In general, this would lead to the augmentation of the tensile strength. However, the plasticizing effect of NMP reduced the strength of the film.

![Stress-strain curves for A and B.](image)

**Figure 5.6: The stress-strain curves for A and B.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14 (± 0.01)</td>
<td>15 (± 0.6)</td>
<td>1180 (± 43)</td>
</tr>
<tr>
<td>B</td>
<td>0.02 (± 0.01)</td>
<td>2.8 (± 0.5)</td>
<td>1200 (± 132)</td>
</tr>
</tbody>
</table>

To support these findings, stress-strain tests were carried out on the annealed sample, BT (see table 5.5). At low strain, the modulus of BT was eight times higher than B. The effect was even more obvious at the higher strain, in that the tensile strength had increased to nine times higher than the parent B. All these arguments suggested that NMP was capable of interfering with the microphase interactions to some extent, thus affecting the final properties.
Table 5.5: Mechanical properties for B and BT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.02 (± 0.01)</td>
<td>2.8 (± 0.5)</td>
<td>1200 (± 132)</td>
</tr>
<tr>
<td>BT</td>
<td>0.16 (± 0.02)</td>
<td>27 (± 0.6)</td>
<td>1250 (± 23)</td>
</tr>
</tbody>
</table>

5.1.5 Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis is capable of delivering detailed information about the morphological behaviour. In this work, a comparison have been made between A and B, regarding to their dynamic mechanical behaviour. The storage modulus of samples A and B are presented in figure 5.7.

Figure 5.7: Storage modulus versus temperature plots for A and B.

The storage modulus of these two samples was measured at 25°C, corresponding to the elastic response under ambient conditions, which can be correlated with the coatings performance in empirical tests such as penetration hardness. Sample A showed a higher modulus (1.9 MPa)
than B (1.3 MPa). The main reason was NMP reduced the Tg of B, thus decreasing the modulus. The slope of the intermediate plateau was flatter in A, meaning that stronger interactions existed in the interphase regions. The interactions were attributed to hydrogen bonding and dipole-dipole interactions. They led to the increase in the storage modulus. A well defined rubbery plateau indicated a highly phase separated morphology. On the contrary, the opposite behaviour was exhibited by B.

Useful information about the degree of phase separation can be extracted from the plot of tan δ versus temperature, as shown in figure 5.8. The dynamic properties obtained from the plots are summarised in table 5.6. The values of tan δ max and the tan δ half-peak widths are related to the structural homogeneity and crosslinking. The height of the intermediate plateau between the two transitions implied some degree of microphase mixing due to the molecular interactions.

![Figure 5.8: Tan δ versus temperature plots for A and B.](image)
As mentioned in chapter 2, Tgs refers to the glass temperature at the soft segment, while Tgh is the glass temperature for the hard segment. As can be seen, both samples showed well defined peaks for both segments and behaved like a semi-miscible system. Tgs of B was shifted to a lower temperature (-46°C), owing to the plasticizing effect of NMP that reduces the glass temperature of the soft segment. Tan δ max value of B was slightly higher than A, indicating that the former had greater chain mobility. The broader peak in the hard segment exhibited by sample A was connected with the breakage of hydrogen bonds. However, the process starts earlier in B (34°C). This is thought due to the presence of the NMP that caused less interaction, thus less, or weaker, hydrogen bonding was formed. Nevertheless, sample B showed a greater degree of mixing between two segments by shifting the Tgh peak to a lower temperature. This was supported by the broad tan δ half-peak width of the soft segment, indicating that the extent of mixing for B was higher. These results were consistent with the study which claimed that solvent retention in the film would affect the DMTA spectra due to plasticization, evaporation or bubble formation.

Table 5.6: Dynamic properties for A, B and for BT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max value</th>
<th>Half-peak width tan δ max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tgs</td>
<td>Tgh</td>
<td>SS*</td>
</tr>
<tr>
<td>A</td>
<td>-36</td>
<td>-</td>
<td>0.37</td>
</tr>
<tr>
<td>B</td>
<td>-46</td>
<td>34</td>
<td>0.40</td>
</tr>
<tr>
<td>BT</td>
<td>-40</td>
<td>-</td>
<td>0.30</td>
</tr>
</tbody>
</table>

SS = Soft segment. HS = Hard segment.

To understand the influence of NMP on the morphology, the tan δ profiles of all samples were compared in figure 5.9. The Tgs peak was shifted from -46°C (B) to -40°C (BT), whereas, the Tgh was shifted from 34°C to a higher temperature. This showed that phase separation was favourable in BT. The Tgh peak became broader, associated with the breakage of the hydrogen bonds at the higher temperature. BT was behaving more like A, with a broad hard segment peak. However, the extent of mixing was higher in BT as indicated by the tan δ half
peak width (table 5.6). This led to the higher modulus, tensile strength and elongation at break. The stress-stain results complement these findings.

![Figure 5.9: Tan δ versus temperature for A, B and for BT.](image)

From the above analysis, it can be concluded that NMP affects both the soft and the hard segments. The shifted Tgs and Tgh peaks of B to lower temperature correspond to the plasticizing effect of the solvent. This also influenced the degree of mixing between the segments. By annealing the NMP-containing sample, both Tg peaks were shifted to higher values, indicating more segment separation. The annealing process has led the sample to behave more likely as the pure PUD, despite the moderate changes in the morphology.

5.1.6 Modulated temperature differential scanning calorimetry

The thermograms obtained by this method can be used in conjunction with the DMTA results. The signal is sensitive to the Tg and can provide the information about the miscibility and the degree of molecular mixing of a polymer blend, about interfaces and about physical ageing and latex structure.\textsuperscript{102,163}
Figure 5.10 shows derivative Cp-temperature profiles for A and B. It seems that the addition of NMP did not give a significant effect on the soft segments. The reason lies in the sensitivity of each technique towards the transition temperature. However, the segmental mixing in B was increased, as the TgH was shifted to a lower temperature. The augmentation of the intermediate plateau in B supported the observation.

Meanwhile, sample A showed more phase separation, corresponding with the TgH that was shifted to a higher value. The reduction of the intermediate plateau, which indicated fewer molecular interactions such as hydrogen bonding, could bring about to the same conclusion. Notably, the Tg values obtained from this technique (table 5.7) are typically lower than those obtained from DMTA, depending on the method, the principle of measurement and the thermal history of the sample. The lower frequency used in these experiments is also a contribution to the difference.
Table 5.7: Transition temperatures for A, B and for BT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (dCp/dT max)</th>
<th>Tgs (°C)</th>
<th>Tgh (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-55 Broad</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>-56 47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT</td>
<td>-53 75</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To strengthen the earlier conclusion about the role of NMP on the morphology, the behaviour of B was compared with BT as shown in figure 5.11. The Tgs was shifted from -56°C (B) to -53°C (BT) and the peak intensity decreased from 0.026 (B) to 0.02 (BT). These observations implied that the chain mobility was restricted to some extent and phase separation was favoured in BT. The latter also showed lower interphase mixing, as indicated by the height of the intermediate plateau. All these findings are consistent with the DMTA data. The NMP evidently has changed the sample morphologies to a certain extent and has influenced the final properties.

Figure 5.11: dCp/dT versus temperature plots of B and BT.
5.1.7 Transmission electron microscopy

This technique offers direct interpretation of the sample morphology in terms of the extent of mixing and the size and the shape of the domains.\textsuperscript{163} The results are used to support the findings from other techniques such as DMTA. Films A and B have been stained with ruthenium tetroxide to give better contrast between the hard and soft segments. Figures 5.12 a) - c) show the micrographs of all samples. The dark shades represent the hard segments, while the lighter ones represent the soft segments. The hard segments which contain more \(-\text{NH}\) groups can be stained by RuO\(_4\), while the soft segments could be intermixed with a few hard segments, thus exhibited the greyish regions in the images.\textsuperscript{99}

Figure 5.12: TEM micrographs for a) A, b) B and c) BT at 100k magnification.
As can be seen, both segments were distributed uniformly throughout the matrix. Sample A showed sharp phase boundaries between the hard and the soft segments. The continuous phase of the soft segments dominated the matrix, while the discrete phase of the hard segments provided crosslink sites and filler-like reinforcement to the soft segments.\textsuperscript{49} On the contrary, the degree of mixing was apparently higher in B due to the absence of the sharp interface between the phases (figure 5.12 b). The interphases (greyish shades) were distributed evenly throughout the matrix and behaved more like a PPG-rich phase. The white spots observed in the micrograph were thought to be thin region. Nonetheless, the annealing process resulted in a somewhat more phase separation as shown by the distinguishable phases (figure 5.12 c).

Undoubtedly, from all the above discussion, it is proven that NMP can have major impacts upon a sample's properties and morphology. The solvent is capable of plasticizing the polymer chains and reducing the Tg to a lower temperature. It is also thought that NMP has the ability to interfere with the particle stability, thus enhancing the particle size. The TEM micrographs showed that the degree of mixing was higher in the NMP containing sample than in the solvent free one. These disadvantage would limit sample applications to the certain areas that need lower tensile strength, but with higher extensibility. On the other hand, the solvent free sample is attractive as it exhibited excellent mechanical properties and could minimise, or totally cut, the solvent cost.
CHAPTER 6

POLYURETHANE-POLYACRYLIC DISPERSIONS
The use of a solvent such as DMF or NMP cannot be avoided in some of PUD syntheses. However, the results in chapter 5 showed that NMP can affect the polymer properties, which make it less attractive than the solvent free PUD. An alternative to replace a solvent is by using reactive diluents. They are capable of regulating the viscosity of prepolymer and lowering Tg and so could aid film formation. Acrylic monomers or co-monomers, are the most popular reactive diluents. They offer excellent coating properties such as high gloss, excellent weatherability, a wide range of glass transition temperatures and are relatively cheaper than PU (see chapter 3). The prime advantage is they segmented IPN can be polymerised at a later stage to form a hybrid polyurethane. Polyurethane-polyacrylic hybrids (PUAs) are well documented in the literature.

In this work, the solvent free PUD was used as a seed, and two types of acrylic co-monomers, MMA/n-BA and styrene/n-BA, have been selected as diluents, (designated as the A series). The latter monomer combination is more hydrophobic than the former, due to the aromatic ring in the styrene molecular structure. This distinction was purposely selected to get more understanding of the factors that could affect the sample properties. The acrylic monomers were copolymerised with the PUD via a seeded emulsion polymerisation with a single batch technique, (see chapter 4). In addition, pure PMMA/PBA and PS/PBA have been synthesised by conventional emulsion polymerisation, (designated as samples E and F). These polyacrylics were used as references, and are mostly encountered in the latex blend systems. Later, the same synthesis technique have been employed to prepare hybrids at fixed 1:1 PU:polyacrylic ratio with the NMP containing PUD used as a seed, (designated as the B series). To complete the study, the hybrids with the same PU:polyacrylic ratio were synthesised via the double batch technique (see chapter 4), in order to study the effect of the different synthesis routes on the sample morphology.
This chapter is divided into two topics as follows.

1. The variation of the polyacrylic composition and its type upon the morphology-property relationships for the A and B series, via the single batch techniques.
2. The synthesis of the hybrid via the double batch technique at fixed 1:1 PU:polyacrylic ratio.

6.1 The variation of the composition and type of acrylic co-monomer (via single batch technique)

6.1.1 Hybrid with solvent free polyurethane dispersions (the A series)

In this section, the first part of the discussion is focused on the PU-PMMA/PBA materials with three different weight ratios as shown in table 6.1 (see also figure 4.8). The second part tackles the PU-PS/PBA system with the same ratios as in the first part, and finally, both of the systems are compared with each other to see the impact given by both polyacrylics on morphology and properties.

Table 6.1: Sample descriptions for A, the A series, E and F.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Solvent-free PUD</td>
</tr>
<tr>
<td>A1</td>
<td>70% PU: 30% PMMA/PBA</td>
</tr>
<tr>
<td>A2</td>
<td>50% PU: 50% PMMA/PBA</td>
</tr>
<tr>
<td>A3</td>
<td>30% PU: 70% PMMA/PBA</td>
</tr>
<tr>
<td>A4</td>
<td>70% PU: 30% PS/PBA</td>
</tr>
<tr>
<td>A5</td>
<td>50% PU: 50% PS/PBA</td>
</tr>
<tr>
<td>A6</td>
<td>30% PU: 70% PS/PBA</td>
</tr>
<tr>
<td>E</td>
<td>PMMA/PBA</td>
</tr>
<tr>
<td>F</td>
<td>PS/PBA</td>
</tr>
</tbody>
</table>

Note: The Tg of all acrylic copolymers were set at 50°C.
6.1.1.1 Fourier transform infra-red spectroscopy

The analysis was made to verify the chemical structure of the PUAs. It also can be used to investigate the hydrogen bonding behaviour of the PU in the presence of a polyacrylic.\textsuperscript{75} Figure 6.1 demonstrates the spectra of the dried films for A1-A3.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ftir_spectra.png}
\caption{FT-IR spectra for the PU-PMMA/PBA-based hybrids (A and E series).}
\end{figure}

All the hybrid samples showed the –NH bonded peaks located at 3312 - 3302 cm\textsuperscript{-1}, which are characteristic of hydrogen bonded –NH groups in the hard segments.\textsuperscript{19} The –C=O free stretching band of the acrylics and the –C=O bonded with –NH, were detected at 1728 cm\textsuperscript{-1} and 1703 cm\textsuperscript{-1}, respectively.\textsuperscript{98,112} There was a weak sign of a urea group absorption band at 1640 cm\textsuperscript{-1} in A. All samples show the –CONH- stretching band in the region of 1533–1534 cm\textsuperscript{-1}, while the –OC\textsubscript{4}H\textsubscript{9} absorption band of BA groups was observed at 841 cm\textsuperscript{-1}.\textsuperscript{83,96} The C-O-C stretching band of PPG was detected at 1096 cm\textsuperscript{-1}, while the –C-O stretching band of aliphatic esters was observed at 1145 cm\textsuperscript{-1}.\textsuperscript{78,168} Undoubtedly, these spectroscopic data indicate the formation of hybrid structures.
The FT-IR spectra of the second set of hybrid samples that consist of PU-PS/PBA are depicted in figure 6.2.

![Figure 6.2: FT-IR spectra of the PU-PS/PBA-based hybrids with A and F.](image)

- The \(-\text{NH}\) bonded bands were detected in the region of 3312-3318 cm\(^{-1}\), indicating the formation of hydrogen bonding in these hybrid samples. The \(-\text{C}=\text{O}\) stretching band of the acrylic was detected at 1703 cm\(^{-1}\) and 1728 cm\(^{-1}\), respectively. The \(-\text{CONH}\) stretching bands were observed at the region of 1533-1534 cm\(^{-1}\), while the \(\text{C}=\text{C}\) stretching vibration of aromatic rings was detected at 1600 cm\(^{-1}\) and 698 cm\(^{-1}\), respectively.\(^{53,78,83,168}\) The \(-\text{OC}_4\text{H}_9\) absorption band was detected at 842 cm\(^{-1}\), attributed to the BA group. These spectroscopic data are the evidence that the samples possess PU-PS/PBA hybrid characteristics.

6.1.1.2 Grafting

Studies have shown that the hybrids involving PU and polyacrylcs can undergo a grafting reaction.\(^{5,78,96}\) \(\alpha\)-Hydrogen from the \(-\text{NH}\) groups in the hard segments can be abstracted by the free radicals either from the decomposition of initiators or from acrylic
monomer/oligomer radicals as shown in scheme 1. In other words, the \(-\text{NH}\) groups provide the reaction site for the grafting.\(^5\)

\[
\begin{align*}
\text{O} & \begin{array}{c}
\text{C} \\
\text{N} \\
\text{R}
\end{array} \text{-H} \text{-R} & + M_n \xrightarrow{\text{Heat or}} \gamma \text{rays} \text{O} & \begin{array}{c}
\text{C} \\
\text{N} \\
\text{R}
\end{array} \text{-M} \text{-R} & \text{R}_1 \\
\text{(a)}
\end{align*}
\]

\[
\begin{align*}
\text{PU} & \xrightarrow{\text{Gamma rays}} \left\{ \begin{array}{l}
\text{PU} + M \\
M_n + \text{PU}
\end{array} \right. \\
& \rightarrow \text{PU-M}\text{-M}_n
\end{align*}
\]

Scheme 1: Grafting reactions in the presence of heat or gamma-rays.\(^5\)

The grafting that involved a chemical initiator e.g. potassium persulphate (K\(_2\)S\(_2\)O\(_8\)), is likely to follow scheme 1(a), while the radicals that were produced by photochemical means e.g. gamma rays, favour scheme 1(b).\(^{110}\) Techniques such as solvent extraction, H\(^1\)-NMR spectroscopy, thin layer chromatography/flame ionisation detection (TLC/FID) and FT-IR spectroscopy have been employed to determine the grafting reaction and its efficiency.\(^{78,96,110}\)

In this work, FT-IR spectra has been used to determine grafting reactions in the samples and it is strongly thought that the grafting reaction follows the mechanism in scheme 1(a). Figures 6.3 a) and b) compare the spectra of \(-\text{CONH}\) absorption peaks at 1531 cm\(^{-1}\) - 1534 cm\(^{-1}\) for all samples. The areas under the peaks have been calculated using the Mattson 300 Unicam software. All samples showed a reduction in the peak area with increasing polyacrylic ratio, regardless with the acrylic type. The area under the curve represents the \(-\text{NH}\) bonding from the urethane linkages. Mathematically, the ratio of the peak area of the hybrid (A\(_h\)) is divided with the peak area of pure PUD (A\(_{ref}\)) x 100%, corresponds to the percentage of ungrafted \(-\text{NH}\) groups in the samples (table 6.2). By subtracting the percentage of ungrafted \(-\text{NH}\)
groups from 100, the percentage of grafting can be calculated. The peak area for pure PUD ($A_{\text{rel}}$) is 6.80.

Figure 6.3: The $-\text{CONH}$ absorption peak at 1531-1534 cm$^{-1}$ for a) samples A1 to A3 and b) samples A4 to A6.
As can be seen, by increasing the polyacrylic content, the grafting percentage increased. This can be explained as follows. As the content of acrylic monomers increased, the chances of the monomer molecules or the polyacrylics contacting the PUD molecules were higher.\textsuperscript{110} Interestingly at 30 wt. % acrylic content, the PMMA/PBA-based hybrids showed higher levels of grafting than its PS/PBA counterpart. However, beyond that ratio, both samples showed nearly the same grafting level, which is not fully understood.

Table 6.2: Percentage of ungrafted $-\text{NH}$ groups.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area under peak at 1531-1534 cm$^{-1}$ ($A_h^+$)</th>
<th>Percentage of ungrafted $-\text{NH}$ groups ($A_h/A_{ref}^* \times 100%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>4.25</td>
<td>63</td>
</tr>
<tr>
<td>A2</td>
<td>3.34</td>
<td>49</td>
</tr>
<tr>
<td>A3</td>
<td>1.25</td>
<td>18</td>
</tr>
<tr>
<td>A4</td>
<td>5.60</td>
<td>80</td>
</tr>
<tr>
<td>A5</td>
<td>3.50</td>
<td>50</td>
</tr>
<tr>
<td>A6</td>
<td>1.25</td>
<td>18</td>
</tr>
</tbody>
</table>

$^*$The areas shown in the second column are the area under peak for hybrid, $A_h$.

$^*$The area under peak for pure PUD ($A_{ref}$) is 6.80.

6.1.1.3 Particle sizing

As can be seen in table 6.3, sample A had the smallest average particle size. With the lower level of polyacrylic ratio, i.e. 30 wt. %, A1 has a size that is similar to A. As polyacrylic ratio increased, the average particle size of the samples increased. With 70 wt. % PMMA/PBA, sample A3 showed the largest average size of 169 nm. This can be explained as follows: by increasing the acrylic content, more monomer tends to be absorbed and swell the PU particles, thus augmenting the size.\textsuperscript{64} These findings were supported by other workers.\textsuperscript{3,62,78,101} As expected, A2 and A3 have bigger particle sizes than the pure polyacrylic, E. This was due to the external surfactant (i.e. SLS) that has been added in E to assist latex stability. On the contrary, the hybrid particle stabilities depended solely upon the internal
stabiliser, the carboxylic salt groups (-COO\textsuperscript{\textprime}NH\textsubscript{4}\textsuperscript{+}) that surround the PU particles.\textsuperscript{78} The reduction of PU content would indirectly decrease the hybrid particle stabilities. The particles tended to aggregate and formed larger particles. The entire sample range showed unimodal distributions, with A3 exhibiting the broadest (figure 6.4).

Table 6.3: Particle sizes for A, A1 to A3 and E.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57 (± 0.30)</td>
</tr>
<tr>
<td>A1</td>
<td>65 (± 0.2)</td>
</tr>
<tr>
<td>A2</td>
<td>114 (± 3.5)</td>
</tr>
<tr>
<td>A3</td>
<td>169 (± 1.5)</td>
</tr>
<tr>
<td>E</td>
<td>103 (± 0.7)</td>
</tr>
</tbody>
</table>

Figure 6.4: Particle size distributions for samples A1 to A3.

Table 6.4 shows the particle sizes for the second hybrid system, PU-PS/PBA. As can be seen, the particle size increased with increasing polyacrylic ratio. The samples showed a similar
Chapter 6 Polyurethane-polyacrylic hybrid dispersions

trend to that observed for the PU-PMMA/PBA samples. The exception was only that sample A6 (70 wt. % PS/PBA) gelled within two months and has the shortest shelf life. Inevitably, sample A6 has been excluded from this work. The particle instability was attributed to the reduced availability of the carboxylate ions built into the PU, that act as the stabiliser. Stated earlier, higher polyacrylic ratios mean less stabiliser is available to stabilise the latex.

Table 6.4: Particle sizes for A4 to A6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57 (± 0.30)</td>
</tr>
<tr>
<td>A4</td>
<td>76 (± 1.3)</td>
</tr>
<tr>
<td>A5</td>
<td>146 (± 2.8)</td>
</tr>
<tr>
<td>A6</td>
<td>(gelled after 2 months)</td>
</tr>
<tr>
<td>F</td>
<td>80 (± 0.4)</td>
</tr>
</tbody>
</table>

Comparatively, the PS/PBA-based samples exhibited larger particle sizes than the PMMA/PBA latexes at the equivalent polyacrylic ratio. The particle diameters of both samples were influenced by the degree of hydrophobicities of acrylic monomers and the availability of the internal stabiliser i.e. carboxylate ions. Styrene imparts more hydrophobicity than MMA, owing to the aromatic group in the styrene molecular structure. Increasing the hydrophobic monomer content would decrease the particle stability faster than the less hydrophobic case. Thus, the sample gels within a shorter time. 168

6.1.1.4 Solubility parameters

The miscibility of the two polymers in the hybrid system influences the latex particle morphology, and thus the final properties of the samples. Miscibility refers to the mixing of two systems at the molecular level. 167 Many factors influence the miscibility such as molecular weight of the polymer, the crosslink density and the structural similarity of the two components. 105, 145 The miscibility based on the latter factor can be predicted by the solubility parameters, δ. Values of the solubility parameter of a polymer can be calculated by using group molar attraction constants developed by Small and Hoy. 106 Because this chapter deals
with the hybrid systems, a prediction regarding the degree of mixing between the two different types of polyacrylics with the PU would be very useful.

Table 6.5 shows the solubility parameter, \( \delta \), for each polymer provided by Hoy, (detailed calculations were shown in Appendix A2). The solubility parameter of the PU in this work is slightly lower than the values found in the literature i.e. 19.4 to 21.5 (Jcm\(^3\))\(^{1/2}\). As can be seen, the PU-PMMA/PBA system exhibited more mixing than PU-PS/PBA, as shown by a smaller difference of the \( \delta \) values between PU and PMMA copolymer. A study\(^5\) had shown that with the less hydrophobic character of the MMA monomers, they were able to polymerise within the PU particles, but also onto the surface of the PU particles. Undeniable, the hydrophobicity of the acrylic monomer could have a major impact on the component miscibility.

Table 6.5: Solubility parameters for the polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Average solubility parameter, ( \delta^* ) (Jcm(^3))(^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU dispersion</td>
<td>19.10</td>
</tr>
<tr>
<td>PMMA/PBA/PMAA</td>
<td>18.20</td>
</tr>
<tr>
<td>PS/PBA/PMAA</td>
<td>17.90</td>
</tr>
</tbody>
</table>

*Calculated using Hoy's molar attraction constants.

6.1.1.5 Stress-strain tests

It is useful to know the effect of acrylic composition and it type on the mechanical properties of these samples. The stress-strain curves in figure 6.5 display the soft and tough behaviour, which is common to elastomers.\(^4\) However, as the polyacrylic weight ratio increased, the samples started to lose their rubbery character and behaved more like glassy materials, which was clearly seen in the case of A3. Table 6.6 shows the mechanical properties that have been extracted from the stress-strain data.
Table 6.6: Mechanical properties for A, A1 to A3 and E.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14 (± 0.01)</td>
<td>15 (± 0.6)</td>
<td>1180 (± 43)</td>
</tr>
<tr>
<td>A1</td>
<td>0.34 (± 0.03)</td>
<td>16 (± 0.1)</td>
<td>610 (± 6)</td>
</tr>
<tr>
<td>A2</td>
<td>0.50 (± 0.01)</td>
<td>15 (± 0.3)</td>
<td>450 (± 12)</td>
</tr>
<tr>
<td>A3</td>
<td>0.20 (± 0.03)</td>
<td>16 (± 0.4)</td>
<td>200 (± 2)</td>
</tr>
<tr>
<td>E</td>
<td>1.73 (± 0.04)</td>
<td>73 (± 3.0)</td>
<td>23 (± 3)</td>
</tr>
</tbody>
</table>

Figure 6.5: Stress-strain curves of A1 to A3.

It has been stated many times in the literature\textsuperscript{5,10} that the morphology of PUAs can be divided into three components: the PU-rich component, the PU polyacrylic-rich component and the polyacrylic-rich component. The dominant one will most affects the materials behaviour.\textsuperscript{62}
In this work, a modulus value was calculated at low strain i.e. 5%, to investigate if any reinforcing effect due to the acrylic phase takes place. From the results, it can be seen that the soft segments dominated the matrix of A, as it exhibited the lowest value of the modulus. Sample A2 showed the highest modulus (0.5 MPa) with 50 wt. % polyacrylic content. However, the modulus decreased when the polyacrylic ratio reached 70 wt. % (sample A3). It was thought that the matrix was then dominated by the polyacrylic phase. The polyacrylic particles tended to aggregate, thus forming weaker interfaces between the particles. This resulted in incomplete particle coalescence, thus reducing the cohesive film strengths, (see figure 6.6). A certain ratio limit has to be set to produce the optimum result. Figures 6.7 a) - c) show the profiles of samples at the different acrylic ratios.

Figure 6.6: A schematic diagram of the morphologies of the samples.
Figure 6.7: Mechanical properties for A1 to A3. a) Modulus at 5% strain. b) Tensile strength. c) Elongation at break.
Interestingly, the hybrids exhibited tensile strengths that were nearly the same values as the pure PU (figure 6.7 b). It can be suggested that sample failure occurred in the PU matrix rather than in the polyacrylic phase. The same findings have been reported by Galcogi et al. However, they did not explain the cause of such behaviour. With very complex morphologies, there were no straightforward answers. On the other hand, elongation at break decreased with increasing polyacrylic ratio, (see figure 6.7 c). The presence of the polyacrylic, which is hard and brittle, could restrict the PPG chain flexibility, thus reducing the sample extensibility. The mechanical properties of the PU-PS/PBA hybrid are shown in table 6.7.

Table 6.7: Mechanical properties for A, A4 to A5 and for F.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14 (± 0.01)</td>
<td>15 (± 0.6)</td>
<td>1180 (±43)</td>
</tr>
<tr>
<td>A4</td>
<td>0.20 (± 0.02)</td>
<td>10 (± 0.9)</td>
<td>850 (± 45)</td>
</tr>
<tr>
<td>A5</td>
<td>0.40 (± 0.01)</td>
<td>15 (± 0.3)</td>
<td>620 (± 2)</td>
</tr>
<tr>
<td>F</td>
<td>1.10 (± 0.1)</td>
<td>38 (± 1.4)</td>
<td>20 (± 1.0)</td>
</tr>
</tbody>
</table>

At low strain, the moduli of the hybrids increased with increasing polyacrylic ratio. The PUA-rich phase was thought to be controlling the polymers' behaviours as the effect of polyacrylic component reinforcement became pronounced, (see figure 6.8 a). At higher strain, A4 exhibited a tensile strength that was lower than that of pure PU. By increasing the polyacrylic content to 50 wt. %, the tensile strength increasing and showed nearly the same value as pure PU (figure 6.8 b). Unfortunately, no comparison can be made for A6, as the sample was omitted from this work. As expected, the elongation at break values decreased with increasing polyacrylic ratio (figure 6.8 c).

By comparing both systems, it shows that the PMMA/PBA-based hybrids behaved like the semi-miscible systems, whereas the PS/PBA-based ones were more like filler-reinforced systems.
Figure 6.8: Mechanical properties for A4 and A5 versus polyacrylic ratio. a) Modulus at 5% strain. b) Tensile strength. c) Elongation at break.
6.1.1.6 Dynamic mechanical thermal analysis

The effects of copolymerising an acrylic with PU, on the resulting morphology can be examined in more detail with DMTA. Figure 6.9 shows the storage moduli for A1 to A3.

As can be seen, at room temperature (25°C), the modulus increased with increasing polyacrylic ratio, which was in agreement with the stress-strain results. The intermediate plateau became flatter, indicating a higher degree of mixing in the interphase regions due to molecular interactions such as hydrogen bonding or dipole-dipole interactions. These interactions increased the storage modulus of the samples, thus increasing their stiffness.

The plot of tan δ versus temperature can be used to verify the above findings, (see figure 6.10). It can be seen that the addition of the polyacrylic did not affect the Tg of the soft component of PUAs, Tgsc (i.e. PPG). The Tgsc values for all samples were in the range of -39°C to -41°C (see table 6.8).
On the contrary, the Tg of the hard component of PUAs, $T_{gH}$ (i.e. the PU hard segments and polyacrylic phase) were shifted to higher temperature values with increasing polyacrylic ratio. The difference between $T_{gSC}$ and $T_{gH}$, $\Delta T_g$, can be used to define the degree of phase separation.95 A3 showed the highest phase separation with a $\Delta T_g$ value of 115°C. The peaks became more resolved with A3 developing a shoulder, which is thought to represent the PU hard segments as it was shifted toward the $T_{gh}$ of PU (figure 6.11). The extent of mixing was increased in both lower and higher temperature regions as the tan $\delta$ half-peak widths became broader with increasing polyacrylic ratio.

It was difficult to distinguish the overlapping $T_{gH}$ peaks of PU and polyacrylcs. The grafting reaction between the components is thought to be a key factor. The FT-IR spectroscopy data showed that by increasing the polyacrylic content, the grafting level increased, thus producing broader peaks. Notably, Tg of the pure PMMA/PBA deviated by 35°C from the theoretical value obtained using the Fox equation due to the frequency effect.163
Table 6.8: Dynamic mechanical properties for A, A1 to A3 and for E.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max value</th>
<th>Half-peak width of tan δ max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tgsc*</td>
<td>Tgh*</td>
<td>ΔTg</td>
</tr>
<tr>
<td>A</td>
<td>-36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A1</td>
<td>-39</td>
<td>69</td>
<td>108</td>
</tr>
<tr>
<td>A2</td>
<td>-39</td>
<td>75</td>
<td>114</td>
</tr>
<tr>
<td>A3</td>
<td>-41</td>
<td>77</td>
<td>115</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>94</td>
<td>-</td>
</tr>
</tbody>
</table>

*Tgsc = Tg of the soft component of PUs. Tgh = Tg of the hard component of PUs.

SC = soft component. HC = hard component.

The PS/PBA-based hybrids showed the same behaviour as the PMMA/PBA-based hybrids (figure 6.12). The samples character were strongly influenced by the hard components, corresponding with the large step height drop in that particular temperature region. The
intermediate plateau was more flatter with increasing acrylic ratio, indicating stronger molecular interactions e.g. hydrogen bonding. Consequently, the storage moduli at room temperature (25°C) increased.

![Figure 6.12: Storage modulus versus temperature for A, A4 to A5 and for E.](image)

The findings were supported with the tan δ-temperature profiles shown in figures 6.13 and 6.14. The Tg_sc showed less significant changes with increasing polyacrylic ratio. Sample A4 showed a broad Tg_H peak with a shoulder, while sample A5 exhibited a more resolved peak. By calculating the tan δ half-peak width of Tg_H, A4 exhibited a higher extent of mixing than A5. Comparatively, the PMMA/PBA hybrids showed more mixing as indicated by the broadened Tg_H peaks and the greater tan δ half-peak width values with increasing polyacrylic ratio. On the contrary, the samples with PS/PBA showed more resolved peaks, indicating higher phase separation. The different morphologies are due to different hydrophobicities of the polyacrylic, and is thought to be a key factor. The degree of hydrophobicity influences the extent of the grafting reaction as demonstrated by the FT-IR spectroscopy analysis. In addition, the polyacrylic content, did not affect the glass transition temperature in the lower temperature region. This implied that the polyacrylic was actively involved in some reactions.
with -NH groups in the PU hard segments. The overlapping \( T_g \) peaks between PU and polyacrylic is thought to be due to the grafting reaction, thus producing the inseparable signals that led to broad peaks.

Figure 6.13: \( \tan \delta \) versus temperature for A and for A4 to A5.

Figure 6.14: \( \tan \delta \) versus temperature for A, A4 to A5 and for F.
Table 6.9: Dynamic properties for A, A4 to A5 and for F.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max value</th>
<th>Half-peak width of tan δ max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tgs*</td>
<td>Tgh*</td>
<td>ATg</td>
</tr>
<tr>
<td>A</td>
<td>-36</td>
<td>Broad</td>
<td>-</td>
</tr>
<tr>
<td>A4</td>
<td>-39</td>
<td>79</td>
<td>118</td>
</tr>
<tr>
<td>A5</td>
<td>-38</td>
<td>76</td>
<td>114</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>90</td>
<td>-</td>
</tr>
</tbody>
</table>

*Tgsc = Tg of the soft component of PUAs. Tgh = Tg of the hard component of PUAs.

6.1.1.7 Modulated temperature differential scanning calorimetry

This technique was used to support the DMTA findings. Figure 6.15 shows the plots of dCp/dT versus temperature for A1 to A3. The Tgsc did not show significant change with increasing polyacrylic ratio (table 6.10). Sample A2 showed more interphase mixing as indicated by the height of the intermediate plateau. Nonetheless, sample A3 showed the broadest Tgh peak, implying higher component mixing. A1 and A2 showed the same values of Tgsc and Tgh, while Tgh of A3 was shifted to a higher temperature value, indicating more phase separation.

Table 6.10: Transition temperatures for A, A1 to A3 and for E.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SC*</th>
<th>HC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-55</td>
<td>Broad</td>
</tr>
<tr>
<td>A1</td>
<td>-52</td>
<td>56</td>
</tr>
<tr>
<td>A2</td>
<td>-52</td>
<td>56</td>
</tr>
<tr>
<td>A3</td>
<td>-52</td>
<td>68</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>65</td>
</tr>
</tbody>
</table>

*SC = soft component. HC = hard component.
Figure 6.15: \( \frac{dC_p}{dT} \) versus temperature for A and A1 to A3.

Figure 6.16: \( \frac{dC_p}{dT} \) versus temperature for A, A4 to A5 and for F.
Meanwhile, the PS/PBA-based hybrids showed the opposite behaviour. The tan δ peaks in both lower and higher temperature regions becoming more resolved, (see figure 6.16). The $T_{gH}$ peaks were shifted to higher values with increasing polyacrylic ratio, (table 6.11). These observations led to the conclusion that phase separation was higher with increasing polyacrylic content. However, the $T_{gSC}$ values were not significantly affected by the polyacrylic content.

Table 6.11: Transition temperatures for A, A4 to A5 and for F.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (dCp/dT max) ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{gSC}^*$</td>
</tr>
<tr>
<td>A</td>
<td>-55 Broad</td>
</tr>
<tr>
<td>A4</td>
<td>-54 54</td>
</tr>
<tr>
<td>A5</td>
<td>-53 60</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
</tr>
</tbody>
</table>

*TgSC = $T_g$ of the soft component. $T_gH$ = $T_g$ of the hard component.

6.1.1.8 Transmission electron microscopy

The TEM allows the study of the particle size and shape, the extent of molecular mixing, miscibility and phase segregation at the nanoscale. As mentioned before, the hybrid samples consist of three phases i.e. the interphase, the PU-rich phase and the polyacrylic-rich phase. The darker shades are the PU phase, while the lighter one is the polyacrylic phase. The interphase, which consists of PU and polyacrylic, is greyish in the images. Figures 6.17 and 6.18 show the micrographs for the PU-PMMA/PBA hybrids with A and E.

As can be seen, sample A2, (figure 6.17 b) showed sharp boundaries between the phases. The particles have a core-shell structure, in which, polyacrylic formed the core, while PU was the shell. A study had shown that the hydrophilic component, (i.e. PU) is preferably located at the shell region of the particles. The same findings have been reported by many workers.
Figure 6.17: TEM micrographs for a) pure PUD, b) 50:50 PU:PMMA/PBA, c) 30:70 PU:PMMA/PBA and d) pure PMMA/PBA, all at 100k magnification.

The hybrid particles were distributed uniformly throughout the matrix and were of an irregular shapes. As the polyacrylic content was increased to 70 wt. %, the boundaries between the phases became unclear, (see figure 6.17 c ). This implied that the component
mixing was apparently higher in the hybrid due to molecular interactions such as hydrogen bonding between the polyacrylic and the PU. These factors would influence the mechanical properties of samples. The TEM micrographs for the PS/PBA-based hybrids are shown in figures 6.18 a) and b).

Figure 6.18: TEM micrographs: a) 30:70 PU:PS/PBA at 100k magnification. b) 50:50 PU:PS/PBA at 120k magnification.

Unlike the PMMAlPBA-based samples, the PS/PBA phases are darker in the images, as RuO$_4$ selectively stains PS.$^{116}$ The unclear boundaries between the particles implied that component mixing was favourable in A4. The greyish regions (interphases) dominated the matrix as in the discrete form. As the polyacrylic content was increased to 50 wt. %, sharp boundaries between the phases can be seen in A5, indicating greater phase separation (figure 6.18 b). It seems that PS/PBA particles aggregated and were distributed in a discrete manner in the PU particles. These phenomena are manifested in the behaviour of a filler reinforced system.

Comparatively, the PMMA/PBA type hybrid was more miscible than the PS/PBA type. The latter showed greater phase separation and acted like a reinforcement to the system. The findings were supported by the previous characterisation techniques.
6.1.2 Hybrids with the NMP containing polyurethane dispersions (the B series)

This section addresses the hybrid of NMP containing PU dispersions and polyacrylic (designated as the B series). The acrylic monomers used were MMA/n-BA and styrene/n-BA and the ratio was fixed at 50:50 wt. % of PU:polyacrylic. The morphology-property relationships are the main concern. The results were compared to the solvent free PUD at the equivalent polyacrylic ratio. Finally, the samples were annealed under the conditions shown in table 6.12.

Table 6.12: Sample descriptions for the B series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>PUD with 20% NMP</td>
</tr>
<tr>
<td>B1</td>
<td>50% PU: 50% PMMA/PBA</td>
</tr>
<tr>
<td>B2</td>
<td>50% PU: 50% PS/PBA</td>
</tr>
<tr>
<td>BT1</td>
<td>Film B1 annealed at 80°C for 16 hours in a vacuum chamber.</td>
</tr>
<tr>
<td>BT2</td>
<td>Film B2 annealed at 80°C for 16 hours in a vacuum chamber.</td>
</tr>
</tbody>
</table>

Note: The Tg of all acrylic copolymers were set at 50°C.

6.1.2.1 Fourier transform IR spectroscopy

Figure 6.19 shows the spectra of the dried B1 and B2 films. As can be seen, samples B1 and B2 showed the \(-\text{CONH}\) stretching band at 1535 cm\(^{-1}\), the \(-\text{NH}\) hydrogen bonded peaks at 3295 cm\(^{-1}\) and the \(-\text{C}=\text{O}\) free stretching band, attributed to polyacrylics, at 1721 cm\(^{-1}\). The aromatic ring of styrene for B2 was detected at 1602 cm\(^{-1}\), while the C=C stretching band was detected at 760 cm\(^{-1}\) and 701 cm\(^{-1}\), respectively. The \(-\text{OC}_{4}\text{H}_{9}\) of n-BA group was observed at 836 cm\(^{-1}\). These spectroscopy data confirmed that the samples possessed hybrid characteristics.

It has been demonstrated earlier (see section 6.1.1.1) that a grafting reaction is possible between the \(-\text{NH}\) group of PU and the polyacrylic. The percentage of grafted \(-\text{NH}\) groups are
shown in table 6.13. Obviously, the grafting percentage was higher in the PMMA/PBA hybrid type in comparison with the PS/PBA type.

Figure 6.19: FT-IR spectra for the B series at 1:1 PU:polyacrylic ratio.

Table 6.13: Percentage of ungrafted –NH groups for the A and B series at 1:1 PU:polyacrylic ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area under peak at 1531-1534 cm(^{-1}) ((A_h^+)^*)</th>
<th>Percentage of ungrafted –NH groups ((A_h/A_{ref}^+ \times 100%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>1.42</td>
<td>22</td>
</tr>
<tr>
<td>B2</td>
<td>6.48</td>
<td>98</td>
</tr>
<tr>
<td>A2</td>
<td>3.34</td>
<td>49</td>
</tr>
<tr>
<td>A5</td>
<td>3.50</td>
<td>50</td>
</tr>
</tbody>
</table>

*The area under the peak for hybrid sample, \((A_h)\)

\(^*\) \(A_{ref}\) for B1 and B2 is 6.60. \(A_{ref}\) for A2 and A5 is 6.80.

The type of acrylic monomer used influenced the results. Factors such as the monomer’s radical reactivity, the molecular structure and the degree of hydrophobicity should be taken
into the account. The study of the radical reactivity is beyond the scope of this research. However, by considering the reactivity ratios of both monomers, it was expected that the MMA monomer radicals are more highly active than the styrene. The former is thought to participate actively in the grafting reaction, thus enhancing the grafting level. In addition, the plasticizing effect brought by the NMP could facilitate the reactions. On the other hand, the bulky structure of styrene could possibly hinder the radicals approach to the grafting site i.e. \(-\text{NH}\) groups, thus reducing the grafting level.

By comparing the grafting percentages for the A and B series at the equivalent polyacrylic ratio, it was found that B1 exhibited the highest grafting percentage, while B2 was the lowest one. It seems that the addition of NMP affected the level of grafting as this effect was not too pronounced in the solvent-free samples, (i.e. A2 and A5).

6.1.2.2 Particle sizing

Table 6.14 shows the results for B1 and B2, while figure 6.20 depicts the comparison for the A and B series at the equivalent polyacrylic ratio. As discussed earlier, the addition of NMP increased the particle size, (see chapter S). Results from table 6.14 show that the PMMA/PBA-based hybrid have bigger particles than the PS/PBA type. Greater chain mobility caused by NMP and lower hydrophobicity of MMA monomer is thought to be key factors that produced the larger particles in B1. Nonetheless, the particle size of B2 did not show significant change relative to the parent B (table 6.14). It is not fully understand why B2 behaved in such manner. A systematic study is needed to investigate of any specific event that takes place between NMP and styrene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>125(± 2.0)</td>
</tr>
<tr>
<td>B1</td>
<td>145(± 1.4)</td>
</tr>
<tr>
<td>B2</td>
<td>128 (± 1.6)</td>
</tr>
</tbody>
</table>
Finally, results from A and B series were compared and presented in figure 6.20. Obviously, B and B1 have bigger particles than their counterparts. However, the PS/PBA-based hybrids showed the opposite behaviour.

6.1.2.3 Stress-strain tests

Figure 6.21 shows the stress-strain curves for B1 and B2, while the mechanical properties for the B series are displayed in table 6.15. As expected, all samples showed the common behaviour of elastomeric materials. At lower strain, the reinforcement effect of polyacrylic was more pronounced in B2 with a modulus value about half of B1, (see table 6.15). However, at higher strain, B1 showed a higher tensile strength than B2, and, surprisingly, both hybrids have lower modulus values than the parent B. This implied that the addition of NMP affected the hybrids strength. In addition, B1 has a poor extensibility, while B2 showed a superior result. The degree of hydrophobicity of the polyacrylics is thought to be a main reason. The PMMA/PBA-based hybrid behaves like a
semi-miscible system, while the PS/PBA-based is more like a filler reinforced system. On the top of that, the plasticization effect by NMP had tremendous influence on the sample final properties.

![Stress-strain curves for B1 and B2.](image)

Figure 6.21: Stress-strain curves for B1 and B2.

To study the effect of NMP, the results have been compared to the annealed samples, BT1 and BT2, (see figures 6.22 a – c and table 6.15). It can be seen that the moduli and the tensile strengths of the samples were enormously higher than the untreated samples. The evaporation of NMP has reduced the plasticization effect to a certain extent, thus enhancing both the modulus and tensile strength. Consequently, the elongation at breaks decreased.

Undoubtedly, annealing process is crucial for the sample that used solvent in its formulation. The previous results demonstrated that samples would exhibit different properties when they were treated under various conditions.
Figure 6.22: Mechanical properties for the B series. a) Modulus at 5% strain. b) Tensile strength. c) Elongation at break.

For completion, the mechanical properties for the A and B series were compared at the 1:1 PU:polyacrylic ratio, as shown in figures 6.23 a) – c). As can be seen, the A series exhibited higher modulus and tensile strength, while the B series showed higher elongation at break. The reason lies in the plasticizing effect contributed by the NMP which reduced the strength of the samples, but also enhanced the extensibility.
Figure 6.23: Mechanical properties for the A series and B series. a) Modulus at 5% strain. b) Tensile strength. c) Elongation at break.
Table 6.15: Mechanical properties for the B series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.02 (± 0.01)</td>
<td>2.8 (± 0.5)</td>
<td>1200 (± 131)</td>
</tr>
<tr>
<td>B1</td>
<td>0.02 (± 0.01)</td>
<td>1.5 (± 0.1)</td>
<td>740 (± 7)</td>
</tr>
<tr>
<td>B2</td>
<td>0.04 (± 0.02)</td>
<td>1.2 (± 0.04)</td>
<td>1210 (± 86)</td>
</tr>
<tr>
<td>BT</td>
<td>0.16 (± 0.02)</td>
<td>27 (± 0.6)</td>
<td>1250 (± 23)</td>
</tr>
<tr>
<td>BT1</td>
<td>0.40 (± 0.02)</td>
<td>23 (± 3)</td>
<td>550 (± 33)</td>
</tr>
<tr>
<td>BT2</td>
<td>0.30 (± 0.03)</td>
<td>23 (± 0.6)</td>
<td>730 (± 25)</td>
</tr>
</tbody>
</table>

6.1.2.4 Dynamic mechanical thermal analysis

Figure 6.24 illustrates the plots of the storage modulus for B1 and B2. The well-defined rubbery plateau of B2 indicated a highly phase-separated morphology, which resulted in slightly higher storage modulus at room temperature, in comparison to B1. B1 showed a gradual drop of the interphase plateau, indicating more component mixing. The plot of tan δ in figure 6.25 can be used to verify this argument.
As can be seen, the $T_{g_{sc}}$ peaks of both samples (-42°C) were shifted slightly higher than the parent B (-46°C). This indicated that the chain mobility induced by NMP has been restricted to some extent with the addition of the polyacrylics. The argument was supported by the tan $\delta$ max values that reduced by about 65% from their parent (table 6.16). B1 showed higher component mixing with a broader $T_{g_H}$ peak and a greater tan $\delta$ half-peak width value. A broad $T_{g_H}$ peak was related to the overlapping peaks of PU and polyacrylic. Molecular interactions, such as hydrogen bonding and the grafting reaction, were thought responsible for the results. In addition, the carbonyl group in NMP could also contribute to the formation of hydrogen bridges with the $-\text{NH}$ groups. Nonetheless, B2 showed more phase separation, corresponding to a greater $\Delta T_g$ value and a more resolved $T_{g_H}$ peak.

To study more about the influence of NMP, comparisons have been made with the annealed samples, BT1 and BT2. It can be see that the $T_{g_{sc}}$ of both samples were not strongly affected by the annealing process. However, the process led to more phase separation in both samples, with BT1 showing the highest $\Delta T_g$ values and a more resolved $T_{g_H}$ peak, (see figure 6.26 a).
On the other hand, BT2 showed nearly the same behaviour as the untreated sample with a slight increase of the $T_{gH}$ value from 65°C (B2) to 69°C, (see figure 6.26 b).

![Figure 6.26: Tan δ versus temperature for a) PU-PMMA/PBA-based hybrids and b) PU-PS/PBA-based hybrids.](image-url)
Table 6.16: Dynamic properties for the B series with A2 and A5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max value</th>
<th>Half-peak width of tan δ max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tgsc*</td>
<td>Tgh*</td>
<td>ΔTg</td>
</tr>
<tr>
<td>B</td>
<td>-46</td>
<td>34</td>
<td>80</td>
</tr>
<tr>
<td>B1</td>
<td>-42</td>
<td>53</td>
<td>95</td>
</tr>
<tr>
<td>B2</td>
<td>-42</td>
<td>65</td>
<td>107</td>
</tr>
<tr>
<td>BT1</td>
<td>-42</td>
<td>73</td>
<td>115</td>
</tr>
<tr>
<td>BT2</td>
<td>-40</td>
<td>69</td>
<td>109</td>
</tr>
<tr>
<td>A2</td>
<td>-39</td>
<td>75</td>
<td>114</td>
</tr>
<tr>
<td>A5</td>
<td>-38</td>
<td>76</td>
<td>114</td>
</tr>
</tbody>
</table>

*Tgsc = Tg of the soft component. Tgh = Tg of the hard component.

To complete the analysis, the dynamic behaviour of the A series, (i.e. A2 and A5) and the B series, (i.e. B1 and B2), at the 1:1 PU:polyacrylic ratio, were compared to study morphology-property relationships, (see figures 6.27 a - d). Obviously, the A series were stiffer than the B series at room temperature, as the former exhibited higher storage modulus values than their counterparts, (figures 6.27 a and c). These arguments were supported by a flatter intermediate plateau in the A series, which implied stronger molecular interactions such as hydrogen bonding. Furthermore, a higher ΔTg value, (see table 6.16) and a more resolved Tgh peak exhibited by the A series, would lead to the same conclusion. On the other hand, the residual NMP reduced the storage modulus of the B series due to its plasticizing effect. Consequently, component mixing was higher in B1 than in A2, corresponding to the broadness of the tan δ peaks, (figures 6.27 b), and the value of the tan δ half-peak width, (see table 6.16). In contrast, B2 showed less component mixing than A5, in both lower and higher temperature regions, (see figure 6.27 d and table 6.17).

To conclude, the type of polyacrylic and the use of NMP, do have a major impact on the polymer’s final properties. The first factor is related to the hydrophobicity of the acrylic monomer, while the second is related to the plasticizing effect.
Figure 6.27: Dynamic properties for the A series (i.e. A2 and A5) and the B series (i.e. B1 and B2), at the 1:1 PU:polyacrylic ratio.

6.1.2.5 Modulated temperature differential scanning calorimetry

The data obtained from the plot of $\frac{dC_p}{dT}$ versus temperature can be used in conjunction with the DMTA results. As can be seen from figure 6.28, B1 showed more
component mixing than B2, as indicated by the height of the intermediate plateau and the broadness of the peaks in both temperature regions. The peaks intensity of the soft components for both samples were lowered to about a half from the parent B, due to the chain mobility that was induced by NMP, and was restricted by the polyacrylic component. Nonetheless, B2 favours more phase separation with two resolved peaks that have been clearly separated. All these findings are consistent with the DMTA data. Table 6.17 shows the glass transition temperatures for the lower and the higher temperature regions.

![Graph](image)

Figure 6.28: dCp/dT versus temperature for B, B1 and for B2.

Overall, the addition of NMP had little effect on $T_g^{SC}$. However, the plasticizing effect was prominent on the $T_g^H$ of B2, as the temperature value was lower than that of the B1. Surprisingly, the findings are contradicted by the DMTA results.

Figure 6.29 a) shows the behaviour of the treated and untreated B1 samples. It can be seen that the annealing process had reduced component mixing in BT1, corresponding to a low height of the intermediate plateau. On the other hand, B2 and BT2 exhibited a more or less identical behaviour, which is in coherent with the DMTA data (figure 6.29 b). It seems that
the annealing process has a moderate influence on the sample morphology. The relative hydrophobicity of PS is thought to be a key factor. Overall, the evaporation of NMP during the annealing process had reduced the plasticizing effect.

Figure 6.29: $dCp/dT$ versus temperature for a) PU-PMMA/PBA-based hybrids and b) PU-PS/PBA-based hybrids with the parent B.
Finally, the A and B series were compared at the 1:1 PU:polyacrylic ratio to investigate the effect of NMP on sample properties.

From figure 6.30, it can be seen that both samples, A2 and B1 possessed the same degree of component mixing, as indicated by the same height of the intermediate plateau. However, B1 showed more phase separation than A2, as the $T_g$ peak was shifted to a higher temperature value, (see table 6.17). It seems that the addition of NMP has led to more phase separation. It is not fully understood why B1 behaved in such a way.

![Figure 6.30: $dC_p/dT$ versus temperature for A2 and B1 at 1:1 PU:PMMA/PBA ratio.](image)

Nonetheless, the addition of NMP did not show a significant effect on the $T_{gsc}$ of the PS/PBA-based hybrids, (figure 6.31 and table 6.17). However, it caused the degree of mixing in the interphase to be reduced to a certain extent, as indicated by the height of the intermediate plateau in B2. In addition, the $T_g$ peak was shifted to a lower temperature value, due to the plasticizing effect of NMP. Meanwhile, A5 showed more component mixing, corresponded to the broadened peaks in both temperature regions.
Chapter 6

Polyurethane-polyacrylic hybrid dispersions

Figure 6.31: \( \frac{dC_p}{dT} \) versus temperature for A5 and B2, at the 1:1 PU:PMMA/PBA ratio.

Table 6.17: Transition temperatures for the B series with A2 and A5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g ) (( \frac{dC_p}{dT} ) max) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_{gsc}^* )</td>
</tr>
<tr>
<td>B</td>
<td>-56</td>
</tr>
<tr>
<td>B1</td>
<td>-54</td>
</tr>
<tr>
<td>B2</td>
<td>-54</td>
</tr>
<tr>
<td>BT</td>
<td>-53</td>
</tr>
<tr>
<td>BT1</td>
<td>-53</td>
</tr>
<tr>
<td>BT2</td>
<td>-53</td>
</tr>
<tr>
<td>A2</td>
<td>-52</td>
</tr>
<tr>
<td>A5</td>
<td>-53</td>
</tr>
</tbody>
</table>

*\( T_{gsc} \) = \( T_g \) of the soft component of PUAs. \( T_{gh} \) = \( T_g \) of the hard component of PUAs.
6.1.2.6 Transmission electron microscopy

Figures 6.32 a) and b) depict the micrographs for the B series. It can be seen that B1 has phases with a core-shell structure and are a mixture of spherical and some of an irregular shape. The polyacrylic phase formed the core with the lighter shade, while PU phase as the shell with the darker shade. The interphase, which consists of PU and polyacrylic, was greyish in the images. The discrete polyacrylic phases were distributed uniformly throughout matrix. PU existed as a continuous phase and dominated the matrix. These characters resulted a sample with a lower strength, but higher extensibility.

Figure 6.32 b) shows the micrograph of B2. It can be seen that the phases are of an irregular shape and the matrix was dominated by the discrete greyish shade of PU-rich phase. This explained why B2 possessed a higher extensibility that could match the parent B.

![Figure 6.32: TEM micrographs of a) B1 and b) B2, all at 100k magnification](image)

Figures 6.33 a) and b) show the micrographs for the annealed samples BT1 and BT2. There was an increase of the dark areas in the matrix, implying more phase separation between PU phase and the polyacrylic phase, particularly in BT1. The phase has changed into uneven
shapes and has a smaller size than the untreated ones. Meanwhile, BT2 did not show a significant change with the annealing process, (figure 6.33 b). The observations for all samples have been supported by other techniques.

Figure 6.33: TEM micrographs of a) BT1 at 100k magnification and b) BT2 at 50k magnification.

To conclude, it has been demonstrated that the addition of NMP affected the hybrid properties. The PMMA/PBA-based hybrid produced a stiffer material as it exhibited a higher grafting level and more component mixing. On the other hand, the PS/PBA-based hybrid showed more phase separation with lower grafting level and less component mixing, thus producing a material with greater extensibility. By annealing those samples, the PMMA/PBA-based sample exhibited a higher phase separation due to evaporation of NMP, whereas the PS/PBA type did not show a significant change with the annealing process. Undoubtedly, the type of polyacrylic used does have an impact to the sample properties.
### 6.2 Hybridisation via the double batch method

An attempt has been made to synthesise the hybrid samples via a double batch method, (see chapter 4). The aim was to investigate the effect of synthesis mode on the morphology-property relationships. Reports\textsuperscript{62,115,116} showed that the multi-stage polymerisation techniques such as a double batch polymerisation, are capable of producing a variety morphologies, such raspberry-like or acorn-like structures, due to thermodynamic and kinetic factors. These factors were greatly influenced by the different interfacial tensions existing in a multi-phase systems\textsuperscript{43,62,114,116}. In this work, the hybrid was synthesised by copolymerising the solvent free PUD with polyacrylic at the fixed 1:1 ratio. The copolymerisation occurred through two stages. Firstly, 20 wt. % of acrylic monomer, acting as diluent at the prepolymer stage, was polymerised. Secondly, the remaining 30 wt. % acrylic monomer was polymerised in the later stage, which made in total of 50 wt. % polyacrylic. The results were compared with the hybrids from the A series (single batch method) at the equivalent polyacrylic ratio. Sample descriptions are shown in table 6.18.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Solvent free PUD</td>
</tr>
<tr>
<td>C1</td>
<td>50% PU: 50% PMMA/PBA</td>
</tr>
<tr>
<td>D1</td>
<td>50% PU: 50% PS/PBA</td>
</tr>
</tbody>
</table>

\textit{Note: The T_g of all acrylic copolymers were set at 50^\circ C.}

#### 6.2.1 Fourier transform infra-red spectroscopy

Figure 6.34 shows the FTIR spectra for samples C1 and D1. It can be seen that the samples showed the \(-\text{NH}\) bond peaks located at 3318 cm\(^{-1}\), corresponding to hydrogen bonding in the hard segments. The \text{C=O} free stretching peaks, attributed to the acrylics, was observed at 1728 cm\(^{-1}\). The \(-\text{OC}_4\text{H}_9\) absorption band of BA groups was observed at 844 cm\(^{-1}\), while the \(-\text{CONH-}\) stretching bands of the urethane links were located in the region of 1527 - 1528 cm\(^{-1}\). The styrene aromatic rings was detected at 1600 cm\(^{-1}\), while the \text{C=C} stretching
vibrations of the benzene rings were observed at 758 cm\(^{-1}\) and 695 cm\(^{-1}\). All these data manifested the hybrid characteristics of both samples.

![FT-IR spectra for CI and D1.](image)

Figure 6.38: FT-IR spectra for CI and D1.

6.2.2 Particle sizing

Table 6.19 shows the particle sizes for samples CI and D1. Both samples have nearly the same particle sizes. To see the effect of different synthesis techniques, the results were compared with a single batch system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57 (± 0.3)</td>
</tr>
<tr>
<td>CI(^d)</td>
<td>88 (± 1.1)</td>
</tr>
<tr>
<td>D1(^d)</td>
<td>89 (± 0.3)</td>
</tr>
<tr>
<td>A2(^s)</td>
<td>114 (± 3.5)</td>
</tr>
<tr>
<td>A5(^s)</td>
<td>146 (± 2.8)</td>
</tr>
</tbody>
</table>

*Note: d = double batch method. s = single batch method.*
Chapter 6 Polyurethane-polyacrylic hybrid dispersions

The double batch technique produced a smaller particle size than the single batch system. A study\textsuperscript{67} has found that the presence of monomer in the first stage disturbed the dispersion mechanism by adsorbing some hydrophilic short chain PU as stabiliser and start a new batch of particle growth. As a consequence, a smaller particle size was produced. On the other hand, a single batch technique allowed the monomers to diffuse into the PU particles and be polymerised, which led to a bigger particle size.

6.2.3 Grafting

The percentage of grafted –NH groups in the PU hard segment can be determined by using the IR spectra of the –CONH absorption peaks at the region of 1527 cm\(^{-1}\) to 1528 cm\(^{-1}\). The area under the peaks has been calculated using the Mattson 300 Unicam software. Table 6.20 presents the percentage of ungrafted –NH groups.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area under peak at 1531-1534 cm(^{-1}) ((A_h^*))</th>
<th>Percentage of ungrafted –NH groups ((A_h/A_{ref}^* \times 100%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>1.17(^*)</td>
<td>17</td>
</tr>
<tr>
<td>D1</td>
<td>3.48(^*)</td>
<td>51</td>
</tr>
<tr>
<td>A2</td>
<td>3.34(^*)</td>
<td>49</td>
</tr>
<tr>
<td>A5</td>
<td>3.50(^*)</td>
<td>50</td>
</tr>
</tbody>
</table>

\(^*\) The area under the peak for hybrid sample, \((A_h)\)

\(^*\) \(A_{ref}\) is 6.80.

It can be seen that the C1 had a higher degree of grafting than D1. The lower hydrophobicity of PMMA allows more contact with the –NH groups, thus increasing the grafting level. Meanwhile, the bulky structure of styrene in D1 might hinder the grafting process, thus reducing the grafting level. The results have been compared with the single batch samples. As can be seen from table 6.20, the PMMA/PBA-based double batch (C1) possessed 38% more grafting than the single batch sample (A2). On the contrary, regardless of
polymerisation technique, both PS/PBA-based samples (D1 and A5) showed nearly the same grafting level.

6.2.4 Stress-strain tests

Figure 6.35 shows the stress-strain curves for samples C1 and D1. As expected, both samples exhibited similar elastomeric behaviour.

![Stress-strain curves for samples C1 and D1.](image)

Figure 6.35: Stress-strain curves for samples C1 and D1.

Table 6.21: Mechanical properties for samples C1 and D1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.16 (± 0.01)</td>
<td>14 (± 0.3)</td>
<td>720 (± 3.0)</td>
</tr>
<tr>
<td>D1</td>
<td>0.26 (± 0.03)</td>
<td>14 (± 0.4)</td>
<td>730 (± 23)</td>
</tr>
</tbody>
</table>
Both C1 and D1 possessed nearly the same value of tensile strength. D1 had a higher modulus at lower strain, indicating the reinforcing effect of PS/PBA, (see table 6.21). Figures 6.36 a) – c) show the mechanical properties at the 1:1 PU:polyacrylic ratio from the double and the single batch techniques.

Figure 6.36: Mechanical properties for a double and a single batch sample at the 1:1 PU:polyacrylic ratio.
It can be seen that samples from a single batch technique exhibited a higher modulus at lower strain than the double batch one. The reinforcing effect clearly influenced the modulus of samples. Regardless of the synthesis technique, surprisingly, all samples exhibited nearly the same tensile strength. It have been postulated that the possibility of the sample's failure occurred in the PU matrix rather than polyacrylic phase or the interphase, as the values were nearly the same as the pure PU i.e. sample A. Nonetheless, the second technique produced the samples with higher extensibility.

To conclude, regardless of the synthesise technique, the PMMA/PBA-based hybrid are stiffer than the PS/PBA-based ones, as they exhibited higher tensile strength and modulus, but with a lower extensibility. The different levels of hydrophobicities of each polyacrylic is thought to be a key factor. The hybrids exhibited about half the value of elongation at break of the parent A.

6.2.5 Dynamic mechanical thermal analysis

Figure 6.37 shows the plot of the storage modulus versus temperature for C1 and D1.

![Graph showing storage modulus versus temperature for C1 and D1.](image)

Figure 6.37: Storage modulus versus temperature for samples C1 and D1.
It can be seen that C1 showed more mixing as indicated by a flatter intermediate plateau and a gradual tail-off. Meanwhile, the well defined rubbery region of D1, means more phase separation. These arguments were supported by a broad tan δ peaks of C1, but a resolved peak of D1, (figure 6.38). Both samples exhibited overlapping peaks, which is thought to be attributed to the grafting reaction between the PU hard segments and the polyacrylic.

![Figure 6.38: Tan δ versus temperature for samples C1 and D1.](image)

Table 6.22: Dynamic mechanical properties for samples C1 and D1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max value</th>
<th>Half-peak width of tan δ max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tg_{sc} Tg_{H} ΔTg</td>
<td>SC^{+}</td>
<td>HC^{+}</td>
</tr>
<tr>
<td>A</td>
<td>-36 - 105 141</td>
<td>0.37 0.13</td>
<td>(-42 &lt;-&gt; -16) 26 Broad</td>
</tr>
<tr>
<td>C1</td>
<td>-37 84 121</td>
<td>0.12 0.09</td>
<td>(-45 &lt;-&gt; -10) 35 (52 &lt;-&gt; 101) 49</td>
</tr>
<tr>
<td>D1</td>
<td>-39 75 114</td>
<td>0.09 0.10</td>
<td>(-48 &lt;-&gt; -4) 44 (62 &lt;-&gt; 95) 33</td>
</tr>
<tr>
<td>A2</td>
<td>-38 76 114</td>
<td>0.09 0.50</td>
<td>Broad</td>
</tr>
<tr>
<td>A5</td>
<td>-38 76 114</td>
<td>0.10 0.65</td>
<td>(-48 &lt;-&gt; -4) 44 (62 &lt;-&gt; 95) 33</td>
</tr>
</tbody>
</table>

*Tg_{sc} = Tg of the soft component of PUA's. Tg_{H} = Tg of the hard component of PUA's.

*SC = soft component. HC = hard component.
The results were compared with the single batch samples. As can be seen from table 6.22, the double batch samples showed more component mixing, as the tan $\delta$ half-peak width value in the higher temperature region was bigger than a single batch samples. The samples also had more phase separation, as indicated by the $\Delta T_g$ values. However, both techniques did not indicate a significant change to the $T_g$ of the soft components.

6.2.6 Modulated temperature differential scanning calorimetry

Figure 6.39 shows the plots of the $dC_p/dT$ versus temperature for C1 and D1. Sample C1 showed more component mixing with a broad transition peak in both lower and higher temperature regions. The broadened peak in the higher temperature region was thought to be two overlapping $T_g$ peaks that belong to the PU hard segments and the polyacrylic.

![Graph showing $dC_p/dT$ versus temperature for samples C1 and D1.]

In contrast, D1 exhibited more mixing in the interphase regions, particularly, in the higher temperature region, as indicated by a profile of the intermediate plateau that gradually increased at above sub-ambient temperature. In addition, D1 also showed more resolved peaks in both temperature regions, indicating more phase separation.
Finally, a comparison was made between the double and the single batch techniques. From figure 6.40 a) and table 6.23, it can be seen that A2 showed more component mixing than C1, as indicated by the height of the intermediate plateau. In contrast, the PS/PBA-based hybrid showed nearly the same level of mixing for both techniques, (figure 6.40 b). Conclusively, the nature of the synthesis can influence the final morphology.

Figure 6.40: dCp/dT versus temperature for a) PMMA/PBA-based hybrid and b) PS/PBA-based hybrid.
Table 6.23: Transition temperatures for C1 and D1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (dCp/dT max) (°C)</th>
<th>Tg sc*</th>
<th>Tg H*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-55</td>
<td></td>
<td>broad</td>
</tr>
<tr>
<td>C1</td>
<td>-53</td>
<td>65,79</td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>-54</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>-52</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>-53</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

*Tg sc = Tg of the soft component. Tg H = Tg of the hard component.

6.2.7 Transmission electron microscopy.

Figures 6.41 a) and b) show the micrographs of C1 and D1, respectively. It can be seen that C1 exhibited non-spherical phases: a structure that could be deviated from the true core-shell latex particles. Dong et al. labelled it as the multi-core, while others referred to it as the lobed-structure. It was proposed that the crosslinking/grafting reaction between the core-shell and the shell-outer shell (bulk) was responsible for the formation of such morphology.

Figure 6.41: TEM micrographs for a) C1 and b) D1, all at 100k magnification.
On the other hand, D1 showed the dark core of the PS/PBA phase, as RuO$_4$ selectively stains PS.\textsuperscript{116} The sample showed more phase separation than PMMA/PBA-type, with the discrete cores were surrounded by the continuous greyish interphase, (figure 6.41 b). There was small area governed by the discrete PU lighter phase. Higher phase separation imparted more flexibility to the sample. The stress-strain test results supported this argument.

Lastly, comparative study has been made of both synthesis techniques. C1 showed more phase separation with sharp interface between the phases, (figure 6.42 a), while, A2 favoured more mixing, as indicated by unclear phase boundaries, (figure 6.42b). On the contrary, the double batch PS/PBA-type hybrid showed more phase separation than the single batch ones, (figure 4.43 a). The latter was dominated by a more discrete polyacrylic phase, (figure 6.43 b), which imparted higher rigidity. Undoubtedly, all these argument proved that the synthesis method does affect the morphology of the samples.

Figure 6.42: TEM micrographs for a) C1 and b) A2, at 100k magnification.
To conclude, the double batch technique allowed the formation of a smaller particle size and a higher grafting level than the single batch ones. The hydrophilicity of PMMA is thought to contribute to the findings. Nonetheless, the single batch samples showed a higher modulus with a lower elongation at break than its counterpart. All samples showed nearly the same tensile strength value and could match their pure PUD parent. It is suggested that the failure occurred in the PU phase rather than polyacrylic phase or the interphase. It also triggered the possibility that the outer layer, or the surface, of the film was governed by PU phase. The behaviour shown by all samples were in agreement with the DMTA and MTDSC data. Phase separation was higher in the double batch samples with two subtle Tg peaks overlapping in the higher temperature region. Component mixing was higher in the single batch samples as measured by the broadness of the tan δ peaks and the tan δ half-peak width value. This statement is supported by the TEM micrographs. All these arguments led to one conclusion i.e. the mode of synthesis does have a major impact on the sample morphology, thus influencing its final properties.
6.3 The hybrid versus the latex blend

It is a common practice to mix two different latex polymers by physical blending. In the case of PU and polyacrylic blends, reports\textsuperscript{64,77,112} showed that a finally film would be composed of distinct phases of each polymer, with the dominant one controlling the final morphology. The blend could not match the advantages offered by the hybrid technique such as higher modulus and tensile strength, while being able to retain the flexibility.\textsuperscript{77} This study was designed to investigate the PU/polyacrylic blend behavior by mixing two types of PUD and polyacrylic. Later, the findings are compared with the hybrid at the equivalent polyacrylic ratio.

Two types of PUD i.e. A (solvent free) and B (containing NMP), were blended with the two types of polyacrylic latex i.e. PMMA/PBA and PS/PBA at three different polyacrylic ratios. The samples were coded as follows: the latex blend with the PUD A was designated as the AP series, while the BP series referred to the blend with PUD B. The mixture was stirred for one hour at room temperature. The resultant latex was dried at room temperature for 5 days prior to further drying in a vacuum chamber at room temperature for 2 days. The dried films were subjected to four characterisation techniques i.e. stress-strain tests, dynamic mechanical thermal analysis, modulated temperature differential scanning calorimetry and transmission electron microscopy.

6.3.1 The AP series

Table 6.23 shows the list of sample descriptions for the AP series. The samples consist of three different acrylic ratios i.e. 30\% wt. \%, 50\% wt. \% and 70\% wt \%. The analysis was focused on the following issues.

i) The effect of acrylic ratio on the morphology-property relationships.

ii) The effect of acrylic type on the morphology-property relationships.

iii) A comparative study of the hybrid and the blend at equivalent acrylic ratio.

Table 6.23: Sample descriptions of the AP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP1</td>
<td>70 wt.% PU: 30 wt.% PMMA/PBA</td>
</tr>
<tr>
<td>AP2</td>
<td>50 wt.% PU: 50 wt.% PMMA/PBA</td>
</tr>
<tr>
<td>AP3</td>
<td>30 wt.% PU: 70 wt.% PMMA/PBA</td>
</tr>
<tr>
<td>AP4</td>
<td>70 wt.% PU: 30 wt.% PS/PBA</td>
</tr>
<tr>
<td>AP5</td>
<td>50 wt.% PU: 50 wt.% PS/PBA</td>
</tr>
<tr>
<td>AP6</td>
<td>30 wt.% PU: 70 wt.% PS/PBA</td>
</tr>
</tbody>
</table>

6.3.1.1 Stress-strain tests

Figure 6.44 shows the stress-strain curves for AP1 to AP3. It can be seen that with increasing polyacrylic ratio, the behaviour was gradually changed from the elastomeric behaviour of PU to the brittle plastic behaviour of PMMA/PBA.118

Figure 6.44: Stress-strain curves for AP1 to AP3.
Sample AP3 showed a yield point, implying the starting point for a plastic deformation. At lower strain, the modulus increased with increasing polyacrylic ratio, (table 6.24), indicating a reinforcement effect by the polyacrylic. However, at 70 wt. % ratio, the tensile strength was drastically dropped by about half of the API and AP2 values.

The same trend was displayed by the PS/PBA-based samples, (i.e. AP4 to AP6) as shown in figure 6.45. It can be seen that above 50 wt. % polyacrylic, the sample behaved like a brittle plastic. The modulus increased with increasing polyacrylic ratio, with AP6 showed a value that was nearly the same as for the pure PS/PBA, (table 6.24). On the other hand, the tensile strength and the elongation at break showed the opposite results. Interestingly, the blend with PS/PBA was more extensible than PMMA/PBA, which gave an earlier postulation that phase separation was favoured in the former sample.

![Stress-strain curves for AP4 to AP6.](image)

Figure 6.45: Stress-strain curves for AP4 to AP6.

It is very useful to compare the findings with the hybrid sample at the equivalent polyacrylic ratio. Figures 6.46 a) – f) show the behaviour with different synthesis techniques.
Figure 6.46: Mechanical properties for the hybrids versus the latex blends for PMMA/PBA-based samples (a – c) and PS/PBA-based samples (d – f) at the equivalent polyacrylic ratio.
The modulus of the hybrids exceeded the blends at ratios up to 50 wt. %. In contrast, the blends exhibited higher tensile strengths under the same ratio limit. The reason lies in the fact that at higher polyacrylic loading, partial flocculation of the particles caused the formation of large polyacrylic phases in the blend. When polyacrylic phase dominated the matrix, one would expect the reduction of strength, (i.e. AP3 and AP6) due to incoherent film formation between PU and polyacrylic. Nonetheless, the elongations at break of the blends matched or nearly exceeded the hybrids at ratios up to 50 wt. %. Beyond that ratio, the blends showed poor results for both properties.

Table 6.24: Mechanical properties for the AP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14 (± 0.01)</td>
<td>15 (± 0.6)</td>
<td>1180 (± 43)</td>
</tr>
<tr>
<td>AP1</td>
<td>0.21 (± 0.1)</td>
<td>22 (± 1.5)</td>
<td>830 (± 40)</td>
</tr>
<tr>
<td>AP2</td>
<td>0.26 (± 0.01)</td>
<td>21 (± 2.4)</td>
<td>450 (± 28)</td>
</tr>
<tr>
<td>AP3</td>
<td>0.32 (± 0.01)</td>
<td>11 (± 1.4)</td>
<td>130 (± 29)</td>
</tr>
<tr>
<td>AP4</td>
<td>0.35 (± 0.04)</td>
<td>18 (± 1.4)</td>
<td>950 (± 48)</td>
</tr>
<tr>
<td>AP5</td>
<td>0.34 (± 0.09)</td>
<td>16 (± 0.6)</td>
<td>590 (± 7)</td>
</tr>
<tr>
<td>AP6</td>
<td>1.0 (± 0.1)</td>
<td>10 (± 1.6)</td>
<td>120 (± 8)</td>
</tr>
<tr>
<td>A2</td>
<td>0.5 (± 0.01)</td>
<td>15 (± 0.3)</td>
<td>450 (± 12)</td>
</tr>
<tr>
<td>A5</td>
<td>0.4 (± 0.01)</td>
<td>15 (± 1.30)</td>
<td>620 (± 2)</td>
</tr>
<tr>
<td>E</td>
<td>1.73 (± 0.04)</td>
<td>73 (± 3.0)</td>
<td>23 (± 3)</td>
</tr>
<tr>
<td>F</td>
<td>1.10 (± 0.10)</td>
<td>38 (± 1.4)</td>
<td>20 (± 1.1)</td>
</tr>
</tbody>
</table>

6.3.1.2 Dynamic mechanical thermal analysis

Figure 6.47 shows the storage modulus versus temperature for AP1 to AP3. At room temperature, the modulus increased with increasing polyacrylic ratio. The intermediate plateau became more flattened, indicating more mixing in the interphase due to stronger molecular interactions such as the dipole-dipole interactions or hydrogen bonding.
Figure 6.47: Storage modulus versus temperature for AP1 to AP3.

Figure 6.48: Tan δ versus temperature for AP1 to AP3.
The plot of tan δ in figure 6.48 supported these arguments. As can be seen, the addition of a polyacrylic reduced the TgSC and TgH by about 5°C from the Tg of the pure components, respectively, (see table 6.25). Kukanja et al. 64 explained the phenomenon as inter-diffusion of PU and polyacrylic components, resulting in a semi-miscible system. Nonetheless, the phase separation was higher, (indicated by the ΔTg value), and the extent of mixing was reduced, (corresponded to the tan δ half-peak width value), with increasing polyacrylic ratio.

The same behaviour was observed in the PS/PBA-based sample, (figures 6.49 and 6.50). The storage modulus increased with increasing polyacrylic ratio. Interestingly, the degree of phase separation was nearly the same for all samples, as indicated by the ΔTg value, (table 6.25). It is not fully understood why the polyacrylic content had only a little influence on the ΔTg. On the other hand, the ratio affected the extent of mixing in both temperature regions, as indicated by the reduction of the half-peak width of the tan δ value. Overall, the amount and the type of polyacrylic influenced behaviour.

Figure 6.49: Storage modulus versus temperature for AP4 to AP6.
Finally, the latex blends were compared with the hybrids at the 1:1 PU:PMMA/PBA ratio. Figure 6.51 a) shows the plots of tan δ versus temperature for the AP2 (blend) and the A2 (hybrid). It can be seen that the hybrid showed more mixing than the blend with a broader tan δ peak and a greater half-peak width value, (table 6.25). On the other hand, the blend showed more resolved peaks, indicating more phase separation. Figure 6.51 b) shows the tan δ plots for the AS (hybrid) and the AP5 (blend), at the 1:1 PU:PS/PBA ratio. Both samples showed resolved peaks, but the hybrid showed a slightly higher mixing in the interphase regions as indicated by the height of the intermediate plateau.

In conclusion, the blends and the hybrids exhibited different behaviours. By varying the polyacrylic ratio, the PMMA/PBA-based sample, (either the hybrid or the blend), showed a more significant effect on morphology than the PS/PBA type. Undoubtedly, the ratio and the type of the polyacrylic did determine the final properties.
Figure 6.51: Tan δ versus temperature plots for the hybrid and the blend a) PU-PMMA/PBA and b) PU-PS/PBA, at the 1:1 PU:polyacrylic ratio.

Table 6.25: Dynamic mechanical properties for the AP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max value</th>
<th>Half-peak width of tan δ max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tgsc</td>
<td>Tgh*</td>
<td>ΔTg</td>
</tr>
<tr>
<td>A</td>
<td>-36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AP1</td>
<td>-41</td>
<td>85</td>
<td>126</td>
</tr>
<tr>
<td>AP2</td>
<td>-43</td>
<td>84</td>
<td>127</td>
</tr>
<tr>
<td>AP3</td>
<td>-44</td>
<td>89</td>
<td>133</td>
</tr>
<tr>
<td>AP4</td>
<td>-42</td>
<td>82</td>
<td>124</td>
</tr>
<tr>
<td>AP5</td>
<td>-43</td>
<td>81</td>
<td>124</td>
</tr>
<tr>
<td>AP6</td>
<td>-44</td>
<td>79</td>
<td>123</td>
</tr>
<tr>
<td>A2</td>
<td>-39</td>
<td>75</td>
<td>114</td>
</tr>
<tr>
<td>A5</td>
<td>-38</td>
<td>76</td>
<td>114</td>
</tr>
</tbody>
</table>

*Tgsc = Tg of the soft component of PUAs. Tgh = Tg of the hard component of PUAs.

*SC = soft component. HC = hard component.
6.3.1.3 Modulated temperature differential scanning calorimetry

Figure 6.52 shows the dCp/dT versus temperature for AP1 to AP3. It can be seen that the degree of component mixing in the interphase did not show a significant change with increasing polyacrylic ratio, as indicated by the height of the intermediate plateau.

![Graph showing dCp/dT versus temperature for AP1 to AP3.]

Figure 6.52: dCp/dT versus temperature for AP1 to AP3.

However, the broadness of the TgH peak, indicated some degree of the hard component mixing. The TgH peak was shifted to a lower temperature which supported these arguments, (table 6.26). The same observations were reported by other workers.64,77 On the other hand, the TgSC value did not showed a significant change with increasing polyacrylic ratio.

Figure 6.53 shows the behaviour of AP4 to AP6. It can be seen that the TgH peak was shifted to a higher temperature with increasing polyacrylic ratio, which indicated more phase separation. This behaviour was totally opposite to the PMMA/PBA-based sample. The hydrophobic character of PS is thought to be a key factor. Nonetheless, the TgSC value did not change with the addition of the polyacrylic.
Finally, a comparative study has been made between the hybrid and the blend at the 1:1 PU:polyacrylic ratio, (figures 6.54 a and b).

Figure 6.53: $\frac{dC_p}{dT}$ versus temperature for AP4 to AP6.

Figure 6.54: $\frac{dC_p}{dT}$ versus temperature for the hybrid and blend of a) PU-PMMA/PBA and b) PU-PS/PBA, at 1:1 PU:polyacrylic ratio.
As can be seen, the hybrids showed more component mixing than the blends, as both $T_{gsc}$ and $T_{gH}$ were shifted inwardly. This observation was pronounced for the PMMA/PBA-based hybrid, which showed the greatest height of the intermediate plateau. All the arguments proved that the synthesis method and polyacrylic type does affect the sample morphology.

Table 6.26: Transition temperatures for the AP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{gsc}$ (°C)</th>
<th>$T_{gH}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-55</td>
<td>Broad</td>
</tr>
<tr>
<td>AP1</td>
<td>-55</td>
<td>59</td>
</tr>
<tr>
<td>AP2</td>
<td>-54</td>
<td>60</td>
</tr>
<tr>
<td>AP3</td>
<td>-56</td>
<td>57</td>
</tr>
<tr>
<td>AP4</td>
<td>-55</td>
<td>64</td>
</tr>
<tr>
<td>AP5</td>
<td>-55</td>
<td>65</td>
</tr>
<tr>
<td>AP6</td>
<td>-56</td>
<td>65</td>
</tr>
<tr>
<td>A2</td>
<td>-52</td>
<td>56</td>
</tr>
<tr>
<td>A5</td>
<td>-53</td>
<td>60</td>
</tr>
</tbody>
</table>

*T_{gsc} = Tg of the soft component of PUAs. $T_{gH} = Tg$ of the hard component of PUAs.

6.4.1.4 Transmission electron microscopy

Figures 6.55 a) and b) illustrate the micrographs for AP3 and A3 at 70 wt. % polyacrylic. Sharp interfaces were observed between the multi-lobed structures of the blended phases and the dark shades of the PU phases. This indicated that phase separation was favourable in the former sample. It is hard to explain the formation of such multi-lobed structures in the blend. On the other hand, the hybrid showed unclear phase boundaries between the cores and the shells, indicating more component mixing. The blend exhibited bigger phase sizes. Unfortunately, the comparison cannot be made on the PS/PBA-blended samples, as they showed very poor contrast.
To conclude, the PMMA/PBA-blended samples showed a greater degree of mixing than the PS/PBA-based samples. The less hydrophobic character of PMMA is thought to be the main reason. The stress-strain tests showed that the dominant phase in the blend could determine the final properties. Nonetheless, the hybrid showed more component mixing than the blend. Interestingly, the blend could match the strength of the hybrid up to a ratio limit of 50 wt. % polyacrylic. However, these results were opposite from those found by other workers.\textsuperscript{64,77,112} They found the blend showed poor mechanical properties at all polyacrylic ratios. Many factors such as the synthesis method, the type and Tg of polyacrylic and the components of the PU, such as the type of diisocyanate and polyol, must be taken into the account for the comparison to be fair.

6.3.2 The BP series

Table 6.27 shows the sample descriptions for the BP series. As mentioned earlier, PUD containing NMP was mixed with polyacrylic at the same three different ratios i.e. 30%
wt. %, 50% wt. % and 70% wt. %. The effects of the type and the ratio of polyacrylic on morphology-property relationships were studied. The films were analysed with three characterisation techniques i.e. stress-strain tests, DMTA and MTDSC. On completion, the results were compared with the hybrid and the AP series, at the 1:1 PU:polyacrylic ratio.

Table 6.27: Sample descriptions for the BP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP1</td>
<td>70 wt.%PU: 30 wt. % PMMA/PBA</td>
</tr>
<tr>
<td>BP2</td>
<td>50 wt.%PU: 50 wt. % PMMA/PBA</td>
</tr>
<tr>
<td>BP3</td>
<td>30 wt.%PU: 70 wt. % PMMA/PBA</td>
</tr>
<tr>
<td>BP4</td>
<td>70 wt.%PU: 30 wt. % PS/PBA</td>
</tr>
<tr>
<td>BP5</td>
<td>50 wt.%PU: 50 wt. % PS/PBA</td>
</tr>
<tr>
<td>BP6</td>
<td>30 wt.%PU: 70 wt. % PS/PBA</td>
</tr>
</tbody>
</table>

6.3.2.1 Stress-strain tests

Figures 6.56 and 6.57 show the stress-strain curves for BP1 to BP3 and BP4 to BP6, respectively. As can be seen, regardless of the type of polyacrylic, the samples displayed the behaviour of brittle materials with a yield point at 70 wt. % ratio. The modulus increased, while the tensile strength decreased with increasing polyacrylic ratio. Overall, the PMMA/PBA-based samples could deliver more or less acceptable properties within the limit of 50 wt. % ratio, (figures 6.58 a – c and table 6.28).

On the other hand, the PS/PBA-based samples showed tensile values that were nearly the same for all ratios, (figure 6.58 b). Probably failure occurred at a weaker interface between the polyacrylic phase and the PU phase in these materials. It is thought that the hydrophobicity and the bulky structure of PS allowed very little inter-diffusion between the polymers, thus forming an incoherent film with weaker molecular interactions between the phases. As expected, elongation at break decreased with increasing polyacrylic ratio, with the PS/PBA type exhibiting a slightly higher value.
Figure 6.56: Stress-strain curves for BP1 to BP3.

Figure 6.57: Stress-strain curves for BP4 to BP6.
Finally, figures 6.59 a)-c) show the comparison between the hybrid and the blend at the 1:1 PU:polyacrylic ratio. It can be seen that the blends exhibited higher moduli and tensile strengths than the hybrids, but had poorer elongation at break. The hybrids possessed higher elongation at break due to enhanced component mixing. The plasticizing effect of NMP and the ability of PU to plasticize the polyacrylic phase explained why the samples were extensible enough to match the parent B^{112}, (see figure 6.59 c and table 6.28).
Figure 6.59: Mechanical properties for the hybrids versus the blends, at the 1:1 PU:polyacrylic ratio.
Table 6.28: Mechanical properties of the BP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.02 (± 0.01)</td>
<td>2.8 (± 0.5)</td>
<td>1200 (± 131)</td>
</tr>
<tr>
<td>BP1</td>
<td>0.30 (± 0.04)</td>
<td>15.0 (± 0.4)</td>
<td>670 (± 28)</td>
</tr>
<tr>
<td>BP2</td>
<td>0.28 (± 0.01)</td>
<td>9.0 (± 0.3)</td>
<td>400 (± 13)</td>
</tr>
<tr>
<td>BP3</td>
<td>0.21 (± 0.01)</td>
<td>6.0 (± 0.3)</td>
<td>295 (± 22)</td>
</tr>
<tr>
<td>BP4</td>
<td>0.13 (± 0.01)</td>
<td>6.0 (± 0.7)</td>
<td>880 (± 80)</td>
</tr>
<tr>
<td>BP5</td>
<td>0.30 (± 0.1)</td>
<td>7.0 (± 0.4)</td>
<td>570 (± 71)</td>
</tr>
<tr>
<td>BP6</td>
<td>0.40 (± 0.04)</td>
<td>6.6 (± 0.3)</td>
<td>310 (± 13)</td>
</tr>
<tr>
<td>B1</td>
<td>0.02 (± 0.01)</td>
<td>1.5 (± 0.1)</td>
<td>740 (± 7)</td>
</tr>
<tr>
<td>B2</td>
<td>0.04 (± 0.02)</td>
<td>1.2 (± 0.04)</td>
<td>1210 (± 86)</td>
</tr>
<tr>
<td>E</td>
<td>1.70 (±0.04)</td>
<td>73.0 (± 3.0)</td>
<td>23 (± 3)</td>
</tr>
<tr>
<td>F</td>
<td>1.10 (±0.10)</td>
<td>38.0 (± 1.4)</td>
<td>20 (± 1.1)</td>
</tr>
</tbody>
</table>

On completion, the BP series were compared with the AP series at an equivalent polyacrylic ratio. Figures 6.60 a) - c) show the mechanical properties for the PMMA/PBA-based samples. The modulus of AP series increased linearly with increasing polyacrylic ratio, while the BP series showed a limit at 50 wt. % ratio to give an optimum property values. The AP series possessed higher tensile strengths than the BP series. The reason lies in fact that NMP plasticized the BP series, thus reducing their strengths. On the other hand, both samples showed reductions in elongation at break with BP displaying unclear trends. Figures 6.60 d) - f) depict the mechanical behaviours for PS/PBA-based samples. The moduli and the tensile strengths of the AP series were greater than the BP series, as the plasticizing effect of NMP becomes the main issue. As expected, both samples became less flexible with increasing polyacrylic ratio.

To conclude, the hybrids displayed far better mechanical properties than the blends. The formation of secondary forces such as hydrogen bonding, grafting reaction and dipole-dipole interactions in the hybrid is thought to be a major contributor. As for the blends, the AP
series showed better mechanical properties than the BP series, due to the plasticizing effect of NMP in the latter.

![Graphs showing mechanical properties for blend series with PMMA/PBA (a to c) and PS/PBA (d to f).](image)

Figure 6.60: Mechanical properties for the blend series with PMMA/PBA (a to c) and PS/PBA (d to f).
6.3.2.2 Dynamic mechanical thermal analysis

Figure 6.61 shows the effect of increasing the PMMA/PBA ratio on the storage modulus of the blend samples. At room temperature, i.e. 25°C, the modulus increased and the intermediate plateau became flatter, which indicated greater component mixing with increasing polyacrylic ratio.

![Figure 6.61: Storage modulus versus temperature for BP1 to BP3.](image)

This argument was supported by the tan δ plots as shown in figure 6.62. The samples showed more mixing as the Tg_H peak became broader and the peak was shifted inwards with increasing polyacrylic ratio. It also can be seen that the Tg_sc of BP1 and BP2 were shifted to about 3°C higher from the parent B. This was thought to because of some degree of mixing occurring in the lower temperature region. Component mixing increased with increasing polyacrylic ratio as shown by the tan δ half-peak width. Among all samples, BP3, which has the highest polyacrylic content, showed less phase separation, as indicated by the ΔTg value, (table 6.29).
Figure 6.62: Tan δ versus temperature for BP1 to BP3.

Figure 6.63: Storage modulus versus temperature for BP4 to BP6.
Figure 6.63 shows the storage modulus for PS/PBA-based blends. It can be seen that by varying the PS/PBA weight content has only a small impact on the modulus. Nonetheless, the samples showed more phase separation as the $T_{gH}$ peak became more resolved with increasing polyacrylic ratio, (figure 6.64). The argument was supported by the reduction of the level of component mixing, as shown by the tan $\delta$ half-peak width values, (table 6.29).

Figure 6.64: Tan $\delta$ versus temperature for BP4 to BP6

Overall, the PMMA/PBA-based samples showed more phase separation than the PS/PBA types with increasing polyacrylic ratio, (table 6.29). Both types showed a certain degree of component mixing, which was most pronounced in the higher temperature region.

Figures 6.65 a) and b) show a comparison between the hybrid and the blend at 1:1 PU:polyacrylic ratio. It can be seen that the hybrids showed more component mixing than the blend, particularly with the PMMA/PBA-based hybrid. Regardless of the synthesis technique, both PS/PBA-based samples showed nearly the same degree of mixing in the higher temperature region.
Figure 6.65: Tan δ profiles for the hybrid versus the blend a) PU:PMMA/PBA and b) PU:PS/PBA, at 1:1 ratio.

Figure 6.66: Tan δ profiles for the blend a) PU:PMMA/PBA and b) PU:PS/PBA, at the 1:1 PU:polyacrylic ratio.
Finally, the AP series and the BP series were compared at the 1:1 PU:polyacrylic ratio, (figures 6.66 a and b). The AP series showed more phase separation than the BP series. The $T_g$ of the BP series was shifted to a lower temperature value, due to the plasticizing effect of NMP.

Table 6.29: Dynamic properties for the BP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ at $\tan \delta$ max ($^\circ$C)</th>
<th>$\tan \delta$ max value</th>
<th>Half-peak width of $\tan \delta$ max ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{gsc}$</td>
<td>$T_{gH}$</td>
<td>$\Delta T_g$</td>
</tr>
<tr>
<td>B</td>
<td>-46</td>
<td>34</td>
<td>80</td>
</tr>
<tr>
<td>BP1</td>
<td>-43</td>
<td>81</td>
<td>124</td>
</tr>
<tr>
<td>BP2</td>
<td>-43</td>
<td>82</td>
<td>125</td>
</tr>
<tr>
<td>BP3</td>
<td>-46</td>
<td>76</td>
<td>122</td>
</tr>
<tr>
<td>BP4</td>
<td>-43</td>
<td>75</td>
<td>118</td>
</tr>
<tr>
<td>BP5</td>
<td>-41</td>
<td>70</td>
<td>111</td>
</tr>
<tr>
<td>BP6</td>
<td>-45</td>
<td>75</td>
<td>120</td>
</tr>
<tr>
<td>B1</td>
<td>-42</td>
<td>53</td>
<td>95</td>
</tr>
<tr>
<td>B2</td>
<td>-42</td>
<td>65</td>
<td>107</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>94</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>90</td>
<td>-</td>
</tr>
</tbody>
</table>

$T_{gsc} = T_g$ of the component of PUA. $T_{gH} = T_g$ of the hard component of PUA.

$^* SC =$ soft component. $HC =$ hard component.

6.3.2.3 Modulated temperature differential scanning calorimetry

Figure 6.67 shows the transition profiles for BP1 to BP3. The $T_{gsc}$ value did not show a significant change with polyacrylic ratio, while the $T_{gH}$ peak was shifted down by about 11°C from pure PMMA/PBA, (table 6.30). The plasticizing effect of the elastomeric PU on polyacrylic was thought as the reason. Component mixing in the interphase showed a small increase, corresponding with the height of intermediate plateau. Figure 6.68 shows the transition profiles for BP4 to BP6. The samples showed a slight increased of phase
separation with increasing polyacrylic ratio, (table 6.30). The level of component mixing in
the interphase was nearly the same, as indicated by the height of intermediate plateau. The
\( T_{gH} \) peak became more resolved with increasing polyacrylic ratio, emphasising a lesser
degree of heterogeneity existed in that particular temperature region.\(^{112}\)

![Figure 6.67: dCP/dT versus temperature for BP1 to BP3.](image)

![Figure 6.68: dCp/dT versus temperature for BP4 to BP6.](image)
Overall, both samples did not show significant change in the \( T_{gsc} \) value with the increasing polyacrylic ratio. In contrast, the \( T_{gh} \) peak was shifted by about 2\( ^\circ \)C to 11 \( ^\circ \)C lower than the \( T_g \) of pure polyacrylic, (table 6.30). The plasticizing effect caused by PU at higher polyacrylic loadings was thought as the reason.\(^{112}\) The PMMA/PBA-based sample showed more component mixing, as indicated by the \( T_{gh} \) value that was lower than the PS/PBA type, (figure 6.69).

![Graph](image)

Figure 6.69: \( \frac{dCp}{dT} \) versus temperature for BP2 and BP5, at 1:1 the PU:polyacrylic ratio.

A comparative study has been made between the hybrid and the blend at the 1:1 PU:polyacrylic ratio. The PMMA/PBA-based hybrid showed more mixing as shown by the broadness of both transition peaks and the height of intermediate plateau, particularly in the lower temperature region, (figure 6.70 a). The blend showed a resolved peak, indicating more phase separation. Regardless of the synthesis method, the hybrid and the blend of PS/PBA-based samples showed nearly the same degree of phase separation, (figure 6.70 b). However, the component mixing in the interphase was slightly lower for the hybrid, as indicated by the height of the intermediate plateau.
Figure 6.70: $\frac{dC_p}{dT}$ versus temperature for the hybrid and the blend a) PU-PMMA/PBA and b) PU-PS/PBA.

Finally, the AP series and the BP series were compared, at the 1:1 PU:polyacrylic ratio as shown in figures 6.71 a) and b).

Figure 6.71: $\frac{dC_p}{dT}$ versus temperature for the blends a) PU-PMMA/PBA and b) PU-PS/PBA.
It can be seen that the addition of NMP affected the transition temperatures of the BP series. The series showed more component mixing by shifting the $T_{gH}$ value to a lower temperature. The mixing was higher, particularly in the temperature region of $0^\circ C - 45^\circ C$. It is not fully understood why the series behaved in that way. Further studies should be undertaken to investigate the connection between the solvent and samples at that particular temperature range.

Table 6.30: Transition temperatures for the BP series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{g (dCp/dT max)}$ ($^\circ C$)</th>
<th>$T_{gsc}$*</th>
<th>$T_{gH}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>-56</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>BP1</td>
<td>-54</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>BP2</td>
<td>-55</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>BP3</td>
<td>-55</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>BP4</td>
<td>-55</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>BP5</td>
<td>-55</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>BP6</td>
<td>-56</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>-54</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>-54</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>61</td>
<td></td>
</tr>
</tbody>
</table>

$^*T_{gsc} = T_g$ of the soft component. $T_{gH} = T_g$ of the hard component.

To conclude, the PU-PMMA/PBA blend samples showed more component mixing, while the PS/PBA-type favoured phase separation. However, the polyacrylic ratio has to be limited up to 50 wt. % to give the comparable results relative to the hybrids. As expected, the hybrids displayed better mechanical properties than the blends. It was found that the type and the ratio of polyacrylic does determine the final properties. The addition of NMP has also affected the properties of both the hybrid and blend samples.
CHAPTER 7

THE MODIFICATION OF THE POLYURETHANE HARD SEGMENTS
CHAPTER 7

THE MODIFICATION OF THE POLYURETHANE HARD SEGMENTS

This chapter addresses the modification of the PU hard segments, based on the results of dynamic mechanical thermal analysis (DMTA) and modulated temperature differential scanning calorimetry (MTDSC). Three cases are outlined. Firstly, the results showed that the PUD hard segment displayed broad peaks in the tan δ–temperature and in the derivative Cp–temperature plots from DMTA and MTDSC, respectively, (see chapter 5). By increasing the hard segment content with a short diol (e.g. neopentyl glycol) or replacing hydrazine with ethylene diamine (EDA), without changing the NCO/OH ratio, was thought might impart more information on the morphology of the soft and the hard segments. Apart from that, the PU-polyacrylic hybrid system showed broad overlapping tan δ peaks, corresponding to Tg of PU and polyacrylic, at the higher temperature region, (see chapter 6). The reason was thought to be due to Tg of polyacrylic (50°C) being closer to the Tg of the PU hard segment. Presumably, if the Tg of the polyacrylic is set lower than 50°C, two separated peaks associated with Tg of PU hard segment and polyacrylic would be seen. Finally, studies revealed that different synthesis techniques, (i.e. single batch versus double batch), affected the sample properties. A summary of all cases are listed as follows:

1. Modify the hard segment content by using NPG or EDA on solvent free PUD.
2. Change Tg of polyacrylic of the C series.
3. Vary the addition mode of acrylic monomer of the D series.

7.1 The incorporation of EDA and short diols into the PU hard segments

This section addresses the modifications of the hard segment of the PUDs. Three types of modifier, namely, ethylene diamine (EDA), neopentyl glycol (NPG) and
dibromoneopentyl glycol (dNPG) were incorporated into the hard segment, (the structural formulae of all can be seen in chapter 4). The NCO/OH ratio of 2 was maintained for all samples. EDA and NPG were incorporated into solvent free pure PUD, while the bromine-containing diol was inserted into PUA, to assist the TEM micrograph analysis. Bromine was added to give better contrast between the core and shell structures. Solvent free PUD was selected as a model, as it offers far superior properties than the NMP-containing PUD, (see chapter 5). On the other hand, only two hybrid samples, A2 and A5, (see chapter 6), have been chosen to incorporate with brominated polyols. Table 7.1 shows sample descriptions with the modification. The analysis was divided into 3 sections according to the type of modifier.

Table 7.1: Sample descriptions and their modification.

<table>
<thead>
<tr>
<th>Modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>AN1</td>
</tr>
<tr>
<td>AN2</td>
</tr>
<tr>
<td>A2</td>
</tr>
<tr>
<td>A5</td>
</tr>
</tbody>
</table>

7.1.1 Ethylene diamine (EDA) as the chain extension agent

In the previous work, solvent-free PUDs, (the A series), were chain-extended with hydrazine. Studies showed that diamine chain extenders such as EDA and hydrazine were capable of forming urea linkages in the hard segment, while the diol types such as ethylene glycol produced urethane linkages. The presence of two –NH groups from urea linkages impart stronger hydrogen bonds, in comparison with one –NH group pertaining to urethane linkages. The urea type bonding possesses a bond energy of 21.5 kJ/mol, while the urethane type is 18.4 kJ/mol. Consequently, the poly(urethane-urea) exhibited higher
rigidity than the polyurethane. The additional amide linkages present in the urea type bonding restricted chain rotation, thus strengthening the sample.\textsuperscript{104} Kim et al.\textsuperscript{71} reported that by using an amine type chain extender with different functionality ($f$) could increase the rigidity of the sample. However, both chain extenders used in this work, hydrazine and EDA, have the same functionality i.e. $f = 2$. Undeniably, the findings from the experiment impart more understanding on the hard segment behaviour.

\subsection{7.1.1.1 Fourier transform IR spectroscopy}

Figure 7.1 shows the spectra for A and AE. Of special interest were the urea groups that has a peak position of 1632-1671 cm$^{-1}$\textsuperscript{71,121-123} It can be seen that the hydrogen bonded urea carbonyl peak was detected at 1636 cm$^{-1}$, which confirmed the formation of urea linkages in AE.

![Figure 7.1: FT-IR spectra for A and AE.](image)

On the other hand, a weaker signal (mere shoulder) of the hydrogen bonded urea linkages was detected at 1658 cm$^{-1}$ in the hydrazine chain extended sample. Urea linkages was greater in AE than A, corresponding to a stronger peak intensity in the former.


7.1.1.2 Particle sizing

Table 7.2 lists the particle size for all samples. The particle size increased by about 21% when hydrazine was replaced with EDA. The presence of two methylene groups in EDA was thought to be a key factor. The groups increased the polymer hydrophobicity, thus increasing water repellence at the dispersion stage and limiting the extent of polymer dissociation. On the top of that, the greater rigidity of polymer chain caused by the urea groups, hindered the migration process of ionic species that were embedded in the macromolecular coils to the particle surface.

Table 7.2: Particle sizes for samples A and AE.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57 (± 0.3)</td>
</tr>
<tr>
<td>AE</td>
<td>76 (± 0.7)</td>
</tr>
</tbody>
</table>

7.1.1.3 Stress-strain tests

Figure 7.2 shows the strain-stress curves for A and AE. Both samples showed the behaviour of elastomeric materials. Table 7.3 shows the mechanical properties for A and AE. It can be seen that both samples have nearly the same modulus at lower strain. Nonetheless, AE exhibited higher tensile strength but with lower elongation at break, than A. The explanations are outlined as follows: EDA possesses two methylene groups, which imparted flexibility to the hard segment. This led to more component mixing, by the greater possibility to form hydrogen bonding between the ether groups of PPG and the -NH groups of urea/urethane groups in the hard segments.

Apart from that, the presence of methylene groups reduced the polarity of the urea linkages, which promoted more component mixing. A study had shown that higher component mixing tends to reduce the energy storage character, thus reducing the extensibility.
Chapter 7

The modification of the polyurethane hard segments

On the contrary, higher polarity of the urea linkages in the hydrazine type\textsuperscript{31}, developed higher cohesion in the hard segments, which favoured more phase separation. All these factors explained why the EDA based sample had higher tensile strength, but less flexible than the hydrazine type. The findings were in the agreement with other workers, who found that the EDA based samples possessed higher crystallinity, which increased the rigidity and brittleness of the film.\textsuperscript{27,31,104} Figure 7.3 showed the molecular structures of the urea linkages for both types of chain extenders.

![Figure 7.3: Schematic diagrams of urea linkages with a) hydrazine and b) EDA.\textsuperscript{31}]

\[ \text{a) } \quad \text{b) } \]
Table 7.3: Mechanical properties for A and AE.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14 (± 0.01)</td>
<td>15 (± 0.6)</td>
<td>1180 (± 43)</td>
</tr>
<tr>
<td>AE</td>
<td>0.15 (± 0.02)</td>
<td>20 (± 0.6)</td>
<td>1010 (± 54)</td>
</tr>
</tbody>
</table>

7.1.1.4 Dynamic mechanical thermal analysis

Figure 7.4 shows the storage modulus for A and AE. At room temperature, AE showed a slightly lower storage modulus value than A.

This can be explained by the presence of two methylene groups in EDA which are capable of ‘plasticizing’ the hard segment, thus reducing the modulus. Sample AE showed a more gradual tail off, which indicated that the sample has more component mixing than sample A. These arguments were supported by a broad tan δ peak–temperature as shown in figure 7.5.
Evidently, the lower polarity of the urea linkages and the higher flexibility of the hard segment, promoted more component mixing in AE. Nonetheless, the incorporation of EDA did not have a major impact on the soft segment, as the dynamic properties did not show significant changes, (table 7.4)

Table 7.4: Dynamic properties for A and AE.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max value</th>
<th>Half-peak width of tan δ max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tgs</td>
<td>Tgh</td>
<td>SS*</td>
</tr>
<tr>
<td>A</td>
<td>-36</td>
<td>Broad</td>
<td>0.37</td>
</tr>
<tr>
<td>AE</td>
<td>-34</td>
<td>Broad</td>
<td>0.38</td>
</tr>
</tbody>
</table>

*SS = Soft segment, HS = Hard segment.
7.1.1.5 Modulated temperature differential scanning calorimetry

Figure 7.6 shows the transition profiles for A and AE. It can be seen that AE showed slightly more segmental mixing with a broad transition peak, especially in the higher temperature region. The Tgh peak that was shifted to a lower temperature value, (table 7.5), supported the arguments. Nonetheless, neither chain extender affected the transition behaviour of the soft segment. All of these observations were in agreement with the DMTA data. The presence of the two methylene groups of EDA is thought to be a key factor.

![Graph showing dCp/dT versus temperature for A and AE.]

**Figure 7.6: dCp/dT versus temperature for A and AE.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (dCp/dT max) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SS*</td>
</tr>
<tr>
<td>A</td>
<td>-55</td>
</tr>
<tr>
<td>AE</td>
<td>-56</td>
</tr>
</tbody>
</table>

*SS = Soft segment. HS = Hard segment.
7.1.1.6 Atomic force microscopy

Atomic force microscopy (AFM) is a scanning probe technique that allows three-dimensional topographical imaging of a surface. Figure 7.7 illustrates the phase images for A and AE.

![Phase images for A and AE.](image)

The dark shade represents the soft segment-rich phase, while the lighter shade is the hard segment-rich phase. The contrast resulted from the differences between the local stiffness of the two segments. The interphase regions are greyish in the images. It can be seen that the hydrazine based bonding, exhibited more spherical phases, while the EDA based displayed more irregular shapes. Both samples exhibited phases separation, with AE showing clearer phase boundaries. Sample A was dominated by the discrete hard segments, while the latter was dominated by the continuous greyish areas, which corresponding to higher component mixing. The results were consistent with the findings from other characterisation techniques.

Overall, the incorporation of EDA, as chain extension agent, had a moderate influence on the sample properties. Both chain extenders are capable of forming urea linkages in the hard
segments. However, the higher polarity of the urea linkages of the hydrazine based sample, relative to EDA, caused higher cohesion between the hard segments. In return, the hydrazine based sample favoured more phase separation than the latter. On the other hand, the two methylene groups in EDA reduced the polarity of the urea linkages, thus promoting more component mixing.

7.1.2 Incorporation of neopentyl glycol (NPG) into the PU hard segments

Branched chain aliphatic diols, such as neopentyl glycol (NPG), were introduced into the PU hard segments as single compounds or as mixtures. Wu et al. combined 1,4-butanediol with NPG to improve the hardness of a sample, due to the latter branched molecular structure. A study showed that the combination of adipic acid and NPG, or mixtures of NPG and hexamethylene glycol as polyols, imparted greater flexibility and increased the hydrolytic stability. In this work, NPG was used to increase the rigidity of the hard segment and was set at two different weight ratios i.e. 2 wt. % and 4 wt. %. Other variables such as the NCO/OH ratio, PPG molecular weight and the type of chain extender remained unchanged.

7.1.2.1 Particle sizing

Table 7.6 shows the particle sizes for A, AN1 and AN2. It can be seen that the particle size decreased with increasing NPG ratio. It seems that the incorporation of NPG, did not affect particle stability, as in the EDA case, (see section 7.1.1). In fact, higher NPG content led to the smallest particle size, (i.e. sample AN2). This phenomenon is hard to explain. With fixed DMPA content throughout the experiment, the incorporation of NPG is thought to be a key factor.

Hypothetically there is a possibility of diol groups facilitating the incorporation of DMPA to some extent, thus leading to a better distribution along the polymer chain. Consequently it produced smaller particle size. The observations were in agreement with the increase in
dispersion viscosity. A study showed that smaller particles produced higher viscosity, as the number of dispersed particles increased.\textsuperscript{121}

Table 7.6: Particle sizes for samples A, AN1 and AN2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
<th>Viscosity (mPa s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57 (± 0.3)</td>
<td>51</td>
</tr>
<tr>
<td>AN1</td>
<td>58 (± 0.3)</td>
<td>53</td>
</tr>
<tr>
<td>AN2</td>
<td>52 (± 0.3)</td>
<td>71</td>
</tr>
</tbody>
</table>

*Data provided by DSM-NeoResins, Holland.

7.1.2.2 Stress-strain tests

Figure 7.8 shows the stress-strain curves for A, AN1 and AN2. The samples lost their elastomeric character with increasing NPG ratio.

![Stress-strain curves for A, AN1 and AN2](image)

Figure 7.8: The stress-strain curves for A, AN1 and AN2.
The modified samples exhibited higher modulus and tensile strength but with lower elongations at break, particularly in AN2, which showed a reduction of 61% from the unmodified sample, (table 7.7). To explain these phenomena, two possibilities are outlined. Firstly, higher component mixing between the segments led to higher tensile strength, but with a less flexible material. Lubnin et al. studied the oligomer formation at the prepolymer stage. They found that hetero-pentamers e.g. IPDI-NPG-IPDI-PPG-IPDI, had an ability to compatibilise with homo-trimers e.g. IPDI-PPG-IPDI or IPDI-NPG-IPDI, thus producing more component mixing. Secondly, the NPG structure itself plays an important role. The presence of two branched methyl groups of NPG could impart a degree of steric hindrance, which perturbed the order of the hard segments. Apart from that, the groups could also restrict the mobility of PPG thus reducing the sample flexibility.

Table 7.7: Mechanical properties of A, AN1 and AN2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Hardness (s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14 (± 0.01)</td>
<td>15 (± 0.6)</td>
<td>1180 (± 43)</td>
<td>41</td>
</tr>
<tr>
<td>AN1</td>
<td>0.31 (± 0.01)</td>
<td>17 (± 0.5)</td>
<td>750 (± 12)</td>
<td>79</td>
</tr>
<tr>
<td>AN2</td>
<td>0.46 (± 0.01)</td>
<td>20 (± 0.9)</td>
<td>460 (± 30)</td>
<td>139</td>
</tr>
</tbody>
</table>


Overall, the addition of NPG has produced more phase mixing, resulting in an increase of modulus and tensile strength. A drawback was the sample became less flexible, as the methyl groups restricted the soft segment mobility.

7.1.2.3 Wide-angle X-ray diffraction

Another factor that could be linked with the increasing of sample stiffness is the presence of crystallinity in the sample. Wide-angle x-ray diffraction was used to provide evidence for crystallinity in the sample. The restriction of chain mobility introduced by the
covalent linkages and the presence of strong interactions through hydrogen bonding, decreased the degree of crystallinity.46

![Figure 7.9: WAXD spectra for AN1 and AN2.](image)

It can be seen that AN1 and AN2 show broad halos at 17.9° and 18.6°, respectively (figure 7.9). The broad halos were caused by scattering from small crystalline structures or from the amorphous regions. With the absence of discrete diffraction peaks in the spectra, it was confirmed that there was no crystalline structure present in these samples, and the broad halos originated from the amorphous phase. The results removed the possibility of crystallinity causing the increase in both modulus and tensile strength. Furthermore, PPG-based PU was unlikely to form crystalline structures due to its liquid nature at room temperature.98

7.1.2.4 Dynamic thermal mechanical analysis

The storage moduli of the modified samples are shown in figure 7.10. It can be seen that at room temperature, the storage modulus increased with increasing of NPG ratio. The modified samples showed stronger molecular interactions, such as hydrogen bonding, as indicated by the flatter intermediate plateau. The Tgly values of the modified samples were
lower than that of the parent A, (figure 7.11). These observations brought the conclusion that component mixing was favoured in the modified samples.

Figure 7.10: Storage modulus versus temperature for A, AN1 and AN2.

Figure 7.11: Tan δ-temperature plots for A, AN1 and AN2.
Nonetheless, increasing the NPG ratio led to more phase separation, indicated by the ΔTg values. In addition, the tan δ peak of the hard segment displayed a shoulder that is thought to correspond to stronger hydrogen bonding, as it moved toward the Tgh value of the parent A. The results also revealed that NPG was able to restrict PPG chain mobility, as indicated by the reduction of the tan δ max value in the lower temperature region, (table 7.8). Surprisingly the Tgs value was reduced with increasing NPG ratio. This cannot be explained, as the previous findings did not show any sign of a plasticizing effect by NPG.

Table 7.8: Dynamic properties for samples A, AN1 and AN2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max at Tg</th>
<th>Half-peak width of tan δ max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tgs*</td>
<td>Tgh*</td>
<td>ΔTg</td>
</tr>
<tr>
<td>A</td>
<td>-36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AN1</td>
<td>-40</td>
<td>67</td>
<td>107</td>
</tr>
<tr>
<td>AN2</td>
<td>-42</td>
<td>83</td>
<td>125</td>
</tr>
</tbody>
</table>

*SS = Soft segment. HS = Hard segment.

7.1.2.5 Modulated temperature differential scanning calorimetry

Figure 7.12 shows the derivative Cp-temperature plots for AN1, AN2 and the parent A. It can be seen that both modified samples have higher interphase mixing than the parent A, as indicated by the height of the intermediate plateau. The methyl groups of NPG are thought to restrict the PPG chain mobility, thus reducing the peak intensity in the lower temperature region.

With increasing the NPG ratio, the Tgh was shifted to the higher temperatures value, (table 7.9), which indicated more phase separation. The incorporation of NPG did not affect the Tg of the soft segment. This observation was contradicted by the DMTA data, which showed a reduction of Tgs value. Different sensitivities of the techniques might be the best explanation. Overall, the findings were in accord with the DMTA data.
Figure 7.12: \( \frac{dC_p}{dT} \) versus temperature for A, AN1 and AN2.

Table 7.9: Transition temperatures for AN1 and AN2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g ) (( \frac{dC_p}{dT} ) max) (( ^\circ C ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>SS*: -55, HS*: Broad</td>
</tr>
<tr>
<td>AN1</td>
<td>SS*: -55, 52</td>
</tr>
<tr>
<td>AN2</td>
<td>SS*: -55, 59</td>
</tr>
</tbody>
</table>

*SS = Soft segment, HS = Hard segment.

7.1.2.6 Atomic force microscopy

Figure 7.13 shows the phase images for A, AN1 and AN2. It can be seen that the modified samples showed more phase separation, corresponding to clear phase boundaries.
The hard segment (lighter shade) of A was distributed as discrete phases, while it existed as a continuous phase in the modified samples. The presence of NPG, which allowed more mixing between the segments, is thought to be key. The area covered by the lighter shade increased with increasing NPG ratio. AN2 showed clear phase boundaries with more spherical soft phase than AN1.

In conclusion, the NPG containing samples exhibited more mixing, resulting from hydrogen bonding between the hard-hard segments and the hard-soft segments. The appearance of a slight shoulder in the tan δ peak of the DMTA verified the formation of weaker hydrogen bonding between the ether groups of PPG and the -NH groups of urethane linkages. The presence of methyl side groups caused a restriction to the PPG chains, thus producing a more rigid material. The groups could also disturb the order of the hard segments, which reduced the degree of phase separation.

7.1.3 Incorporation of dibromoneopentyl glycol (dNPG) into the PU hard segments

The aim of incorporation of dibromoneopentyl glycol (dNPG) was to assist the TEM analysis of the hybrid samples from the A series, (see chapter 6). Some samples failed to
display good contrast between the polyacrylic and the PU. By incorporating brominated polyol into the PU hard segments, it was thought that this could impart better contrast due to the higher electron density provided by the bromine atoms.\textsuperscript{43} It was hoped to see clear contrast between the soft and the hard segments in the image, without the use of a staining agent such as ruthenium tetroxide. In addition, it was also interesting to investigate the effect of dNPG to the morphology and the properties of the sample.

Two hybrid samples, A2 (PU-PMMA/PBA) and A5 (PU-PS/PBA), at 1:1 PU:polyacrylic ratio were selected. Each sample contained 4 wt. % of dNPG. After the modification, A2 was designated as A2D, while A5 as A5D.

7.1.3.1 Particle sizing

Table 7.10 shows the particle sizes for the modified and unmodified samples. It can be seen that the particle sizes of the modified samples were smaller than the unmodified ones. It is not fully understood why the samples behaved in such a way. In fact the behaviour was similar with the NPG containing samples, which showed smaller particle sizes than their parents. Both cases showed that the addition of dNPG or NPG should increase the hydrophilicity of particles. However, the viscosity results showed unclear trends.

Table 7.10: Particle sizes for samples A, the modified and the unmodified samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
<th>Viscosity (mPa s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57 (± 0.3)</td>
<td>51</td>
</tr>
<tr>
<td>A2D</td>
<td>55 (± 0.1)</td>
<td>64</td>
</tr>
<tr>
<td>A5D</td>
<td>59 (± 0.1)</td>
<td>72</td>
</tr>
<tr>
<td>A2</td>
<td>114 (± 3.5)</td>
<td>52</td>
</tr>
<tr>
<td>A5</td>
<td>146 (± 2.8)</td>
<td>69</td>
</tr>
</tbody>
</table>

*Data provided by DSM-NeoResins, Holland.
Chapter 7  
The modification of the polyurethane hard segments

7.1.3.2 Stress-strain tests

Figure 7.14 shows the stress-strain curves for the modified samples. It can be seen that the samples lost their elastomeric character with the addition of dNPG.

![Stress-strain curves for samples A, A2D and for A5D.](image)

A5D showed a yield point, implying the starting point for a plastic deformation. Both modified samples exhibited higher modulus and tensile strength, but showed reduced elongations at break, compared to the unmodified samples, (table 7.11). The addition of dNPG did not give significant changes to the modulus at the lower strain. However, the tensile strength of the modified samples increased by about 53 % from the unmodified ones. In addition, the incorporation of dNPG enhanced the hardnesses of the samples.

Overall, the PMMA/PBA based modified samples possessed higher tensile strengths and hardnesses, but lower elongations at break. On the other hand, the PS/PBA based showed higher elongation at break, indicating more phase separation. The different levels of hydrophobicities possessed by the two polyacrylics, were though to be a key factor.
Table 7.11: Mechanical properties for A, the modified and the unmodified samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength at break (MPa)</th>
<th>Elongation at break (%)</th>
<th>Hardness (s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14 (± 0.01)</td>
<td>15 (± 0.6)</td>
<td>1180 (± 43)</td>
<td>41</td>
</tr>
<tr>
<td>A2D</td>
<td>0.46 (± 0.02)</td>
<td>25 (± 0.8)</td>
<td>410 (± 2.5)</td>
<td>110</td>
</tr>
<tr>
<td>A5D</td>
<td>0.53 (± 0.11)</td>
<td>23 (± 0.3)</td>
<td>520 (± 3.4)</td>
<td>107</td>
</tr>
<tr>
<td>A2</td>
<td>0.50 (± 0.01)</td>
<td>15 (± 0.3)</td>
<td>450 (± 12)</td>
<td>79</td>
</tr>
<tr>
<td>A5</td>
<td>0.40 (± 0.01)</td>
<td>15 (± 1.3)</td>
<td>620 (± 2.0)</td>
<td>60</td>
</tr>
</tbody>
</table>

* Measured with a Koenig instrument. Data provided by DSM-NeoResins, Holland.

7.1.3.3 Dynamic thermal mechanical analysis

Figure 7.14 shows the storage modulus versus temperature for samples A2D and A5D. It can be seen that A2D showed stronger molecular interactions i.e. hydrogen bonding than A5D with the plateau gradually tailing off.

![Figure 7.14: Storage modulus versus temperature for samples A, A2D and A5D.](image-url)
Both modified samples were dominated by the hard components and indicated more mixing than the pure PUD sample.

Figure 7.15 shows that A2D has more mixing in the higher temperature region, as indicated by the broadness of the tan δ peak and a greater half-peak width value, (table 7.12). Meanwhile, A5D showed a resolved peak, indicating more phase separation.

Finally, the results of the modified and the unmodified samples have been compared, (figures 7.16 a and b). The addition of dNPG had a great impact on the mobility of the soft segments as the height of tan δ max value was reduced to about 84% from the parent A, (table 7.12). In fact, the values were lower than the unmodified hybrids. The extent of mixing was higher in the modified samples due to the order in the hard segment was not only disturbed by the methyl side groups, but also by the bigger bromine substituents in dNPG. Interestingly, dNPG had little effect on Tg of both modified and unmodified PS/PBA based samples. On the other hand, the TgH value of the modified PMMA/PBA based hybrid was shifted 23°C
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higher than the unmodified sample, A2. Again, the hydrophilicity of PMMA relative to PS, is thought to be a key factor.

Figure 7.16: Tan δ versus temperature for a) PMMA/PBA based samples and b) PS/PBA based samples.

Table 7.12: Dynamic properties for A, the modified and the unmodified samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ at $\tan \delta$ max ($^\circ$C)</th>
<th>$\tan \delta$ max</th>
<th>Half-peak width of $\tan \delta$ max ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ sc*</td>
<td>$T_g$ h*</td>
<td>$\Delta T_g$</td>
</tr>
<tr>
<td>A</td>
<td>-36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A2D</td>
<td>-39</td>
<td>98</td>
<td>137</td>
</tr>
<tr>
<td>A5D</td>
<td>-35</td>
<td>76</td>
<td>111</td>
</tr>
<tr>
<td>A2</td>
<td>-39</td>
<td>75</td>
<td>114</td>
</tr>
<tr>
<td>A5</td>
<td>-38</td>
<td>76</td>
<td>114</td>
</tr>
</tbody>
</table>

$^*T_g$ sc = $T_g$ of the soft component of PUAs. $T_g$ h = $T_g$ of the hard component of PUAs.

7.1.3.4 Modulated temperature differential scanning calorimetry

Figure 7.17 shows the derivative Cp-temperature plots for samples A, A2D and A5D. It can be seen that A2D showed more mixing, as indicated by the height of the intermediate
plateau and a broader transition peak, particularly in the higher temperature region. In contrast, A5D showed more resolved peaks, indicating more phase separation.

Figure 7.17: $\frac{dC_p}{dT}$ versus temperature for samples A, A2D and A5D.

Figures 7.18 a) and b) show the comparison between the modified and the unmodified samples.

Figure 7.18: $\frac{dC_p}{dT}$ versus temperature for a) PMMA/PBA based hybrids and b) PS/PBA based hybrids.
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It can be seen that the PMMA/PBA based modified sample showed more phase separation, as the transition peak was shifted to a higher temperature value, (figure 7.18 a). A broadened transition peak in the higher temperature region indicated more hard component mixing. In contrast, the PS/PBA based had similar Tg values for both modified and unmodified samples, (table 7.13). Interestingly, the unmodified samples showed more mixing in the lower temperature region, while their counterparts displayed more mixing at the higher temperature region.

In conclusion, the PMMA/PBA based modified samples showed more mixing than the PS/PBA based. However, the addition of dNPG did not give a significant change in the Tg for both modified samples in the lower temperature region. All the results were in agreement with the DMTA data.

Table 7.13: Transition temperatures for A, the modified and the unmodified samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (dCp/dT max) (°C)</th>
<th>Tgsc*</th>
<th>Tgh*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-55</td>
<td>Broad</td>
<td></td>
</tr>
<tr>
<td>A2D</td>
<td>-52</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>A5D</td>
<td>-50</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>-52</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>-53</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

* Tgsc = Tg of the soft component of PUAs. Tgh = Tg of the hard component of PUAs.

7.1.3.5 Transmission electron microscopy

Figure 7.19 shows the TEM images for the modified sample A2D and the unmodified sample A2. Both samples were cryogenically microtomed prior to analysis. Unfortunately, an attempt to get clear images failed. According to Lubnin et al.43, the image needs to be recorded immediately upon radiation, as the high energy electron beam ablates the bromine-containing phase. Inevitably, the sample needed to be stained with RuO4 vapour prior to analysis.
Figure 7.19: TEM micrographs. a) – b) PMMA/PBA based samples, at 100k magnification. c) - d) PS/PBA based samples, at 100k and 120k magnifications, respectively.

Doubled-staining the sample made the analysis more difficult as the core-shell structure became unclear, as seen in the unmodified sample, A2 (figure 7.19 b). However, the area
covered by the lighter shade increased and was distributed as a semi-continuous phase in the matrix, implying more mixing. The same observations were displayed by the PS/PBA based samples. The phase boundaries became unclear in the modified sample, (figure 7.19 c). This can be explained as the bulky structure of dNPG disturbing the order of the PU hard segments, thus promoting more mixing.

To solve the problem, the embedding latex technique was employed, (refer to chapter 4). A few drops of sample latex was embedded on to the secondary single-phase latex that had latex particles bigger than the sample i.e. 150 to 200 nm. Later, the dried resultant film was embedded into an epoxy resin prior to being microtomed. However, the film needed to be stained with RuO₄ to prevent, or minimise, electron beam damage.

Figure 7.20 shows the micrograph of A2D that employed the above technique. It can be seen that the core-shell structure of the sample latex was clearly distributed within the secondary latex matrix.

Figure 7.20: TEM micrograph for A2D prepared by the embedded latex technique. The image was provided by DSM-NeoResins, Holland.
Drawbacks of this technique are as follows. Extra precautions must be taken as the electron beam could easily damage the sample. The selection of the secondary latex as a support matrix is very crucial, as factors such as particle size, solubility and side reactions with the sample particle could affect the result. Furthermore, the addition of dNPG had changed the morphology and the properties of the sample. One should consider all these factors before employing this technique.

7.2 Tg variation in the polyacrylic phase

The previous DMTA and MTDSC data, (see chapter 6), showed the overlapping transition peaks between PU and polyacrylic, particularly in the higher temperature region. It was thought to be because the Tgs of both components were nearly the same. In this section, Tg of PMMA/PBA was lowered to 20°C in order to minimise the interference from the polyacrylic component on the PU hard segment. It was expected to see two tan δ peaks in the DMTA data. The samples were synthesised via two methods, i.e. the single batch and the double batch. Solvent-free PUD was used as the seed. The results have been compared with the samples that had a polyacrylic Tg of 50°C, including samples A2 from chapter 6. Notably, sample A2 was synthesised via the single batch technique, but all the acrylic monomer was added after the dispersion stage. Sample descriptions are shown in table 7.14. The samples were designated as the C series with the PU:PMMA/PBA ratio fixed, at 1:1 for all samples.

Table 7.14: Sample descriptions for the C series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Solvent free PUD.</td>
</tr>
<tr>
<td>C1</td>
<td>Double batch technique. Tg of PMMA/PBA is 50°C.</td>
</tr>
<tr>
<td>C2</td>
<td>Single batch technique. Tg of PMMA/PBA is 20°C.</td>
</tr>
<tr>
<td>C3</td>
<td>Double batch technique. Tg of PMMA/PBA is 20°C.</td>
</tr>
<tr>
<td>A2</td>
<td>Single batch technique. Tg of PMMA/PBA is 50°C.</td>
</tr>
</tbody>
</table>
7.2.1 Particle sizing

Figure 7.21 shows the particle size distributions for samples A, A2, C1, C2 and E. C2 was selected to represent C3, as both samples have the same particle size and the same distribution. Sample C1 displayed a slightly broader distribution than C2, while A2 displayed the broadest distribution and the biggest particles, (table 7.15). It also can be seen that samples with Tg of 50°C had bigger particle size than samples with Tg of 20°C. It is not fully understood how Tg could affect the particle size. Notably, the acrylic monomer was added after the dispersion in A2. A study has found that the presence of monomer in the first stage disturbed the dispersion mechanism. These authors suggested that the monomer was able to adsorb some hydrophilic short chain PU as stabiliser and start a new batch of particle growth, thus producing a smaller particle size.

On the other hand, when all monomers were added after the dispersion, there were no hydrophilic groups available to stabilise them, as most of the groups were firmly anchored to PU particles after chain extension. Inevitably, the monomer tended to swell into PU particles, thus resulting in a larger particle size as shown by sample A2. It seems that Tg value and the
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synthesis technique played important roles in controlling the particle sizes. The viscosity may be considered the same for the C series, except that A2 showed nearly the same value as the pure PU.

Table 7.15: Particle sizes for A, the C series and A2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
<th>Viscosity (mPa s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57 (± 0.3)</td>
<td>51</td>
</tr>
<tr>
<td>C1</td>
<td>88 (± 1.1)</td>
<td>41</td>
</tr>
<tr>
<td>C2</td>
<td>66 (± 0.1)</td>
<td>39</td>
</tr>
<tr>
<td>C3</td>
<td>66 (± 0.2)</td>
<td>40</td>
</tr>
<tr>
<td>A2</td>
<td>144 (± 3.5)</td>
<td>52</td>
</tr>
</tbody>
</table>

*Data provided by DSM-NeoResins, Holland.

7.2.2 Stress-strain tests

Figure 7.22 shows the stress-strain curves for the C series and A2. It can be seen that the modulus at 5% strain did not show a significant change except in A2.

Figure 7.22: The stress-strain curves for the C series.
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The C series showed values nearly the same as pure PU. This indicated that no reinforcing effect of PMMA/PBA at lower strains. As expected, C2 and C3 exhibited lower tensile strengths as Tg of PMMA/PBA was reduced to 20°C, thus resulting in more flexible samples. On the other hand, C1 and A2 showed higher tensile strengths and hardnesses.

Comparison can be made between the single and the double batch samples, (table 7.16). Although C2 and A2 were single batch samples, by varying the mode of acrylic addition, the former showed lower tensile strength, but higher elongation at break, due to more phase separation. Meanwhile, A2 possessed greater hardness, but lower extensibility, corresponding to more mixing. All of these arguments concluded that Tg of polyacrylic and the synthesis method have major impacts on the mechanical properties of the sample.

Table 7.16: Mechanical properties for sample A and for the C series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Hardness (s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14 (± 0.01)</td>
<td>15 (± 0.6)</td>
<td>1180 (± 43)</td>
<td>41</td>
</tr>
<tr>
<td>C1</td>
<td>0.16 (± 0.01)</td>
<td>14 (± 0.03)</td>
<td>720 (± 3.0)</td>
<td>57</td>
</tr>
<tr>
<td>C2</td>
<td>0.14 (± 0.03)</td>
<td>11 (± 0.4)</td>
<td>830 (± 37)</td>
<td>37</td>
</tr>
<tr>
<td>C3</td>
<td>0.15 (± 0.02)</td>
<td>12 (± 0.6)</td>
<td>780 (± 6.0)</td>
<td>32</td>
</tr>
<tr>
<td>A2</td>
<td>0.50 (± 0.01)</td>
<td>15 (± 0.3)</td>
<td>450 (± 12)</td>
<td>79</td>
</tr>
</tbody>
</table>


7.2.3 Dynamic mechanical thermal analysis

Figure 7.23 shows the storage modulus for A, the C series and for A2. As expected, C2 and C3 showed the lower storage modulus values at room temperature due to Tg of polyacrylic being reduced to 20°C. On the other hand, C1 and A2, which were copolymerised with higher Tg 50°C acrylic monomer, showed more rigidity, as indicated by a flatter intermediate plateau. C2 and C3 showed more mixing than C1, as indicated by the broadness
of the tan $\delta$ peaks, (figure 7.24) and the $\Delta T_g$ values in table 7.17. As the sample became more flexible, the chance to form hydrogen bridges between the hard and the soft segments increased, thus promoting more mixing.

Figure 7.23: Storage modulus versus temperature for A, the C series and A2.

Figure 7.24: Tan $\delta$ versus temperature for A, the C series and for A2.
Comparison could also be made between the double and the single batch samples. It can be seen that the double batch samples produced broad tan δ peaks, (i.e. C1 and C3), while the single batch produced more resolved peaks, (i.e. C2 and A2). However, regardless to Tg of polyacrylic, the C series exhibited a subtle shoulder on the right of the tan δ peak, probably representing Tg of the polyacrylic as the values were closer to the Tg of PMMA/PBA, (i.e. 94°C). This could be explained as acrylic monomer from the first stage was able to adsorb some hydrophilic short chain PU as stabiliser and start as a new site for particle growth. This suggested the possibility to develop a PU-rich phase or a polyacrylic-rich phase, which led to a broader tan δ peak and the development of the shoulder.

Table 7.17: Dynamic properties of the A, the C series and A2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max value</th>
<th>Half-peak width tan δ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tgsc</td>
<td>Tgh</td>
<td>ΔTg</td>
</tr>
<tr>
<td>A</td>
<td>-36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C1</td>
<td>-36</td>
<td>71</td>
<td>105</td>
</tr>
<tr>
<td>C2</td>
<td>-35</td>
<td>53</td>
<td>88</td>
</tr>
<tr>
<td>C3</td>
<td>-36</td>
<td>53</td>
<td>88</td>
</tr>
<tr>
<td>A2</td>
<td>-39</td>
<td>75</td>
<td>114</td>
</tr>
</tbody>
</table>

*Tgsc = Tg of the soft component of PUAs. Tgh = Tg of the hard component of PUAs.

*SC = soft component. HC = hard component.

7.2.4 Modulated temperature differential scanning calorimetry

Figure 7.25 shows the transition profiles for A, the C series and for A2. It can be seen that C2 and C3 showed more mixing than C1, as indicated by the intermediate plateau and Tg value in the higher temperature region that have been shifted to lower temperature, (table 7.18). Interestingly, A2 showed nearly the same degree of mixing as C2 and C3. All of these arguments showed that the Tg of polyacrylic and the synthesis method have a significant impact on the mechanical properties.
Figure 7.25: $dC_p/dT$ versus temperature for A, the C series and for A2.

Table 7.18: Transition temperatures for A, the C series and for A2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ ($dC_p/dT$ max) ($^\circ$C)</th>
<th>$T_{g_{sc}}^*$</th>
<th>$T_{g_{H}}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-55</td>
<td>Broad</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>-53</td>
<td>65,79</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>-54</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>-53</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>-52</td>
<td>56</td>
<td></td>
</tr>
</tbody>
</table>

* $T_{g_{sc}} = T_g$ of the soft component of PUAs. $T_{g_{H}} = T_g$ of the hard component of PUAs.

To conclude, samples with a $T_g$ of $20^\circ$C exhibited lower tensile strength and stiffness than the samples with a $T_g$ of $50^\circ$C. The former favoured more mixing, as indicated by broad tan $\delta$ peaks and the $\Delta T_g$ values of the DMTA. Comparatively, the double batch sample produced broad tan $\delta$ peaks, while the single batch produced a resolved peak. Regardless to the $T_g$ of the polyacrylic, a subtle shoulder appeared on the right of the tan $\delta$ peak. The shoulder disappeared when the monomer was added after the dispersion stage. The presence of acrylic
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monomer prior to dispersion is capable of disturbing the dispersion mechanism. Finally, $T_{g,sc}$ has not been affected significantly either by the synthesis method or by the $T_g$ of the polyacrylic.

7.3 Variation of the acrylic monomer addition sequence

This section addresses the various addition modes of acrylic monomer that needed to be copolymerised with solvent free PUD, to form the hybrid. Polyacrylic type was limited to PS/PBA only and the PU:polyacrylic ratio was 1:1. The samples were designated as the D series. Table 7.19 shows the sample descriptions. The details can be further referred to in chapter 4.

Table 7.19: Sample descriptions with various addition modes of the acrylic monomer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis technique</th>
<th>Acrylic monomer sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>First stage - (pre-polymer mixing). 20 wt. % acrylic monomer was added.</td>
</tr>
<tr>
<td>A</td>
<td>Pre-polymer mixing</td>
<td>Solvent-free PUD</td>
</tr>
<tr>
<td>D1</td>
<td>DB*</td>
<td>A diluent.</td>
</tr>
<tr>
<td>D2</td>
<td>DB</td>
<td>A non-diluent.</td>
</tr>
<tr>
<td>D3</td>
<td>SB*</td>
<td>A non-diluent.</td>
</tr>
<tr>
<td>D4</td>
<td>SB</td>
<td>A diluent.</td>
</tr>
<tr>
<td>D5</td>
<td>SB</td>
<td>Only n-BA monomer as a diluent.</td>
</tr>
<tr>
<td>A5</td>
<td>SB</td>
<td>All acrylic monomer.</td>
</tr>
</tbody>
</table>

*DB = double batch. SB = single batch.

In the first stage, 20 wt. % acrylic monomer was added either as a diluent or after the prepolymer stage was completed, but prior to dispersion (non-diluent). If the monomer was polymerised after the dispersion stage, the sample was classified as the double batch. If otherwise, it was classified as the single batch. The remaining 30 wt. % was added at the second stage and polymerised, which made the overall total of 50 wt. % polyacrylic. The $T_g$
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of PS/PBA was set at 50°C. The results have been compared with the single batch sample A5 from chapter 6. Notably, in A5, all the acrylic monomer was added after the dispersion. The morphology-property relationships are of special interest, particularly with the DMTA and MTDSC data.

7.3.1 Particle sizing

Table 7.20 shows the particle sizes for A, the D series and for A5. It can be seen that the mode of addition did not give significant effects for the D series, as all samples showed nearly the same particle size. However, the monomer must be added prior to dispersion/chain extension or bigger particles, would otherwise form, (i.e. sample A5).

Table 7.20: Particle sizes for A, the D series and for A5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter (nm)</th>
<th>Viscosity (mPa s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57 (± 0.3)</td>
<td>51</td>
</tr>
<tr>
<td>D1</td>
<td>89 (± 0.3)</td>
<td>36</td>
</tr>
<tr>
<td>D2</td>
<td>89 (± 0.2)</td>
<td>36</td>
</tr>
<tr>
<td>D3</td>
<td>89 (± 0.8)</td>
<td>38</td>
</tr>
<tr>
<td>D4</td>
<td>88 (± 0.1)</td>
<td>39</td>
</tr>
<tr>
<td>D5</td>
<td>84 (± 0.7)</td>
<td>39</td>
</tr>
<tr>
<td>A5</td>
<td>146 (± 2.8)</td>
<td>69</td>
</tr>
</tbody>
</table>

*Data provided by DSM-NeoResins, Holland.

As mentioned earlier, the reason lies in the fact that the presence of monomer in the first stage, disturbed the dispersion mechanism, thus resulting in a larger particle size. To strengthen the argument, the particle size distribution of D1, (i.e. represented the D series) was plotted with A5 in figure 7.26. All samples showed unimodal distributions. When the acrylic monomer was added before dispersion, the distribution was narrowed, (i.e. sample D1). However, when the monomer was added after the dispersion stage, a broad distribution was displayed by A5. These results were consistent with the viscosity data. Bigger particles
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tend to reduce the viscosity due to lower number of dispersed particles.\textsuperscript{121} However, A5 was the most viscous, probably due to grafting reactions between the polyacrylic and PU, (see chapter 6).

Figure 7.26: Particle size distributions for samples A, A5, D1 and F.

7.3.2 Stress-strain tests

Figure 7.27 shows the stress-strain curves for samples A, the D series and for A5. It can be seen that D1 and D3 showed elastomeric behaviour, while D2, D4 and D5 behaved like rigid materials. D1 and D3 showed lower modulus and tensile strength, but higher elongations at break, indicating more phase separation between the soft and the hard components, (table 7.21). Even though both samples were synthesised via different techniques, they exhibited similar trends. The latter groups, i.e. D2, D4 and D5, showed a pronounced reinforcing effect of the polyacrylic, as emphasised by the higher modulus and tensile strength with moderate elongation at break. Interestingly, D1 and D2, (both were the second batch samples), displayed different behaviours. D1 showed more phase separation (higher elongation), while the latter showed more interphase mixing, (higher modulus and tensile strength). It is useful to compare the single batch groups with A5 that possessed higher strength, but poorer elongation. It is suggested that A5 favoured more mixing with the
grafting reactions between PU and polyacrylic, (see chapter 6) causing greater restriction to the sample flexibility. There were no straightforward explanations for the complex systems, like the D series. However, the samples showed some trends that could be outlined as follows. The single batch sample with acrylic monomer as a diluent showed more phase separation, while the non-diluent one favoured more mixing. In contrast, the double batch samples showed the opposite results.

![Stress-strain curves for samples A, the D series and A5.](image)

Figure 7.27: Stress-strain curves for samples A, the D series and A5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 5% strain (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.11 (± 0.03)</td>
<td>15 (± 0.6)</td>
<td>1180 (± 43)</td>
</tr>
<tr>
<td>D1</td>
<td>0.26 (± 0.03)</td>
<td>14 (± 0.6)</td>
<td>730 (± 23)</td>
</tr>
<tr>
<td>D2</td>
<td>0.36 (± 0.04)</td>
<td>19 (± 0.4)</td>
<td>640 (± 10)</td>
</tr>
<tr>
<td>D3</td>
<td>0.23 (± 0.01)</td>
<td>13 (± 0.4)</td>
<td>660 (± 4.5)</td>
</tr>
<tr>
<td>D4</td>
<td>0.34 (± 0.05)</td>
<td>20 (± 0.7)</td>
<td>650 (± 15)</td>
</tr>
<tr>
<td>D5</td>
<td>0.42 (± 0.05)</td>
<td>20 (± 0.2)</td>
<td>675 (± 22)</td>
</tr>
<tr>
<td>A5</td>
<td>0.40 (± 0.01)</td>
<td>15 (± 0.31)</td>
<td>620 (± 2.0)</td>
</tr>
</tbody>
</table>
7.3.3 Dynamic mechanical thermal analysis

Figure 7.28 shows the storage modulus for the D series. It was hard to see the difference when all samples were plotted on the same axis. However, it was obvious that sample A showed a well defined rubbery plateau, indicating more phase separation. On the other hand, the hybrids were dominated by the hard components, as indicated by big drops of the plateau height in the higher temperature region.

![Storage modulus for A, the D series and for A5.](image)

Figure 7.28: Storage modulus for A, the D series and for A5.

Figure 7.29 depicts the tan δ plots for all samples. It can be seen that the D series exhibited resolved peaks with a shoulder at the left. These shoulders were associated with the interphase that had weaker hydrogen bonding, corresponding to the shoulder peak temperature that was lower than the TgH value, (table 7.22). D4 and D5 showed the most resolved peaks and exhibited much greater phase separation, as indicated by the ΔTg value, (table 7.22). Notably, both single batch samples used acrylic diluents in their syntheses. Probably, longer contact time of the monomers with the PU short chain resulted in more
component mixing in the higher temperature region. In contrast, sample A5, in which the monomers were added after dispersion, showed a clean resolved peak without a shoulder.

![Graph](image)

**Figure 7.29: Tan δ versus temperature for A, the D series and for A5.**

**Table 7.22: Dynamic properties for A, the D series and for A5.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ max value</th>
<th>Half-peak width of tan δ max (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tg_sc*</td>
<td>Tg_H*</td>
<td>ΔTg</td>
</tr>
<tr>
<td>A</td>
<td>-36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D1</td>
<td>-37</td>
<td>84</td>
<td>121</td>
</tr>
<tr>
<td>D2</td>
<td>-40</td>
<td>81</td>
<td>121</td>
</tr>
<tr>
<td>D3</td>
<td>-35</td>
<td>85</td>
<td>120</td>
</tr>
<tr>
<td>D4</td>
<td>-42</td>
<td>81</td>
<td>123</td>
</tr>
<tr>
<td>D5</td>
<td>-38</td>
<td>85</td>
<td>123</td>
</tr>
<tr>
<td>A5</td>
<td>-38</td>
<td>76</td>
<td>114</td>
</tr>
</tbody>
</table>

*Tg_sc* = Tg of the soft component of PUs. Tg_H* = Tg of the hard component of PUs.

*SC = soft component. HC = hard component.
7.3.4 Modulated temperature differential scanning calorimetry

Figure 7.30 shows the transition profiles for the D series. It was hard to see the difference when all the samples were plotted on the same axis. Therefore, the samples were plotted according to their synthesis method as shown in figures 7.31 a) and b). The double batch sample, D1, showed more mixing than D2, as indicated by the height of the intermediate plateau, but with the same degree of phase separation, (table 7.23). The single batch sample, D3, showed more interphase mixing, while D5 showed the least.

Interestingly, the most mixed sample from the single batch was D3 and the least mixed sample from the second batch was D2, in which, both have in common their synthesis methods, i.e. acrylic monomer was added after the prepolymer stage was completed (a non-diluent). Even though both samples employed the same addition mode of the monomer, it was the synthesis technique that determined the final properties. It also showed that by using monomer as a diluent in the double batch technique, produced more interphase mixing, (as shown by D1). By plotting the least mixed samples from the results above against A5, it can be seen that the single batch sample showed more mixing, particularly in the higher temperature region, (figure 7.32). Sample A5 showed the lowest extent of mixing, as indicated by the intensity of the peak in the higher temperature region.

![Figure 7.30: dCp/dT versus temperature for A, the D series and for A5.](image-url)
The modification of the polyurethane hard segments

Figure 7.31: dCp/dT versus temperature for the D series that have been synthesised via a) double batch and b) single batch methods.

Figure 7.32: dCp/dT versus temperature for D2, D5 and for A5.
To conclude, the mode of addition and the synthesis technique did not give significant changes in $T_g$ or the degree of phase separation. However, they affected the degree of mixing in the interphase regions, particularly in the higher temperature region. It was suggested that the presence of acrylic monomers as either diluents or non-diluents, were able to disturb the dispersion mechanism. These suggestions were supported by the appearance of a shoulder in the DMTA tan $\delta$ profiles. However, no shoulder was observed when the all monomer was added after the dispersion step. It is recommended in future to lower the acrylic content to 5%, 10% or 15% in the first stage for the single batch technique, to ascertain the relationship between the shoulder and the acrylic monomer content.

Table 7.23: Transition temperatures for A, the D series and for A5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ ($dC_p/dT$ max) ($^\circ$C)</th>
<th>$T_{gsc}^*$</th>
<th>$T_{gH}^*$</th>
</tr>
</thead>
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<tr>
<td>A</td>
<td>-55</td>
<td>Broad</td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>-54</td>
<td>62</td>
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</tr>
<tr>
<td>D2</td>
<td>-59</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>D3</td>
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</tr>
<tr>
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<td>61</td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>-55</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>-53</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

$T_{gsc} = T_g$ of the soft component of PUAs. $T_{gH} = T_g$ of the hard component of PUAs.
CHAPTER 8

CONCLUSIONS AND FUTURE WORK
CHAPTER 8

GENERAL CONCLUSIONS AND FUTURE WORK

This chapter briefly presents the conclusions drawn from the results obtained in chapters 5, 6 and 7. A number of recommendations for future work is also suggested.

8.1 Pure polyurethane dispersions (PUDs)

Waterborne systems have not escaped from the pressure of environmental legislation to reduce the VOC that originated from a small quantity of common co-solvent, N-methyl-2-pyrrolidone (NMP). The solvent is important to PUDs as it acts as a processing and coalescing aid in film formation. However, by careful design and selection of materials, it is possible to produce solvent free PUDs, as shown in chapter 5. Two types of PUD i.e. solvent free and NMP containing PUDs were synthesised via the prepolymer mixing method. Results showed that NMP can have a major impact upon both the morphology and properties. It remains in the film and is capable of plasticizing the polymer chains and reducing the Tg to a lower temperature. In addition, as a polar solvent, NMP is capable of hydrogen bonding with both urethane groups and ether groups, thus promoting more mixing between the soft and the hard segments. As a consequence, the samples possess lower strength but higher elongation, which limit the sample applications to certain areas. By annealing the sample near to NMP boiling point, i.e. 200°C, the sample increases its strength, but retains its flexibility. On the other hand, the solvent-free sample is attractive as it exhibits excellent mechanical properties and could minimise, or totally cut out, the solvent cost.

8.2 Polyurethane–polyacrylic hybrid dispersions

The use of solvents such as NMP is proven to affect the sample properties. Another alternative is to replace the solvent by using acrylic monomer or co-monomer as diluents. In
this work, two types of acrylic co-monomers, MMA/n-BA and styrene/n-BA, were copolymerised with solvent free PUD. These monomer pairs are different in their levels of hydrophobicity. The acrylic weight ratio was varied at 30 wt. %, 50 wt. % and 70 wt. % and the Tg was set at 50°C. Later the NMP containing PUD was synthesised with both types of acrylic co-monomer, but only at a fixed 1:1 PU:polyacrylic ratio.

8.2.1 Solvent free and NMP containing hybrids

The solvent-free hybrids increased their strength, but reduced their extensibility with increasing polyacrylic ratio. This is due to polyacrylic phase, which is hard and brittle. However, Tg in the lower temperature region was not affected significantly with increasing polyacrylic ratio. The PMMA/PBA based hybrids favoured more mixing, while the PS/PBA based samples showed more phase separation. Higher grafting levels in the former samples was another factor that contributed to higher mixing. Higher hydrophilicity of the PMMA/PBA based sample is thought to be the main reason. In addition, the stress-strain tests revealed that the PMMA/PBA based samples behaved like semi-miscible systems, while their counterparts acted like reinforced systems.

The comparison had been made between the solvent free and the NMP containing hybrids. The addition of NMP has affected the hybrid sample properties. The solvent free samples were stiffer than the NMP containing samples, as the former showed more phase separation. Again, the ability of NMP to plasticize the polymer chain is thought to be the key factor.

8.3 Latex blends versus hybrids

This work was conducted to study the difference between the latex blends and the hybrids properties. In the latex blends, two types of PUD i.e. solvent free and NMP containing PUDs were blended with two types of polyacrylic latexes i.e. PMMA/PBA and PS/PB at the equivalent ratio as employed in the hybrids. Notably, the hybrid was prepared via seeded emulsion polymerisation.
8.3.1 Solvent free latex blends

Both blended samples increased their modulus and tensile strength, but these dropped when the polyacrylic ratio exceeded 50 wt. %%. Higher polyacrylic contents caused the formation of incoherent films that had weaker interfaces between the PU and the polyacrylic phases. In comparison, the PMMA/PBA blended samples showed more mixing than the PS/PBA based samples. Then, higher hydrophilicity of PMMA/PBA is thought to be the main reason. The stress-strain results showed that the dominant phase determined the final properties. The hybrids showed more mixing than the blends due to molecular interactions such as hydrogen bonding. However, the blends could match the strength of the hybrids up to a ratio limit of 50 wt. % polyacrylic.

8.3.2 NMP containing latex blends

The same behaviour can be seen in the NMP containing latex blend samples. The PMMA/PBA blended samples showed more mixing than the PS/PBA based samples. The polyacrylic ratio has to be limited up to 50 wt. % to give the results comparable to the hybrids. By comparing the solvent free and the NMP containing blended samples, the latter showed more mixing due to the plasticizing effect of NMP. The addition of NMP has been found to affect the properties of both the hybrid and the blend samples.

8.4 Hybridisation via the double batch method

In this work, the hybrid was synthesised by copolymerising the solvent free PUD with a polyacrylic via the double batch method, at a fixed 1:1 ratio. The results were compared with the hybrids from the single batch method at the equivalent polyacrylic ratios. The double batch technique allowed the formation of smaller particle size and higher grafting level, particularly in the PMMA/PBA based sample. The lower hydrophobicity of PMMA, relative to PS, is thought to be the main reason. Both double batch samples were more flexible than the single batch ones. Regardless of the synthesis method, all samples showed
nearly the same tensile strength values and could match their pure PUD parent. It is suggested that the failure occurs in the PU phase rather than polyacrylic phase or the interphase. The tan δ peak traces and the derivative Cp profiles, showed broad transition peaks in the higher temperature region for the double batch samples, especially for the PMMA/PBA based samples. The sample also showed a higher extent of mixing as indicated by the tan δ half-peak width value. Tg in the lower temperature region had not been affected significantly by the synthesis mode. However, the double batch samples showed more phase separation as Tg in the higher temperature region was shifted to higher values. These arguments were supported by TEM micrographs that showed more phase separation. The mode of synthesis and the type of polyacrylic do have a major impact on the sample morphology and properties.

8.5 Modification of the PU hard segments

The modification of PU hard segments is based on the results of the DMTA and MTDSC from chapters 5 and 6. Previous results showed that the PU hard segments displayed a broad transition peak and the segments were well-separated from the soft segments. The PU hard segments was modified with neopentyl glycol (NPG), dibromoNPG (dNPG) and ethylene diamine (EDA).

8.5.1 EDA as the chain extension agent

The incorporation of EDA as the chain extension agent gave a moderate influence on the sample properties. Both EDA and hydrazine are capable of forming urea linkages in the hard segments. However, the higher polarity of the urea linkages of hydrazine based sample, relative to EDA, caused higher cohesion of the hard segments. In return, the hydrazine based sample exhibited more phase separation than the latter. The two methylene groups in the EDA molecular structure is responsible by reducing the polarity of the urea linkages, thus promoting more mixing. The tan δ peak and the derivative Cp profiles supported these
arguments. The reduction in polarity had affected the sample properties. The EDA based sample produced bigger particles and was stiffer than the hydrazine based sample.

8.5.2 Incorporation of NPG and dNPG

The incorporation of the NPG short diol into the PU hard segments promoted more mixing, resulting from hydrogen bonding between the hard-hard segments and the hard-soft segments. The appearance of a small shoulder in the tan δ peak of the DMTA verified the formation of weaker hydrogen bonding between the ether groups of PPG and the –NH groups of the urethane linkages. The presence of methyl side groups caused restriction to the PPG chains, thus producing a more rigid sample. In addition, the groups were capable of disturbing the order of the hard segment, which reduced the degree of phase separation. Apart from that, the addition of NPG caused smaller particles and the samples lost about half of their extensibility.

By incorporating brominated polyol, dNPG, into the PU hard segments of the hybrid, better contrast between the core-shell was observed in the TEM micrographs. The PU shell appeared as dark in the images due to the higher electron density provided by the bromine atoms. Tedium preparation work is a drawback of this technique. The brominated samples needed to be embedded into a secondary single phase latex that has bigger latex particles, prior to microtoming. In addition, the film needed to be stained with RuO₄ to prevent, or minimise electron beam damage on the bromine containing phase. The selection of a secondary latex as the support matrix is very important to avoid any side reaction with the sample. It also has been proved that the addition of dNPG affected the morphology and properties, as shown by an enormous increase in strength and a reduction in extensibility. One should consider all aspects before employing this technique.

In comparison, the image of the brominated samples that have been straight cryogenically microtomed, (without be embedded in the secondary latex), failed to show a true core-shell structure. However, some morphology changes were observed from the images. The phase boundaries became unclear with dNPG incorporation due to the bulky structure of dNPG,
which disturbed the order of the PU hard segments, thus promoting more mixing. The observations were supported by the tan δ traces and the derivative Cp profiles.

8.5.3 Variation of the Tg of polyacrylic in the PU-PMMA/PBA double batch hybrid sample

Previous studies showed that the tan δ peak of DMTA displayed broad overlapping tan δ peaks, corresponding to the Tg of PU and the polyacrylic, in the higher temperature region. The reason was thought due to the Tg of polyacrylic (50°C) being closer to the Tg of PU hard segments. In this study, a new Tg value was set at 20°C to reduce the interference from polyacrylic component on to the PU hard segment signal. The hybrid was synthesised via the single and the double batch techniques. The results were compared with the samples that have Tg of 50°C.

The stress strain tests revealed that the modulus had not been affected significantly by either the synthesis modes or the Tg of polyacrylic. In fact, all the hybrids showed values that were nearly the same as the pure PU. This indicated that there was no reinforcing effect of PMMA/PBA at low strains. However, samples with Tg of 20°C exhibited lower tensile strength and hardness than the sample with Tg of 50°C. By lowering the Tg, the sample become softer and more flexible, thus increasing the chance to form hydrogen bridges between the hard and the soft segments. Consequently, the samples showed more mixing, as indicated by the broad tan δ peaks and the ΔTg values from DMTA.

Comparatively, the double batch sample produced a broad tan δ peak, while the single batch produced a resolved peak. Notably, both techniques used the acrylic monomers as diluent. Regardless of the Tg of the polyacrylic, a subtle shoulder appeared on the right of the tan δ peak. The shoulder disappeared when the monomer was loaded after the dispersion stage. The presence of acrylic monomer prior to dispersion is thought to disturb the dispersion mechanism.
8.5.4 Variation of addition mode of the styrene/n-BA co-monomer

Results from previous studies have revealed that different synthesis techniques, (single batch versus double batch), affected the sample properties. In this work, it was found that by using different routes to introduce styrene/n-BA co-monomers into the PU dispersion and varying the synthesis technique, did not have significant effects on Tg and the degree of phase separation. However, they affected the degree of mixing in the interphase, particularly in the higher temperature region. The single phase samples with diluents showed more phase separation, while the double batch one showed more mixing. These arguments were supported by the derivative Cp results from MTDSC. Regardless of the addition mode, all samples showed a shoulder on the left side of tan δ peak. These shoulder were associated with the interphase that had weaker hydrogen bonding. However, no shoulder was observed when all the monomer was added after the dispersion stage. The presence of acrylic monomer prior to dispersion undeniably, disturbed the dispersion mechanism.

8.6 General conclusions

The studies here have highlighted the effect of NMP as co-solvent on PUDs and PUAs. The type, the composition, Tg and the addition mode of acrylic monomer, as well as the synthesis technique all significantly affect the morphologies and properties of the hybrids. The advantage of the hybrids has been highlighted with respect to latex blend systems. The polarity of the chain extender and the structure of short diols have major impact on the morphology of the PU hard segments. A summary of all samples and some results, (i.e. particle sizes, stress-strain tests and Tg from the DMTA and MTDSC), can be referred to in Appendix A3.

8.7 Future work

Extensive work have been carried out to achieve the objectives of this research. Every topic was carefully designed to give optimum information. Nonetheless, some parts of this
work can be improved to get a better understanding, or more accurate results by the following suggestions.

1. Literature proved that crosslinking or grafting reactions between the PU and the polyacrylic can improve the mechanical properties. In this study, the effect is less significant as it was overshadowed by the primary molecular interactions such as hydrogen bonding. To study this effect, in detail, a hydroxylacrylate material such as hydroxyethylacrylate$^{65,110}$ can be used to bring the reactive acrylic function to the PU chain, thus allowing crosslinking or grafting reactions with the polyacrylic.

2. The appearance of a shoulder on the tan δ peak of DMTA was related to the disturbance of dispersion mechanism due to the presence of acrylic monomer prior to dispersion. The separation between the shoulder and the tan δ peak affected the properties. To date, little information or evidence is available regarding this field. It is recommended to undertake a systematic approach to give a better understanding of this complex relationship.

3. The dCp/dT-temperature profile can be used to estimate the weight fraction of the individual components in the interphase by using a multiple Gaussian function peak resolution analysis.$^{77,107,164}$ It would be interesting to compare the amount of PU-rich phase or polyacrylic-rich phase quantitatively between the hybrids and the blends to get a better understanding of the morphology-property relationships of both samples.
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APPENDICES
### APPENDIX A1

1.1 Standard characterisation for latex dispersions (data provided by DSM-NeoResins).

1.1.1 PU dispersions.

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<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Solids (wt.%)</th>
<th>Viscosity (mPa s)</th>
<th>Absorbance* (%)</th>
<th>MFFT (°C)</th>
<th>Hardness** (s)</th>
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</table>

1.1.2 PU-polyacrylic dispersions.

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<th>Sample</th>
<th>pH</th>
<th>Solids (wt.%)</th>
<th>Viscosity (mPa s)</th>
<th>Absorbance* (%)</th>
<th>MFFT (°C)</th>
<th>Hardness** (s)</th>
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<td>41.7</td>
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* A qualitative measurement of particle size.
** Film hardness was measured by a Koenig instrument and expressed in Koenig's.
1.3 Determination of NCO content with di-n-butylamine (DBA) back-titration.

This method is used to determine the NCO content (%) in a diisocyanate intermediate or the free NCO available in a prepolymer (ASTM 1638). Standard DBA solution is prepared by dissolving the reagent in toluene. Later, the solution is reacted with diisocyanate as shown in scheme 1.

\[
\text{RNCO} + (\text{C}_4\text{H}_9)_2\text{NH} \rightarrow \text{RNHCON(C}_4\text{H}_9)_2
\]

Scheme 1

The reaction is rapid to form a clear solution. Three drops of a 1% alcoholic of bromophenol blue and methanol are added. An excess of amine is titrated with 1.0 N hydrochloric acid. The end point is reached with the disappearance of blue colour to yellow that persists for at least 15 seconds. By carrying out a blank titration, the NCO content can be calculated using the equation below.

\[
\% \text{NCO} = 42 \times M \times \frac{V_2 - V_1}{1000W} \times 100
\]

where,
- \(W\) = weight of sample (g) of the diisocyanate or prepolymer.
- \(V_1\) = volume (ml) of HCl solution required for titration of the sample.
- \(V_2\) = volume (ml) of HCl solution required for titration of the blank sample.
- \(M\) = molarity of HCl (1.0 N).
- 42 = relative molecular mass of the isocyanate group.

1.4 Fox's equation.

The Fox equation describes the Tg of a miscible blend of two polymers or copolymer or a plasticized polymer.

\[
\frac{1}{T_g \text{copolymer}} = \frac{W_a}{T_{g_a}} + \frac{W_b}{T_{g_b}}
\]

where \(W_a\) and \(W_b\) are the weight fraction of polymer A and polymer B while \(T_{g_a}\) and \(T_{g_b}\) are their glass transition temperatures, respectively.
Appendices

Systems which obey the Fox equation are considered to display intimate and uniform mixing, while those that display two Tgs are considered to be poorly mixed. When the blended polymers are completely miscible, the glass transition of the resulting system is situated between the Tgs of the parent materials in proportion to the amount of each phase present in the blend.

Example 1.1: To calculate Tg of MMA/n-BA/MAA with Fox equation.

A monomer ratio of each is as follows.
MMA = 75 %, Tg = 105°C (378 K)
n-BA = 25 %, Tg = -48°C (225 K)

If the amount of total monomers is 100g;

\[
\frac{1}{T_{g_{copol}}} = \frac{0.75}{378} + \frac{0.25}{225}
\]

\[
T_{g_{copol}} = 323 \text{ K} = 50^\circ \text{C}.
\]

1.5 Basic recipe calculation for solvent-free PUDs

1.5.1 NCO/OH ratio

This is the ratio of the equivalent-number of NCO groups of the diisoyanates to the equivalent-number of OH groups of the hydroxylated compounds. The equivalent weight of the isocyanate groups is 42. The ratio is always bigger than one to produce the -NCO terminated prepolymer. By increasing the NCO/OH ratio, would increase the stress-strain properties due to an increase in the degree of interchain hydrogen bonding, which led to the formation of more rigid films. By decreasing the ratio, the tensile strength decreased due to lower number of the hard segments being available. In this work, the NCO/OH ratio was set at 2.
1.5.2 Hydroxyl number of PPG

The number is defined as the amount of KOH (mg) which is equivalent to the amount of hydroxyl groups in one gram of sample.\(^{128}\) The OH value was provided by the supplier i.e. 55.5 mg KOH/g.

1.5.3 Prepolymer composition

The prepolymer has the following solid components i.e. IPDI, PPG and DMPA (5 wt. %)

Example 1.2

Let say IPDI has y wt. % and PPG has z wt. %.

Take the basis as 100g.

\[ y = 95 - z \]

From the set NCO/OH ratio, the wt. % of IPDI and PPG can be calculated.

\[
\frac{\text{NCO}}{\text{OH}} = 2 = \frac{\frac{y}{\text{Mass}_{\text{IPDI}}} \times f_{\text{IPDI}}}{\frac{5}{\text{Mass}_{\text{DMPA}}} \times f_{\text{DMPA}} + \frac{z}{\text{Mass}_{\text{PPG}}} \times \frac{\text{OH-value}}{\text{Mass}_{\text{PPG}}}}
\]

where

\[ y = 95 - z \]

\[
\begin{align*}
\text{Mass}_{\text{IPDI}} &= 222 \text{ g/mol}, & \text{functionality } (f) &= 2 \\
\text{Mass}_{\text{DMPA}} &= 134.1 \text{ g/mol}, & f &= 2 \\
\text{Mass}_{\text{PPG}} &= 56100 \text{ g/mol}, & \text{OH-value} &= 55.5 \text{ mg KOH}
\end{align*}
\]

Insert all the values in equation 1.

\[ \therefore \text{IPDI} = 30.68 \text{ wt. %, PPG} = 64.32 \text{ wt. % and DMPA} = 5 \text{ wt. %}. \]

Total solids in prepolymer is 100 wt.%.

Total required solids in prepolymer is 650 g.
Let say, the percentage of catalyst required in the recipe is 0.02 wt. %

\[ \text{Weight of catalyst in 650g prepolymer} = 0.0002 \times 650 = 0.13 \text{g}. \]

The remaining solid contents in the prepolymer is 650 g - 0.13 g = 649.87 g

To calculate the weight of each component in the prepolymer:

- wt. of IPDI in prepolymer = \( 0.3068 \times 649.87 = 199.37 \approx 199 \text{g}. \)
- wt. of PPG in prepolymer = \( 0.6432 \times 649.87 = 417.9 \approx 418 \text{g}. \)
- wt. of DMPA in prepolymer = \( 0.05 \times 649.87 = 32.49 \approx 32.50 \text{g}. \)
- Total solids in prepolymer = 649.63 \approx 650 \text{g}

### 1.5.6 Calculation of TEA content.

The weight of prepolymer in the reactor vessel is 650 g.

\[ \text{wt. \% of DMPA} = 5 \% = 0.05 \]
\[ \text{wt. of DMPA} = 650 \times 0.05 \times 1 \text{ (100 \% solid content in prepolymer)} = 32.5 \text{ g} \]
\[ \text{Moles of DMPA} = \frac{32.5}{Mass_{\text{DMPA}}} = \frac{32.5}{134.12} = 0.242 \text{ moles} \]

1 mol of DMPA reacts with 1 mol of TEA (for 100 \% neutralization)

\[ :. 0.242 \text{ moles DMPA} \times \text{mass}_{\text{TEA}} \]
\[ 0.242 \times 101.2 = 24.5 \text{ g TEA}. \]

Note:

For the NMP-containing PUD or double batch PUA that used a 20 wt. \% NMP or acrylic monomer, the weight of DMPA = 650 \times 0.05 \times 0.8 (80 \% solid content in the prepolymer).

\[ = 26 \text{ g}. \]
1.5.7 Calculation of hydrazine (HYD) content

The weight of prepolymer required to be dispersed is 650g. The percentage of NCO in the prepolymer can be calculated from DBA back-titration method i.e. 5.54 % NCO.

\[ \text{Weight of NCO terminated prepolymer} = 650g \times 0.0554 = 36.01g \]

Change into mol

\[ \frac{36.01g}{42g/mol} = 0.857 \approx 0.86 \text{ mol NCO} \]

1 mol NCO reacts with 0.85 mol HYD (85 % chain extension)

\[ 0.86 \times 0.85 = 0.73 \text{ mol HYD.} \]

Change into weight (g).

\[ 0.73 \text{ mol HYD} \times \frac{32 g/mol}{2 \text{ (functionality of HYD)}} = 11.7g \text{ HYD.} \]

Concentration of HYD in solution is 15.2 % (provided by supplier)

100g of solution has 15.2 g HYD

\[ \frac{11.7g \text{ HYD} \times 100g \text{ solution}}{15.2g \text{ HYD}} = 76.9 \approx 77g \text{ HYD in solution.} \] (A)

1.5.8 Calculation of the amount of water required for 35 wt. % solids content.

Total solids in dispersion = 650g (prepolymer) + 11.7g (hydrazine)

\[ = 661.7 \approx 662g. \]

The required solid content = 35 wt %.

\[ \frac{662}{0.35} = 1891g \text{ dispersions} \] (B)

The amount of water required for 35 wt % solids content = (B)-(A)-650g = 1164g water.
1.6 Basic recipe calculation of PU-polyacrylic hybrid dispersions (sample A2).

Example 1.3: Required 50:50 wt.% PU:polyacrylic with both polymers have 35 wt. % solids content

Weight of dispersions is 1500g.
The total of solids in 1500g PUA dispersions = 1500g x 0.35 = 525 g solids.

For 50:50 wt % PU:polyacrylic ratio, the calculations will be:
PUD = 525 x 0.5 = 261.52 g.
Acrylic = 525 x 0.5 = 261.52 g.

Note: for other ratio such as 70:30 wt. % PU:polyacrylic, the calculations will be:
PU = 525 x 0.7 = 367.5 g.
Acrylic = 525 x 0.3 = 157.5 g.

Therefore, the weight of PU in dispersion (for 50:50 wt % ratio)
PU = 261.52/(35 wt. % solids) = 261.52/0.35 = 747.2 g.
Acrylic = 261.52 g/(100 % solids) = 261.52 g. (I)

1.6.1 Calculation the amount of t-BHPO, FeEDTA and iso-ascorbic acid.

To calculate the weight of each material required to anticipate with acrylic reaction:
Weight of acrylic monomer x the percentage required from each material.

Therefore, the weight of t-BHPO = weight of acrylic x 3.158 wt % (used by DSM-NeoResins)
= 261.52 x 0.03158 = 8.258 g ≈ 8.26 g t-BHPO. (II)

However, the t-BHPO solution has 10 wt. % solids (provided by manufacturer).
∴ 8.26 g x 10 % = 0.826 g solids in t-BHPO in solution.

Weight of FeEDTA = 261.52 x 0.44 % = 1.15 g FeEDTA. (III)

However, the FeEDTA solution has 1 wt. % solids.
∴ 1.15 g x 1 % = 0.0115 g solids FeEDTA in solution.
Weight of iso-ascorbic acid = 261.32 x 43.5 % = 113.76 ≈ 113.8 g iso-ascorbic acid. (IV)

However, iso-ascorbic acid solution has 1 wt. % solids.

∴ 113.8 x 1 % = 1.138 g solids in solution.

The amount of water required for 35 wt. % solids = 1500g - ((I) + (II) + (III) + (IV))

= 368.07 ≈ 368 g water.

Example 1.5: The weight of both polymers can also be determined by fixing the weight of PUD.

Required 70:30 wt % PU:polyacrylic.

Take the basis of PUD weight of 700g.

PU = weight of PUD x solid content (%)
    = 700g x (0.35)
    = 245g

Therefore, the amount of acrylic required is 245g x \( \frac{30\%}{70\%} \) = 105 g.

Total weight (g) = 245 (PUD) + 105 (polyacrylic)
    = 450g.

PUD 245g / 350g = 0.7  = 70 wt. %.
Acrylic 105g / 350g = 0.3  = 30 wt. %.

The rest of calculations to determine the wt. % of catalyst, initiator etc. are the same as in example 1.4.
APPENDIX A2

2.1 Calculation for NMP content.

The percentage of the evaporated NMP obtained from the TGA technique is shown in figure 2.1.

![Graph showing weight loss of NMP at 200°C.](image)

Figure 2.1: Weight loss of NMP at 200°C.

Example 2.1

The calculation to find the amount of NMP evaporated for B treated at 80°C for 16 hours.

From the graph (figure 2.1), the weight loss obtained at 200°C is 97.8%. Therefore, the amount of the NMP evaporated is 2.2%.

To convert the units from percentage into the mass

\[
2.2 \% \times \text{sample weight (mg)}
\]

\[
= \frac{2.2}{100} \times 22.157 \text{mg}
\]

= 0.487 mg \approx 0.49 \text{ mg.}

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2.2 Solubility parameters.

The solubility parameter, $\delta$, was calculated using group contribution theory. The sum of various molar attraction constants of the particular polymer, $G$, is divided by the molar volume of the component, $V$, as shown in equation 1. The molar attraction constants are obtainable from Small and Hoy's tables. Table 2.1 shows the detail calculations.

$$\delta = \left( \frac{\Sigma G}{V} \right) = \left( \Sigma \frac{G}{M_{o}} \right) \rho$$

Equation 1

where,
- $\delta$ = Solubility parameter (J/cm$^3$)$^{1/2}$
- $G$ = Molar attraction constant (J/cm$^3$)$^{1/2}$/mol$^{-1}$
- $\rho$ = Polymer density (g/cm$^3$)
- $M_{o}$ = Molar mass

Table 2.1: The calculation of the solubility parameter.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Group</th>
<th>n</th>
<th>Molar attraction constant* $G$ [J cm$^{-3}$/mol$^1$]</th>
<th>$\Sigma G$</th>
<th>$\Sigma G$</th>
<th>$\delta$ (J/cm$^3$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Small</td>
<td>Hoy</td>
<td>Small</td>
</tr>
<tr>
<td>PMMA</td>
<td>-CH$_2$</td>
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<td>272</td>
<td>272</td>
<td>269</td>
<td>1592</td>
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<tr>
<td></td>
<td>-CH$_3$</td>
<td>2</td>
<td>438</td>
<td>876</td>
<td>606.8</td>
<td>1609.5</td>
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<tr>
<td></td>
<td>-COO-</td>
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<td>634</td>
<td>634</td>
<td>668.2</td>
<td>100.12</td>
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<tr>
<td></td>
<td>&gt;C&lt;</td>
<td>1</td>
<td>-190</td>
<td>-190</td>
<td>65.5</td>
<td>1.19</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>1609.5</td>
<td>18.92</td>
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<td>-CH$_2$</td>
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<td>272</td>
<td>269</td>
<td>272</td>
<td>2217</td>
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<tr>
<td></td>
<td>-CH$_3$</td>
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<td>1076</td>
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<tr>
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<td>57</td>
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<td>15.50</td>
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<td>PS</td>
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<td>272</td>
<td>269</td>
<td>272</td>
<td>1833</td>
</tr>
<tr>
<td></td>
<td>&gt;CH-</td>
<td>1</td>
<td>57</td>
<td>57</td>
<td>176</td>
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<tr>
<td></td>
<td>Phenyl</td>
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<td>104.1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1833</td>
<td>1843.4</td>
<td>18.49</td>
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</table>

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The A series consists of PU and PMMA/PBA. To estimate the miscibility between the two polymers, the solubility parameter of each will be compared. The closer the solubility parameters of the two components are, the greater the miscibility. The calculations shown below are based on the Hoy values. Firstly, to calculate the solubility parameter of PMMA/PBA copolymer, one must know the weight fraction of each monomer (φ) used in the formulation as shown in table 2.2.

By using equation 1,

\[
\delta_{\text{PMMA/PBA/PMMA}} = 0.714(19.13) + 0.266(15.55) + 0.02(20.93)
\]

\[
= 18.21 \text{ (J/cm}^3)\text{)}^{1/2}
\]
\[ \delta_{\text{PS/PBA/MAA}} = 0.729(18.6) + 0.251(15.55) + 0.02(20.93) \]
\[ = 17.87 \text{ (J/cm}^3\text{)}^{1/2} \]

\[ \delta_{\text{PU}} = 0.307(19.5) + 0.641(19.21) + 0.052(14.89) \]
\[ = 19.07 \text{ (J/cm}^3\text{)}^{1/2} \]

Comparatively, \( \delta_{\text{PU}} \) is closer to \( \delta_{\text{PMMA/PBA}} \) rather than \( \delta_{\text{PS/PSA/PBA}} \). It is predicted that the PU-PMMA/PBA hybrid will exhibit more component mixing than PU-PS/PBA.

Table 2.2: Monomer weight fraction.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer weight fraction, ( \phi ) (%)</th>
<th>MMA</th>
<th>n-BA</th>
<th>MAA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA/PBA copolymer</td>
<td></td>
<td>71.4</td>
<td>26.6</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>72.9</td>
<td>25.1</td>
<td>2</td>
</tr>
<tr>
<td>IPDI PPG DMPA</td>
<td></td>
<td>30.7</td>
<td>64.1</td>
<td>5.2</td>
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</table>