Damping characteristics of unfilled- and filled-polyurethane/poly(ethyl methacrylate) simultaneous interpenetrating polymer networks

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DAMPING CHARACTERISTICS OF UNFILLED AND FILLED -
POLYURETHANE / POLY(ETHYL METHACRYLATE)
SIMULTANEOUS INTERPENETRATING
POLYMER NETWORKS

by

Thanida Pabunruang,

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

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Institute of Polymer Technology and Materials Engineering
August 2000

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ABSTRACT

A series of polyurethane (PUR) / poly (ethyl methacrylate) (PEMA) simultaneous interpenetrating polymer networks (IPNs) with different PUR/PEMA composition ratios was prepared and characterised. For each IPN, the glass transition behaviour was determined by dynamic mechanical thermal analysis (DMTA) and modulated-temperature differential scanning calorimetry (M-TDSC), whereas the morphology was examined by transmission (TEM) and scanning electron microscopy (SEM). Finally, the mechanical and thermal properties were investigated using tensile testing and thermogravimetric analysis (TGA).

Firstly, a semi-miscible IPN with a very broad tan δ versus temperature curve was required, since the IPN will be the most effective acoustic and vibration absorbing material. Characterisation of different PUR/PEMA IPN compositions revealed an individual character for each IPN. The potential as a material for damping applications was exhibited by the 70PUR/30PEMA IPN which had a broad loss factor ≥ 0.3 spanning a temperature range of 132°C. TEM micrographs of this IPN revealed a multiphase morphology where the mixing between the two polymers was extensive. From the tensile tests, as might be expected, the tensile strength at break and modulus of elasticity at ambient temperature increased with increasing PEMA ratio. At high PUR contents, the elongation to failure exhibited a similar trend. However, the value reached a maximum at the 70/30 composition. Further increase in the PEMA content resulted in a deterioration of the properties.

Secondly, a number of fillers of varying geometries were incorporated into the 70PUR/30PEMA IPN. The fillers were silica, talc, calcium carbonate and mica. Filler dispersion was investigated by TEM and SEM. The effects of fillers and filler content were studied in terms of glass transition temperature, dynamic mechanical analysis, thermal analysis and also mechanical properties. Although not every filler affected the glass transition temperature, they changed the dynamic mechanical properties. Silica and talc enhanced the damping ability of the IPN, whereas a moderate increase in the maximum loss factor was observed from calcium carbonate. Improved tensile strength was only shown by the IPN filled with very fine silica particles.
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CHAPTER 1

INTRODUCTION AND OBJECTIVES
CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 Introduction

A large number of polymers are now commercially available with a wide range of mechanical, thermal, and other properties\(^{(1)}\). Their applications have been spreading in numerous fields varying from small household items to specialty uses for the medical field, electronic devices, and other purposes. In spite of this, the development of novel polymers is needed and is now of great interest to scientists. In the past few decades, multicomponent polymer materials have been introduced and extensively studied ranging from glass reinforced thermosets, rubber toughened plastics to polymer blends\(^{(1-3)}\). Polymer blends, blocks, and grafts, of existing polymers, and/or combining them with suitable fillers provide further options for investigation and application.

A more recent type of multicomponent polymer is widely known as interpenetrating polymer networks (IPN). This is a unique type of polymer blend, defined as a combination of two or more polymer networks, at least one of which is synthesised and/or crosslinked in the immediate presence of the other\(^{(4,5)}\). IPNs possess several interesting characteristics in comparison to normal blends. Formation of IPNs is the only way of intimately combining crosslinked polymers, the resulting mixture exhibiting (at worst) only limited phase separation\(^{(4)}\). Normal blending or mixing of polymers results in a multiphase morphology due to the well known\(^{(6)}\) thermodynamic incompatibility of polymers. However, if mixing is accomplished simultaneously with crosslinking, phase separation may be kinetically controlled by permanent interlocking of entangled chains\(^{(6)}\). Advantages of IPNs\(^{(4)}\) are that their mechanical properties can be changed over a wide range by changing the ratio of components and conditions used in their preparation. Furthermore, the mechanism for controlling domain size and shape can be accomplished by introducing crosslinking into the polymer networks.
Many industrial products have been publicly identified as containing IPNs. These products include such diverse materials as tough plastics, ion-exchange resins, artificial teeth, controlled drug delivery agents, contact lenses, and sound- and vibration-damping materials(4).

Among these applications, IPNs are an important class of materials for damping purposes with several interesting characteristics in comparison to homopolymers and polymer blends where efficient damping is limited to a temperature range of the glass transition temperature indicated by one or two narrow dynamic mechanical loss peaks(3). An IPN can have a broad glass transition over a wide range of temperature and frequency. In the other words, the effective energy absorbing material can be obtained from semi-miscible polymer system(6). When the loss modulus or loss tangent is high, particularly in the glass transition region, polymers are capable of damping out noise and vibration by absorbing mechanical energy and converting this energy partially into heat through viscous deformation(7). The application of polymers as damping materials is particularly good due to their high efficiency combined with versatility, relatively low cost, and their ease of application.

Investigations into energy absorption of IPNs have been widely carried out(9). Firstly, several attempts were made to produce new types of IPNs, ionomer-containing, gradient IPN, etc., and to study their characteristics. Afterwards, more work has been done to examine the formation of multicomponent IPN systems. Many investigations on the morphology, phase separation, and transitional behaviour have been published(9). The attempt to study filled IPNs has also been addressed. However, it appears to have been less intensively researched(8). Such studies are of great importance in elaborating principles of producing composite polymeric materials.

The literature(10-15) shows that the combination of a glassy polymer and another which is rubbery at room temperature can produce IPNs possessing a wide range of properties and transition temperatures depending upon the composition ratio and which component forms the continuous matrix. In this study, the simultaneous polymerisation technique was used for the preparation of IPNs, consisting of an
elastomeric polyurethane phase and a glassy poly(ethyl methacrylate) phase. Polyurethane shows some unique properties, including excellent elasticity, excellent abrasion resistance and damping properties, high impact strength, and elongation, which have been widely used in many applications\textsuperscript{16}. However this polymer could not be utilised in some applications for the low mechanical modulus and low strength. While poly(ethyl methacrylate) possesses high mechanical modulus\textsuperscript{17}, it is too brittle to be used in many instances. Hence, a blending technique can be applied utilizing IPNs of two polymer components that can improve deficiencies of each individual material. The PUR/PEMA IPNs were prepared in an effort to obtain semi-miscible behaviour, thus to achieve the desired broad range of energy absorption. Furthermore, a number of fillers were incorporated into the IPNs in order to investigate the effect of concentration, particle size and shape of the fillers on the mechanical properties and dynamic mechanical behaviour of these IPNs. The filling of polymers with mineral substances is one of the methods not only of reducing the cost of polymeric materials but also of improving their properties.

1.2 Objectives of the Study
The purposes of this research were to prepare and characterise high damping unfilled and filled IPNs based on polyurethane/poly(ethyl methacrylate), PUR/PEMA, with a high energy absorbing ability spanning over a broad temperature range.

The approaches in this research were to:
(1) study and synthesise semi-compatible polyurethane/poly(ethyl methacrylate) simultaneous IPNs;
(2) investigate the effect of synthesis variables including cross-linking and composition ratio on IPN morphology, i.e. the phase domain size and shape;
(3) elucidate the relationship between IPN morphology and dynamic mechanical and general mechanical properties;
(4) develop high damping filled IPNs by the incorporation of several types of mineral fillers, which are different in particle size, shape and chemical structure;
(5) examine the effect of fillers on the damping properties, morphology and other properties of filled IPNs by the application of modulated-temperature differential scanning calorimetry, dynamic mechanical thermal analysis, high-resolution TGA, electron microscopy and other characterisation techniques.
CHAPTER 2

BACKGROUND AND LITERATURE REVIEW
2.1 Interpenetrating Polymer Networks

2.1.1 An Introduction to Interpenetrating Polymer Networks

Definition.
An interpenetrating polymer network (IPN) is a special type of polymer blend containing networks of two or more polymers, at least one such polymer being polymerised and/or crosslinked in the presence of the other\(^4\). The original concept of interpenetrating polymer networks was adopted because, in the limiting case of high miscibility between crosslinked polymers I and II, the networks can be visualized as containing extensive molecular interpenetration on a molecular scale and throughout the entire macroscopic sample\(^5,18\). In practice, most IPNs consist of chemically distinct polymers. As a result, incompatibility and some degree of phase separation usually occurs\(^19\). On the other hand, the crosslinked network and entanglement of the chains mean that gross phase separation is unlikely to occur\(^20\). The two components remain intimately mixed, and the extent of microphase separation can be controlled by the method of polymerisation which leads to different types of IPNs\(^20\).

Types of IPNs and Synthesis.
Several different types of IPN have been synthesised and investigated. A classification of the different IPN types follows.

- **Simultaneous IPNs (SIN).** Monomer I and II, and/or prepolymer plus their cross-linking agents, and initiators are introduced simultaneously and polymerised by non-interfering reactions. Interference is minimized if monomer I reacts by radical chain polymerisation, while the other reacts by step polymerisation reaction\(^19,21\). See Figure 2.1(b).
• **Sequential IPNs.** In this case, polymer network I is made first. Monomer II, plus cross-linking agent and initiator, are swollen into network I and polymerised in situ. See Figure 2.1(a).

(a) Sequential Interpenetrating Polymer Network

![Sequential Interpenetrating Polymer Network Diagram]

(b) Simultaneous Interpenetrating Network

![Simultaneous Interpenetrating Network Diagram]

**Figure 2.1** A schematic of two basic polymerisation methods of IPNs (a) Sequential IPN. (b) Simultaneous interpenetrating polymer network (SIN).
• **Latex IPNs.** In this system, two networks are made in the form of latexes by a two-stage emulsion polymerisation. An emulsion of a crosslinked polymer I is first formed. Then, monomer II, initiator, and cross-linking agent are added and polymerised\(^{(21)}\).

• **Gradient IPNs.** This IPN type is deliberately made so that the overall composition varies from location to location on the macroscopic level. For example, a film can be made with network I predominantly on one surface, network II on the other surface, and a gradient in composition throughout the interior\(^{(4)}\). This can be achieved by swelling polymer network I in monomer mix II and polymerising before homogeneity is achieved by diffusion\(^{(21)}\).

• **Thermoplastic IPNs.** An IPN of two linear polymers in which the chemical crosslinks have been replaced by physical crosslinks. Because of this, this material softens and flows at elevated temperature, but behaves as a thermoset at temperature of use\(^{(4)}\).

• **Semi-IPNs.** IPNs in which one or more polymers are crosslinked and one or more polymers are linear or branched\(^{(4)}\).

• **Filled IPNs.** IPN containing inorganic (or organic) fillers\(^{(21)}\).

**History and Nomenclature of IPNs.**

The invention of IPNs was made by Aylsworth in 1914, before the birth of concept of the macromolecules proposed by Staudinger\(^{(4,21)}\). The IPN investigated was the world’s first rubbery toughened plastic of phenol-formaldehyde composition with natural rubber and sulfur\(^{(22)}\). The term “interpenetrating polymer network” was created by Miller in 1960\(^{(23)}\). His research concerned homo-IPNs consisting of divinylbenzene crosslinked polystyrene as both the first and second networks. The principal interest in IPNs started in the late 1960’s, as indicated by the publications by various research teams\(^{(9,23-26)}\).

In spite of the fact that the research on IPNs has been carrying on for several decades, no nomenclature system for IPNs has yet been formally organised. Use of the term net- to indicate a network and the term -inter- to indicate IPN is one of suggested prefix and connective proposals\(^{(4)}\). Thus, an IPN of polyurethane and poly(ethyl
methacrylate) might be written in the proposed way as: net-polyurethane-inter-net-poly(ethyl methacrylate). Most publications, however, use the simple slash notation to indicate the combination of two polymer networks. The above IPN, therefore, becomes: polyurethane/poly(ethyl methacrylate) interpenetrating polymer network, or PUR/PEMA IPN. For reasons of simplicity, as well as, to be in agreement with other IPN literature, the latter method will be used in this study.

Table 2.1 IPN commercial materials(27).

<table>
<thead>
<tr>
<th>IPN component</th>
<th>Application</th>
<th>Manufacturer</th>
<th>Trade Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUR-polyester-</td>
<td>Sheet moulding</td>
<td>ICI Americas Inc.</td>
<td>ITP</td>
</tr>
<tr>
<td>styrene</td>
<td>compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rubber-PP</td>
<td>Tough plastic</td>
<td>Shell Research BV</td>
<td>-</td>
</tr>
<tr>
<td>EPDM-PP</td>
<td>Tyres, belts, gaskets, and hoses</td>
<td>Monsanto</td>
<td>Santoprene</td>
</tr>
<tr>
<td>Anionic-cationic</td>
<td>Ion exchange resins</td>
<td>Rohm &amp; Haas</td>
<td>-</td>
</tr>
<tr>
<td>EPDM-PP</td>
<td>Outdoor weathering</td>
<td>Du Pont</td>
<td>Somel</td>
</tr>
<tr>
<td>EPDM-PP</td>
<td>Paintable automotive parts</td>
<td>Exxon</td>
<td>Vistalon</td>
</tr>
<tr>
<td>Acrylic-based</td>
<td>Artificial teeth</td>
<td>Dentsply International</td>
<td>Trubyte</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bioform</td>
</tr>
<tr>
<td>Vinyl-phenolics</td>
<td>Damping compounds</td>
<td>Hitachi Chemical</td>
<td>-</td>
</tr>
<tr>
<td>Acrylic-urethane-</td>
<td>Sheet moulding</td>
<td>Freeman Chemical</td>
<td>Acpol</td>
</tr>
<tr>
<td>PS</td>
<td>compounds</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Applications of IPN Technology

Many IPNs are combinations of an elastomer and a plastic. Consequently, the resulting IPNs exhibit properties of either reinforced rubbers or impact-resistant plastics, depending upon which phase predominates(4). Other applications to date include ion exchange resins(28), coatings and paint in latex form(29-30), and latex printing ink compositions(31). Recently, an interesting application in the medical field is as devices for drug delivery systems(32) and artificial teeth(33), and sound and vibration damping materials (34-36). The latter application is discussed elsewhere in this chapter.
A number of IPNs are now commercially available with a wide range of applications. Some of these commercial materials are listed in Table 2.1(27).

2.1.2 Morphology of IPNs

2.1.2.1 Morphology and Phase Separation.

Most IPNs and other multicomponent polymer systems investigated to date exhibit phase separation. The phases vary in domain size and shape, interfacial bonding and degree of continuity. These features constitute the morphology, and the morphological detail strongly influences, in turn, the physical and mechanical behaviour(21). For instance, an incompatible polymer pair exhibits two glass transitions, one for each polymer. After a certain degree of miscibility is reached only one transition is observed. Two major mechanisms of phase separation in multicomponent polymer systems are usually considered: nucleation and growth, and spinodal decomposition(7, 37,38).

Nucleation and Growth(7,19,37,38)

For nucleation and growth, the transition of the system from one-phase to two-phase involves the generating of initial fragments, called nuclei, of a new and more stable phase. Figure 2.2 shows a multicomponent system of composition C_o with a nucleus of composition C'_a, while the concentration in the immediate vicinity of the nucleus is represented by C_a. The growth mechanism can be described as the molecules within the phase of concentration C_o diffusing into the phase of lower concentration C_a (i.e. down hill diffusion), where the molecules making up nucleus are held strongly together. This process proceeds as the system decomposes, and nuclei grow resulting in two-phase system with finely dispersed droplets of domains whose sizes increase with time. During the growth mechanism, the concentration within the nucleus remains constant at C'_a, so does the second phase at C_a. Eventually, the droplets become larger by coalescence or coarsening and two large phases of composition C'_a and C_a appear.
Spinodal Decomposition\(^{(7,19,37,38)}\)

Spinodal decomposition is a kinetic process of generating a spontaneous and continuous growth of new phase within an unstable matrix of the first phase. This process is the commonly observed phenomenon in polymer blend phase separation. While nucleation and growth kinetics tend to produce spheres of the second phase, interconnected "cylinders" tend to form in spinodal decomposition. These "cylinders" grow by increasing their wave amplitude. The initial growth mechanism involves exchanging of mass across the boundary. As the molecules of new phase continuously diffuse uphill from the low concentration region into a cylinder domain, the system will decompose into two phases of compositions \(C_s\) and \(C_o'\), see Figure 2.3. Purer phases form with time, but the domains are about the same size as the early stage of phase separation. Later, coarsening and coalescence may cause important changes, such as, increasing the domain sizes and sometimes changing the domain shapes (Figure 2.4). However, these changes may be impeded by crosslinking, which keep domains small. The spinodal decomposition mechanism and the corresponding phase structure are shown in Figure 2.3.

![Figure 2.2](image)

*Figure 2.2* A schematic concentration profile of the nucleation and growth mechanism with the corresponding phase structure; (a) one-dimensional evolution of concentration profiles; (b) two-dimensional pictures of the resultant phase structures\(^{(37)}\).
Figure 2.3 A schematic concentration profile of spinodal decomposition mechanism with corresponding phase structure; (a) one-dimensional evolution of concentration profiles; (b) two-dimensional pictures of the resultant phase structures\(^{(27)}\).

Figure 2.4 Coarsening during the latter stage of spinodal phase separation\(^{(27)}\).
Multi-component polymer systems can exhibit a number of morphologies. In general, the resulting morphology is most likely to be a dispersed-phase matrix type in which the minority phase can be spherical, fibrous or lamella-like\(^\text{(19)}\). Many of them exhibit some degree of dual phase continuity, defined as the continuity of both phase I and phase II domains throughout the macroscopic sample. In other words, interlocking three-dimensional network of phases\(^\text{(4,19)}\), as shown in Figure 2.5. Highly interconnected phases with dual phase continuity are often encountered from the spinodal decomposition phase separation mechanism\(^\text{(38)}\).

![Figure 2.5 Dual phase continuity\(^\text{(19)}\).](image)

2.1.2.2 Factors Influencing IPN Morphology

The morphology of an IPN is its predominant feature. Because of their dual crosslinked nature, both constituent networks influence the morphology. There are many factors that control the morphology of IPNs. The major ones include immiscibility and miscibility of the polymers, crosslink densities of the two networks, polymerisation method and conditions, and also the IPN composition ratio\(^\text{(4,5,21)}\). While these factors may be interrelated, they can often be varied independently.

**Immiscible and Miscible of Polymers.**

Mixing of polymers is not as straightforward or predictable as the mixing of low molecular liquids. Nearly all two-polymer compositions when blended do not mix, but form separate phases or domains within the mixture. Such blends are defined as immiscible\(^\text{(2)}\). In the vast majority of cases cited in literature miscibility is defined in terms of the behaviour of a macroscopic property, usually single glass transition
temperature\(^{(2,39,40)}\). Miscibility, therefore, implies a level of homogeneity within the mixture, such that any separate domains present are smaller than the segmental size responsible for the glass transition. In a pragmatic sense, miscibility occurs when the system appears to be homogeneous in the type of test applied in the study\(^{(2,39,40)}\).

Kaplan\(^{(41)}\) has introduced the notion of a miscibility number, \(N\), such that in general;

\[
N = \frac{\text{Experimental probe size}}{\text{Domain size}}
\]  

(2.1)

In the case where miscibility is defined in terms of glass transition behaviour the experimental probe size is the segmental length associated with the \(T_g\) relaxation process. When \(N\) tends towards infinity, the system appears to be miscible. A value of about one indicates partial miscibility whereas a value of zero indicates immiscibility.

\[\text{Miscible, } N \to \infty\]
\[\text{Partially miscible, } N \to 1\]
\[\text{Immiscible, } N \to 0\]

\[\text{: Probe size}\]

**Figure 2.6** Variation of miscibility number with domain size\(^{(40,41)}\).

IPN morphology, i.e. the phase domain size and shape, and the miscibility, can be characterised by several techniques. Approximate limits of useful ranges of these techniques to study blend morphology are shown in Figure 2.7\(^{(2)}\).

In thermodynamic terms, the basic criterion for the miscibility of two polymers is that the Gibbs free energy of mixing, \(\Delta G_m\), is negative, as determined by the following equation\(^{(2,5,10)}\).
\[ \Delta G = \Delta H_m - T \Delta S_m \] (2.2)

where \( \Delta H_m \) is the enthalpy of mixing, \( T \) the absolute temperature in K, and \( \Delta S_m \) the entropy of mixing. Since the entropy change on mixing two polymers is small or negligible, miscibility is usually only achieved if the enthalpy of mixing is negative, which can be achieved in some cases involving specific intermolecular interactions, such as hydrogen bonding.

**Figure 2.7** Approximate ranges of techniques to study blend morphology of: 1) interatomic; (2) molecular; (3) filler aggregates, compatibilised blends; (4) reinforcements, non-compatibilised blends; (5) voids.

The morphology of IPNs can vary from a microphasic separation with phase domain sizes of 5 nm and less to a macrophase morphology. The more miscible the polymer system, the smaller the phase domains it exhibits. Many polymer pairs are classified as being either immiscible or miscible. To be considered miscible, a polymer pair usually must exhibit a range of compositions and temperatures where total miscibility occurs. Otherwise, the polymer pair is considered immiscible. Examples of selected immiscible and miscible polymer pairs are listed in Table 2.2.
A degree of miscibility between constituent polymers is an important factor that controls the morphology, because solution of monomers, or swelling of networks during polymerisation is needed. Phase separation generally proceeds in the course of polymerisation, but the resulting phase domain size is smaller for higher miscibility systems.

**Table 2.2 Selected immiscible and miscible polymer pairs**

<table>
<thead>
<tr>
<th>Polymer I</th>
<th>Immiscible polymer pair</th>
<th>Miscible polymer pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Polybutadiene</td>
<td>Poly(2,6-dimethyl phenylene oxide)</td>
</tr>
<tr>
<td></td>
<td>Poly(methyl methacrylate)</td>
<td>Poly(vinyl methyl ether)</td>
</tr>
<tr>
<td></td>
<td>Poly(dimethyl siloxane)</td>
<td></td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Polyethylene</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EPDM</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td></td>
<td>Poly(butylene terephthalate)</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td></td>
<td>Poly(acrylic acid)</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td></td>
<td>Poly(vinylidene fluoride)</td>
</tr>
</tbody>
</table>

Two systems of poly(ethyl acrylate)-based sequential IPNs differing in miscibility have been investigated. The effect of monomer miscibility on IPN morphology was examined by scanning electron microscopy. First, the system of poly(ethyl acrylate)/polystyrene (PEA/PS) IPN was prepared. The resulting IPN exhibited clearly incompatible morphology. When styrene monomers in the IPN component were replaced by methyl methacrylate monomer (MMA), the coarse cellular structure became progressively smaller in size and less distinct, Figure 2.8. As MMA completely replaced styrene monomer, fine and more interpenetrating structures were found containing dispersed phase domains less than 10 nm in size. This can be considered as a result of high miscibility, since PEA and PMMA are chemically isomeric, having structures shown as follow. As miscibility is increased, initial phase separation will take place later during the polymerisation of the second component. As a result greater mixing of the two networks occurs, and, so more interpenetrating on a molecular scale exists in final product.
Level of Crosslinking Density

This factor is also important in determining the network morphology, since it is the presence of crosslinking that limits the degree of phase separation in IPNs compared to other multicomponent polymer systems\(^3\).

Distinct phase separation with a cellular domain structure was found in the study of styrene-butadiene rubber/polystyrene (SBR/PS) IPNs\(^{43}\). The level of crosslinking of both networks was altered in order to study the influence of the degree of crosslink density on the morphology. Electron micrographs of IPNs showed smaller network II (PS) domain sizes, as the crosslink density in polymer network I (SBR) was increased, Figure 2.9. On the other hand, variation of crosslink density in the PS network had
little effect on the IPN morphology, indicating that the first network exerted the major control of morphology\(^{(43)}\).

![Figure 2.9](image)

**Figure 2.9** Electron micrographs of 20SBR/80PS IPNs. The rubber is crosslinked with (a) 0.1%, and (b) 0.2%dicumyl peroxide\(^{(43)}\).

A series of polyurethane/polymethylacrylate (PUR/PMA) sequential IPNs was studied by Hourston and McCluskey\(^{(44)}\). The IPNs were investigated by using dynamic mechanical analysis, and tensile testing. In addition, the morphologies were studied by transmission electron microscopy. It was clear that there was phase separation in all the IPNs. Tightening the second formed network (PMA) did not produce a
dramatic effect. As the divinylbenzene, the PMA crosslinking agent, content was increased, the PMA domains were only marginally reduced in size. Some evidence in the electron micrographs suggested that the PMA component became more continuous as the crosslinking level was increased.

**Polymerisation Method and Condition**

In sequential IPNs, the network formed first appears to have the greater degree of continuity\(^5\), even though it may be the minor component by weight. When the polymers are reversed in sequence, the new morphology is again controlled principally by the first network\(^5\). For simultaneous IPNs, the networks form during the same time period, although not necessarily at the same rate, and more complex morphologies result\(^5\). An example was the SIN of 75/25 polyurethane/ poly (methyl methacrylate) studied by Kim et al\(^45\). The reaction rates of the two components were found to be similar, so the majority component probably formed a network first and became the more continuous phase.

A number of studies have been conducted in order to compare IPN morphology prepared from the simultaneous with the sequential techniques. Fox et al\(^46\) used PUR and poly(n-butyl acrylate-co-n-butyl methacrylate) as the constituent polymers in the study of the influence of sequential and simultaneous polymerisation on IPN morphology. They found some evidence that indicated greater phase separation in the simultaneous IPNs. However, a contrasting result has been reported. Akay et al\(^13\) prepared a variety of simultaneous and sequential IPNs based on PUR and PMMA. Scanning electron micrographs confirmed that IPNs synthesised by the simultaneous process appeared to be more homogeneous than the ones prepared by sequential process. The samples were also evaluated in terms of dynamic and static mechanical behaviour. It was found\(^13\) that much higher elongation to failure and greater tensile strength were obtained from the simultaneous IPNs.

Synthesis conditions were also reported to have a significant effect on morphology and properties of IPNs. Hourston et al\(^47\) investigated the PUR/PMA IPNs system of a fixed composition (50/50 weight ratio) prepared at 200 MPa under a range of
temperatures. All the dynamic mechanical analysis results indicated improved mixing as the synthesis temperature decreased. The IPN synthesised at 120°C showed the most phase-separated structure, with very poor tensile strength. This was probably a consequence of thermal damage to the PUR network. At high temperature, the exothermic heat of polymerisation of methyl acrylate could lead to excessive temperature rise, capable of degrading the already formed PUR network.

**IPN Composition Ratio.**

The composition ratio of each polymer exerts significant effects on IPN properties. Any given property of an IPN is the function of the properties of the constituent polymers and of the interactions between them. The combination of a glassy polymer with another which is rubbery can produce IPNs possessing a range of properties depending upon the composition ratio and which component forms the continuous matrix\(^{12,13}\). IPNs, therefore, may be produced to exhibit a range of properties from reinforced elastomers to high impact plastics.

Akay *et al.*\(^{13}\) examined the system of sequential PUR/poly(methyl methacrylate) IPNs with different composition ratios. They reported that an increase in the PMMA content produced the expected trends in the mechanical properties: an increase in hardness, elastic modulus and tensile strength and a decrease in impact strength. Elongation to failure exhibited a maximum value corresponding to the unique damping characteristics of an intermediate composition IPN. An improvement of low temperature impact strength was observed in the IPNs compared with pure PMMA. Similar results were found in the study of IPNs from hydroxy-terminated polybutadiene-based PUR and PMMA\(^{48}\).

Kim *et al.* investigated PUR/PMMA\(^{45,69}\) SINs and PUR/PS IPNs\(^{50}\) with varied composition ratios. They found that phase inversion occurred between 20-40% in the composition range of the second network. When either component exceeds 85% the morphology became more complicated. This work, and that of Touhsaent *et al.*\(^{51}\), both reported that phase domain size and continuity depended sensitively on reaction rates for the two components, as well as on composition.
The IPN composition determines the relative amounts of the two phases present after polymerisation. Increasing amounts of polymer II generally leads to increasing domain sizes\(^3\), but the effect also depends on the polymerisation method. For IPNs based on PEA/PS, Huelck \textit{et al.}\(^4\) found only a slight increase in domain sizes as the composition ranged from 75/25 to 25/75. The corresponding result was found from a study of SBR/PS system\(^5\). Note that in sequential IPNs, an upper limit on the amount of polymer II is set by the equilibrium swelling of monomer II plus initiator and crosslinker into the first network.

2.1.3 Behaviour of IPNs

General Properties

Three main parameters that are crucial in determining the properties of IPNs are generally considered as follow: i) the properties of the constituent polymers, ii) the phase morphology, and iii) interaction between the phases\(^6\). As for other multi-component polymer systems, some properties, such as density\(^7\), of IPNs, in particular cases, can be accounted for approximately by the simple averaging of properties of the constituent polymers.

On the contrary, optical transparency, one simple way of confirming miscibility, is more complex. Miscible amorphous IPNs are transparent whilst IPNs exhibiting phase separation are usually observed as white, opaque materials due to increased scattering as the size of the phase domains approaches the wavelength of light\(^8\). IPNs of two amorphous, transparent, and incompatible polymers, such as PEA and PS, are hazy and translucent in thin sheet form, because the phase domains have different refractive indices and scatter light. However, if the IPN consists of two polymers whose the refractive indices nearly match, the resulting IPN can be clear\(^9\). Optical clarity is a necessary, but not sufficient, criterion for blend miscibility of amorphous constituents. So, any conclusions drawn from such observation must be confirmed by another technique.
Glass Transition Behaviour.
The study of glass transitions is essential with morphological studies of polymers. While homopolymers and random copolymers exhibit single, sharp glass transitions, polymer blends, in general, and IPNs in particular, show two such transitions, one for each phase. The intensity of each transition is related to the overall composition and phase continuity while shift and broadening of the transition indicate the extent of molecular mixing\(^{(5)}\).

Curtius et al.\(^{(53)}\) examined the typical behaviour of IPNs based on an incompatible polymer pair, cis-polybutadiene/polystyrene (PB/PS). Two separate transitions were observed for all IPN compositions. The shift and broadening of the transitions were minimal. See Figure 2.10. The morphology of these IPNs were examined by electron microscopy and found to exhibit a relatively sharp phase domain separation.

![Figure 2.10 Modulus-temperature behavior of incompatible cis-PB/PS IPNs\(^{(53)}\).](image)

Completely compatible IPNs are rare. However, single broad transitions have been found for a semi-compatible polymer pair, PEA/PMMA\(^{(42)}\). Figure 2.11. The broad transition reasonably results from an extensive overlap of the two primary transitions.
as the parent polymers are isomeric, or, more probably, believed to be the combined transitions of all possible compositions that could contribute independent transitions.

![Figure 2.11 Modulus-temperature behaviour of semi-compatible PEA/PMMA IPNs](image)

**Figure 2.11** Modulus-temperature behaviour of semi-compatible PEA/PMMA IPNs.(42)

### 2.1.4 Polyurethane-Based Simultaneous IPNs

As mentioned earlier, SINs are an IPN sub-class. The preparation involves mixing of monomers or prepolymers with their initiators and crosslinkers to form a homogeneous fluid, which is then simultaneously polymerised by independent reactions.(4.21) A major advantage of this process over sequential IPNs is its simplicity.(19) This process does not require the swelling step of network I in monomer mix II. Furthermore, the mixture can be pre-polymerised until just short of the gel point, followed by pumping into a mould or die, with continued polymerisation(21). Many papers have been published on SINs. Park *et al.*(54) proposed several parameters which were crucial in controlling the extent of miscibility in SINs: composition ratio; crosslink density; compatibility of polymer pair; chain mobility; degree of polymerisation and relative polymerisation rates of constituent polymers.

The effect of pendant chain length on the damping factor (tan δ) has been examined by Chen and his research group.(55) A series of polyurethane-based SINs was synthesised containing methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), and ethyl acrylate (EA), respectively, as monomers for network
two. Microphase-multiphase structures and the widening of the glass transition peaks were observed. Dynamic mechanical properties exhibited significantly higher loss tan δ peaks for PUR/PEMA and PUR/PEA than those for PUR/PMMA and PUR/PMA IPNs. The structures of the main chain of the four SINs are the same, while the pendant chains are slightly different. Because of the greater flexibility of the longer pendant group, the ethyl group behaves as a diluent allowing a greater degree of chain motion.

Kim and co-workers\(^{(49,56)}\) investigated the mechanical properties of PUR/PMMA SINs. The hardness behaviour reflected the observed phase inversion where the hardness rapidly decreased at 60-70% PUR concentration corresponding to the results from an electron microscopic study. The maximum ultimate tensile strength was observed from the 85PUR/15PMMA IPN and was mostly due to the reinforcing effect of the dispersed glassy PMMA phase. The IPNs did not show any reinforcement in the ultimate tensile strength. This indicated that the reinforcement in the ultimate tensile strength was not directly related to interpenetration (by increased physical entanglement crosslinks), but indirectly related by reducing the rigid phase domain sizes and increasing the adhesion between the two phases, thus enhancing the reinforcing effect.

Hourston and Schafer\(^{(57-59)}\) conducted a study of PUR/PEMA SINs with respect to morphology and phase continuity using mechanical and dynamic mechanical methods and electron microscopy. Dynamic mechanical data revealed tan δ transitions with shoulders for the intermediate compositions from 70/30 to 40/60 PUR/PEMA which was an indication of a semi-miscible system. TEM micrographs confirmed a co-continuous system at the 70/30 and 40/60 mid-range compositions. For the remaining compositions only one peak, indicating a higher degree of miscibility, was observed. Tensile testing revealed a strong synergistic effect at the 70/30 composition with maxima occurring at this composition for both the elongation at break and the toughness index.
Influence of the relative rates of network formation on the dynamic properties of PUR/poly(methyl acrylate) SINs has been determined\(^{(60)}\). IPNs synthesised without PUR catalyst, dibutyltin dilaurate, at 80°C exhibited two loss factor peaks. Under these reaction conditions, both reactions were believed to proceed simultaneously. By conducting the polymerisation at 35°C together with catalyst, the PUR network was completely formed before the onset of the PMMA polymerisation. As a result, improved component mixing was shown by one broad loss factor maximum.

Other studies on polyurethane-based IPNs have been widely investigated because of the distinctive properties of PUR, the high versatility of its chemistry, the relatively easy synthesis and the outstanding mechanical properties. Besides the above literature, many other PUR-based IPNs have also been studied. Examples include PUR/polyester\(^{(35,61)}\), PUR/polyacrylate\(^{(51)}\), PUR/siloxane\(^{(62,63)}\), PUR/epoxy\(^{(64)}\), and PUR/polystyrene\(^{(34,58)}\) IPNs.

2.2 Dynamic Mechanical Behaviour and Damping with IPNs

2.2.1 Dynamic Mechanical Properties of Polymers

Materials under the influence of an applied strain are categorised depending on the nature of their responses. Perfect viscous liquids obey Newton’s law of viscosity, the applied stress being directly proportional to the strain rate. Perfectly elastic materials obey Hooke’s law, the applied strain being proportional to the stress. Polymeric materials are neither completely elastic nor viscous, but exhibit both behaviours and, so, are termed viscoelastic\(^{(7)}\). The ability of polymers to damp vibration and absorb sound is a function of their viscoelastic nature, specifically their glass transition behaviour.

When energy is applied to a viscoelastic polymeric material, part of it is stored as mechanical energy represented through the storage modulus, \(E'\), while the rest of it is converted into heat through viscous deformation. The latter part is the loss modulus \(E''\). Figure 2.12 is a simple illustration of this behaviour\(^{(7)}\). As a viscoelastic ball is dropped onto a perfectly elastic floor, it bounces back to a height \(E'\), a measure of
the energy stored elastically during the collision between the ball and the floor. The quantity $E''$ represents the energy lost as heat during the collision.

\[ E' \]

\[ E'' \]

Figure 2.12 Simplified definitions of $E'$ and $E''$ (7).

Because of the viscoelastic nature, the magnitude of the strain ($\varepsilon$) in a polymer is a function of time as well as stress ($\sigma$). In dynamic mechanical analysis, as a polymer is under sinusoidal stress at constant amplitude, the resulting strain lags behind the stress by the angle $\delta$. The stress and strain at time $t$ are given by the following equations (7.65):

\[
\sigma = \sigma_0 \sin(\omega t + \delta) \quad (2.3)
\]

\[
\varepsilon = \varepsilon_0 \sin(\omega t + \delta) \quad (2.4)
\]

where $\omega$ is the cyclic frequency, $\sigma_0$ and $\varepsilon_0$ are the strain and stress amplitudes, respectively. Equation 2.3 can be expanded to

\[
\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \quad (2.5)
\]

It can be seen that the stress is made up of two components, one in phase ($\sigma_0 \cos \delta$) and the other 90° out of phase with the strain ($\sigma_0 \sin \delta$).

The stress-strain relationship, therefore, is as follows.

\[
\sigma = \varepsilon_o E' \sin \omega t + \varepsilon_o E'' \cos \omega t \quad (2.6)
\]
where
\[ E' = \left( \frac{\sigma_o}{\varepsilon_o} \right) \cos \delta = \frac{C}{B} \quad \text{(figure 2.13)} \quad (2.7) \]
\[ E'' = \left( \frac{\sigma_o}{\varepsilon_o} \right) \sin \delta = \frac{D}{B} \quad \text{(figure 2.13)} \quad (2.8) \]

---

**Figure 2.13** Sinusoidally varying stress and strain in a dynamic mechanical experiment \(^{65}\).

For a viscoelastic polymer, \( E' \) characterises the ability of the polymer to store energy (elastic behaviour), whereas \( E'' \) reveals the tendency of the material to dissipate energy (viscous behaviour). Dividing the loss modulus by the storage modulus leads to the loss tangent:

\[ \frac{E''}{E'} = \left( \frac{\sigma_o / \varepsilon_o}{\sigma_o / \varepsilon} \right) \sin \delta = \tan \delta \quad (2.9) \]
This means that \( \tan \delta \) is the ratio of the energy stored to the energy lost per cycle. These moduli define a complex modulus \( E^* \) by the equation:

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

(2.10)

as represented by Figure 2.14.

**Figure 2.14** Diagram for complex modulus (7).

The maximum in \( E'' \) and \( \tan \delta \) are sometimes used as the definition of \( T_g \). In Figure 2.15, the \( E' \) and \( E'' \) display maxima at \( T_g \). The presence of two \( T_g \)s is taken as an indication of immiscibility. In Figure 2.16, low frequency storage modulus is plotted as a function of temperature. The solid lines represent the behaviour of homopolymers A and B and the broken lines that of the 50:50 blend. The sudden drop of modulus is
associated with onset of molecular thermal motions in the Tg region. The four schematics show: 1) miscible, 2) immiscible, 3) partially miscible, and 4) semi-miscible blends. The last has a fine dispersion and a broad Tg region^{(2)}.

![Figure 2.16](image)

Figure 2.16 Schematic representation of the temperature dependence of storage modulus for polymer A and B (solid lines), and their 50/50 blends (broken lines). (1) miscible blend, (2) immiscible blend, (3) limited miscibility, (4) semi-miscible blend^{(2)}.

2.2.2 Damping with Polymers and IPNs

Sound and vibration damping are important in the world today, as they are by-products from the use of machinery in both the workplace and the household^{(66)}. An unpleasant noise affects physically and mentally human health, whereas vibration can cause fatigue in products leading to failure, malfunction and low performance levels. A damping property is required for many purposes, such as for the automotive industry, aircraft, tall buildings, and submarine technology.

Viscoelastic polymers have been found to be very interesting in this respect^{(4,67)}. In the vicinity of the glass transition temperature, T_g, of a polymer, a dynamic equilibrium exists between frozen chain segments (glassy state) and segments that are free to move (rubbery state)^{(68,69)}. As a frozen segment obtains energy through mechanical deformation, the onset of coordinated molecular motion converts it to thermal energy. The most common types of damping materials involve simple homopolymers or
copolymers whose efficient damping is limited to the Tg range of approximately 20-
30°C. Many techniques have been investigated to achieve damping over a wider
temperature range. Multicomponent systems such as mechanical blends have been
used to broaden the transition range and so result in high-performance energy-
absorbing materials. Partial miscibility is aimed at in these systems. If both polymers
are immiscible, then a limited damping capability as indicated by the two separate Tg
peaks with little inter-transition damping is observed from dynamic mechanical
analysis. On the other hand, two miscible polymers result in one relatively narrow
transition peak having little or no advantage over a homopolymer.

Among the different types of multicomponent polymeric materials for sound and
vibration damping, IPNs are very useful because of their broad glass transition
regions. An introduction of crosslinks into both polymers restricts the domain sizes
and enhances the degree of molecular mixing. Many IPNs exhibit micro-
heterogeneous morphologies. When the domains are in the order of 10-20 nm, the
whole system is substantially interphase. Subsequently, the glass transition
temperature tends to be very broad and stretches over a range between the transitions
of the two polymers, which also means a broad active frequency range of damping.

For most IPNs, there exist a certain miscibility in structure and also forced miscible
action. Usually, a broader glass transition indicates that the phases are not
completely homogeneous. The width of the peak depends on the Tgs of the two
homopolymers. If the system is partially miscible and the difference of the Tg of the
two homopolymers is about 50°C, the temperature range of tan δ > 0.3 can approach
100°C. If the difference of the Tgs is too great, the width of the peak is great, but the
height must be lower. As a result, the damping power is poor. The height and width of
the damping peak can not be adjusted independently. The area under the peak is
essentially constant. The damping peak must be maximised so that the
requirements for the application are met.

Chang et al. characterised the integral of the loss modulus versus temperature to
develop a relationship between the extent of damping and the contribution from each
molecular structure over a broad range of acrylic, vinyl, and styrenic polymers. They found that the area under curve was a molecular characteristic which was determined by the molecular structure of the polymer material. This analysis may help to select polymers with specific damping characteristics.

2.2.3 Extensional and Constrained Layer Damping

The application of an IPN as an energy absorbing material was first reported by Huelck et al.\(^{(42)}\). The material was latex IPNs based on a pair of compatible polymers, poly(ethyl acrylate) and poly(methyl methacrylate). The IPNs were observed to exhibit high values of tan\(\delta\) over a broad temperature range. The ability of both IPN and homopolymer to absorb sound and damp vibration is a function of their viscoelastic nature, specifically at glass transition temperature where the onset of large segmental movements begins.

Four mechanisms of sound attenuation can occur: (i) scattering by inhomogeneities e.g. in filled polymer, (ii) redirection, (iii) mode of conversion at boundaries in polymeric foams and (iv) intrinsic absorption by conversion to heat with viscoelastic materials\(^{(4)}\). Two basic engineering mechanisms for the use of polymers in damping, extensional and constrained layer, are in common use\(^{(5,7)}\). See Figure 2.17. Extensional or free layer damping is an application of a single layer coating on the vibrating surface. In this case, the energy dissipation evolves primarily from the flexural and extensional motions of the damping layer\(^{(21,59)}\). A further improvement in damping can be obtained from a two-layer system with a viscoelastic damping layer under a stiff constraining layer. The additional constraining layer responds with vibrations that are out-of-phase with the substrate. The resulting shearing action on the intermediate damping layer causes a significant increase in energy dissipation into heat over an extensional system. Extensional dampers tend to work best when the polymer is at the low temperature (stiff) end of the glass-transition range, whereas constrained layer damper tends to work best in the high-temperature (rubbery) range\(^{(75)}\).

When a viscoelastic polymer is adhered to a vibrating substrate, internal friction created by segmental chain motions results in heat build up within the polymer and
absorption of the vibrational waves. Equations describing the performance of damping for extensional and constrained layer systems are given below.

For an extensional layer damping system:

\[
\tan \delta_{\text{system}} = k \left( \frac{E_2}{E_1} \right) \left( \frac{H_2}{H_1} \right)^2 \tan \delta_2
\]  \hspace{1cm} (2.11)

For an constrained layer damping system:

\[
\tan \delta_{\text{system}} = k \left( \frac{E_3}{E_1} \right) \left( \frac{H_3}{H_1} \right)^2 \tan \delta_2
\]  \hspace{1cm} (2.12)

\(k\) is a constant, \(E\) and \(H\) are the Young's modulus and the layer thickness and the subscripts 1, 2 are 3 refer to the substrate, the viscoelastic layer and the constraining layer, respectively.

Figure 2.17 Two mechanisms for the use of polymers in damping$^{(19)}$. 
2.3 Fillers: types, sources, and properties

Fillers are defined as additives in solid form which are physically dispersed in the polymer matrix without significantly affecting the molecular structure of the polymer, but differing from polymer in respect to their chemical composition and morphologies\(^{(78)}\). The major purposes of adding fillers into polymer systems are to improve properties or reduce cost\(^{(77,78)}\). Inert fillers or extender fillers increase the bulk and lower the production cost, while active fillers produce specific improvements in certain mechanical or physical properties and are, thus, also known as reinforcing fillers\(^{(77)}\). The addition of fillers is known to affect several properties of polymers, such as: colour, density, mechanical properties, thermal conductivity, electric conductivity, gas permeability, chemical reactivity, weather resistance, transparency, flammability etc.\(^{(1)}\). The result of filler incorporation mainly depends on filler properties, particle size and shape, interaction between filler-polymer and dispersion of filler in the matrix\(^{(79)}\).

Fillers can be divided into two broad categories based on their chemical types: organic and inorganic fillers. Organic fillers have sub-categories including lignins, cellulosics, proteins and synthetics. On the other hand, inorganic fillers include carbonates, hydroxides, oxides, silicates, sulphates, carbon, metal powders and so on. See Table 2.3\(^{(78)}\). A brief outline of the mineral fillers used in this research is given in the following section.

2.3.1 Silica.

Silica is one of the most abundant minerals on earth\(^{(74)}\). The crystalline form of silica, quartz, has the highest hardness of common minerals. Silica is resistant to heat and chemicals, with low coefficient of thermal expansion, high thermal conductivity, good electrical properties and transparency. Several types of silica are used as fillers.
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Table 2.3 Different types of inorganic fillers

<table>
<thead>
<tr>
<th>Silicates</th>
<th>Carbonates</th>
<th>Metals/powders/fibers</th>
<th>Miscellaneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium silicate</td>
<td>Calcium carbonate</td>
<td>Aluminum</td>
<td>Barium ferrite</td>
</tr>
<tr>
<td>Talc</td>
<td>Barium carbonate</td>
<td>Copper</td>
<td>Magnetite</td>
</tr>
<tr>
<td>Mica</td>
<td>Magnesium carbonate</td>
<td>Bronze</td>
<td>Molybdenum</td>
</tr>
<tr>
<td>Clay</td>
<td>carbonate</td>
<td>Zinc</td>
<td>disulphide</td>
</tr>
<tr>
<td>Silica</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

- **Natural silica.**

Sand, quartz, quartzite, novaculite, tripoli and diatomaceous earth are naturally occurring silica and differ relatively to their particle sizes, degree of crystallinity and hardness. Some deposits contain mostly large primary particles, over 600 µm in size, while others may contain primary particles of under 100 µm. The crystalline form of silica, quartz, has the highest hardness of common minerals with a Moh hardness of 7 and a density of about 2.6 g/cm³.

- **Synthetic silica.**

Most of the reinforcing silicas are synthetic. By means of manufacturing processes, very fine particles with large surface area, very high SiO₂ content (>99%), low bulk density, hydrophobic, high oil absorption and generally spherical primary particles are obtained. The synthetic product obtained by the vapour process is frequently termed fumed silica. This process is Degussa’s invention developed by application of carbon black production technology. The size of primary grains of fumed silica is usually in the range of 7 to 30 nm, which is relative to the final product specific surface area having the range of 400 to 100 m²/g. Synthetic silica, unlike natural quartz, is shown by X-ray analysis to be amorphous. Moreover, it can be employed in low quantity to achieve specific effects in polymers such as reduction in shrinkage and crack.
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formation, reinforcement, improvement in dimensional stability under heat, increase in hardness etc\(^{(80,81)}\).

2.3.2 Mica.
Three naturally occurring types; muscovite, phlogopite, and biotite are important representatives of this group of fillers. Muscovite is one of the most common types of the micas and occurs in a wide variety of geological environments because of its stability. Phlogopite is found in metamorphosed magnesium-rich limestones, dolomites and ultrabasic rocks. Biotite, similar to muscovite, is also widespread\(^{(81)}\). Out of three micas mentioned above, muscovite and phlogopite are the only minerals used with muscovite being the most popular. Application of micas is influenced by their colour. Muscovite is almost colourless, phlogopite has a golden brown colour, whereas biotite is black\(^{(79)}\).

Mica flake fillers are plate-like crystalline aluminosilicates with thickness in the range of 1 to 3 \(\mu\)m and the diameter in the range of 10-450 \(\mu\)m. Mica has excellent mechanical, electrical, and thermal properties, rather low surface area, mostly in the range of 2-15 \(m^2/g\)\(^{(81)}\). Well-manufactured grades do not contain much water (usually in the range of 0.1 - 0.2\%), and pH about 7.5.

2.3.3 Calcium Carbonate.
The most widely used filler for plastics, sealants, and coatings is calcium carbonate, usually employed in the form of naturally occurring carbonate or whiting; limestones, dolomites and marble dust. Precipitated calcium carbonate is also widely used. From the point of view of chemical composition, grades of calcium carbonate contain 95-98\% of \(CaCO_3\), depending on sources and method of manufacture. The specific surface area of calcium carbonate is usually in the range of 2-13 \(m^2/g\), directly proportional to the grain size distribution. Calcium carbonate shows little porosity\(^{(82)}\). Grain size distribution is tailored to the application, and a great number of grades are available. Most grades have 35-39\% of grains with diameters smaller than 2 \(\mu\)m. Moisture content should be less than 0.2\% and the product does not have a tendency to absorb moisture, unless it contains calcium oxide or other impurities. The major
disadvantage of calcium carbonates is their reactivity with acids, causing production of enormous quantities of gaseous carbon dioxide\(^{(83)}\).

- **Natural Calcium Carbonate**
  Natural carbonate is mainly calcite, a rhombohedral crystal (sp.gr. = 2.70-2.72, Moh hardness = 3.0, pH = 9-10). Commercial deposits contain less than 3% magnesium carbonate and traces of other impurities, such as iron and sulfur. Ground carbonates are pure white with a mean particle size of 6 to 20 \(\mu m\). Wet grinding gives higher purity products as fine as 0.8 \(\mu m\)\(^{(76)}\).

- **Limestones**
  Limestones are less pure forms with calcite crystals embedded in soft carbonaceous materials and clays. Crushing and grinding of limestones to coarse sizes for routine applications are standard practice\(^{(83)}\).

- **Precipitated and synthetic calcium carbonates**
  Precipitated calcium carbonates are available in highly pure form with particle sizes down to 0.5 \(\mu m\). Compared to dry or wet ground carbonates, precipitated types have much higher surface area, finer particle size, and narrower particle-size distribution. Oil or polymer absorption is much higher for these porous carbonates and viscosity development is much greater\(^{(83)}\).

2.3.4 **Talc**

Talc is a hydrated silicate mineral widely used in the polymer industry. Commercial talcs are predominantly magnesium silicate. There is little variation in the chemical composition of talc; sometimes small amounts of Al or Ti substitute for Si\(^{(84)}\). Morphology and impurities can vary according to the mining locality with particle size ranging from 1 \(\mu m\) for paint applications to over 15 \(\mu m\) for coarse fillers. Specific surface area is typical for a medium porosity material in the range of 3-20 m\(^2\)/g\(^{(85)}\). The other important feature of talc composition is the presence of about 5% of water, which is chemically combined in a magnesium oxide layer. Talc may lose this water only on heating over 800\(^{\circ}\)C, but, if this happens, the platelet structure is completely lost and its properties are changed\(^{(86)}\). The planar surfaces of the platelet structure are held together by very weak van der Waals forces, and, therefore, talc can be delaminated at relatively low shearing forces, accounting for the slippery feel of talc.
A platelet structure provides talc-filled materials with unique features, such as high resistivity and low gas permeability because the diffusion path is so complicated. Several other properties of talc are structure related, including its lubricating effect, caused by easy delamination, low abrasiveness, because talc is the softest mineral with a Moh hardness of 1.0-2.0, and hydrophobic properties of its surface with excellent wetting and dispersion in plastics and other organic media\(^{(84,85)}\).

**Table 2.4 Types of mineral fillers\(^{(79)}\)**

<table>
<thead>
<tr>
<th>Filler</th>
<th>Main mineral</th>
<th>Chemical composition</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (natural)</td>
<td>Quartz</td>
<td>SiO₂</td>
<td>Cubic</td>
</tr>
<tr>
<td>Silica (synthetic)</td>
<td>-</td>
<td>SiO₂</td>
<td>Aggregated</td>
</tr>
<tr>
<td>Mica</td>
<td>Muscovite</td>
<td>K(_2)(Al(_2)Si(<em>4)O(</em>{10}))(OH)(_2)</td>
<td>Platey</td>
</tr>
<tr>
<td>Mica</td>
<td>Phlogopite</td>
<td>K(_2)Mg(_2)(Al(_2)Si(<em>4)O(</em>{10}))(OH)(_2)</td>
<td>Platey</td>
</tr>
<tr>
<td>Talc</td>
<td>Talc</td>
<td>3MgO.4SiO(_2).H(_2)O</td>
<td>Platey</td>
</tr>
<tr>
<td>Chalk whiting</td>
<td>Calcite</td>
<td>CaCO(_3)</td>
<td>Spherical</td>
</tr>
</tbody>
</table>

**2.4 Incorporation of Fillers into a Polymer Matrix**

At the present time, not only powdered fillers, but also polymeric reinforcing materials based on synthetic fibres, are being used extensively to produce filled and reinforced polymers. The most important requirement of any filler is that it should be effective, for the purpose which it has been designed for, at an economic level\(^{(87)}\). When a filler is added to a polymer with the specific idea of reinforcement, it is expected that the reinforcing filler component, which is strong and stiff, should bear most of the load or stress applied to the system while the polymer, which is of low strength, fairly tough and extensible, should effectively transmit the load to the filler. Good mechanical strength can be achieved only by uniform and efficient stress transfer through a strong interfacial bond between the filler and the polymer\(^{(78,88)}\).

Fillers can be mixed with polymers in a number of ways, dependent on the nature of both ingredients. The mixing process should be able to break any filler aggregates, securing total wetting of each particle by the matrix and uniformly distribute the
particles throughout that matrix. Three possible mechanisms of the action of a filler in polymers can be described.

Case I: By means of the mixing process, the filler is only physically dispersed in a polymer matrix with no interaction at all. The filler then behaves as a diluent or an extender and is expected to weaken the material by its presence.

Case II: The filler is physically present in the polymer and its surface is wetted by the polymer caused by either the inherent polymer affinity for the filler or an suitable surface treatment of the filler to provide this affinity. Physical bonds are formed resulting in an increase in the frictional resistance to the movement of the filler, therefore leading to an increase in tensile strength and a decrease in elongation at break. The extent of an increase in mechanical properties is dependent on the strength of bonding between the filler and the polymer.

Case III: The filler develops true chemical bonding with the polymer matrix resulting in an exceptional strengthening effect. In this case, the chemical bonding can be improved to enhance the mechanical performance of the composite by appropriate filler surface treatment.

2.5 Effects of Fillers on Interpenetrating Polymer Networks

Investigations on IPNs have been widely carried out by various research groups, as evidenced by a significant number of reviews and articles. There have been two lines of research: firstly, investigations aimed at obtaining new types of IPN (ionomer-containing, gradient etc.) and studying their characteristics; secondly, studies of the formation processes of these complex multicomponent systems. Investigations of filled IPNs have been carried out somewhat less intensively, although such studies are of great importance in producing composite polymeric materials.

It is known that introducing fillers into a reaction system at the stage of formation of crosslinked polymer could essentially affect the reaction. Lipatov et al. investigated the kinetics of curing, the microphase separation process and the viscoelastic properties of IPNs based on crosslinked PUR and linear poly(butyl
methacrylate) with the presence of two fillers; talc and polymerised triethylene glycol dimethacrylate. It was found that introducing filler into the reaction mixture changed the reaction kinetics and the degree of microphase separation, which in turn affected the properties of the IPNs. The data obtained by DMTA, DSC and the degree of segregation for filled semi-IPNs showed that the presence of filler resulted in inhibition of the microphase separation process on account of a local increase in viscosity near the solid interface, i.e. compatibility is increased.

Lipatov et al.\(^{91}\) was particularly interested in the thermodynamic state of reinforced IPNs. The free energy of mixing two networks in an IPN based on PUR and poly(ester acrylate) was determined by the vapour sorption method. They found that the constituent networks were not miscible. The unfilled IPN characterised by DMTA exhibited the two tan $\delta$ peaks close to the Tgs of the IPN components. Introduction of fillers; aerosil, aluminium dioxide, and dispersed cured poly(ester acrylate) led to the disappearance of the two peaks and the formation of only one broad transition. This effect may be attributed to some structural changes in the IPNs and to an increase in compatibility.

A study of filler effect on formation and properties of polyurethane-based IPNs was undertaken by Sergeeva and co-workers\(^{92}\). The main feature of IPN formation was reported to be the simultaneous occurrence of chemical crosslinking and microphase separation. Fillers introduced into the IPNs at their formation stage influenced both processes; on one hand, they affected the chemical reaction rate and changed the structure of the networks being formed; in particular the number of crosslinks in the chemical network; on the other hand, the adsorption interaction with one or several components changed the microphase separation rate, resulting in non-equilibrium structure formation with various degrees of component segregation, differing from that of unfilled systems.

Effects of fillers on the acoustic properties of simultaneous IPNs have been conducted by Ting and his research group\(^{93}\). A number of fillers; mica, alumina trihydrate, and ethylene homopolymer, were incorporated in PUR/epoxy IPNs. The IPNs were
prepared by the mixing of two components. One component contained the isocyanate and epoxy resin, and the other contained the polyol, chain extender, catalyst, filler and plasticizer. The mixtures were reacted via the one-shot, simultaneous polymerisation technique. The corresponding acoustical measurement was evaluated as the dynamic Young’s modulus, $E'$, and loss factor, tan $\delta$. It seemed to suggest that the Young’s modulus was not affected by the ethylene homopolymer and alumina fillers as much as by mica.

Using mica and calcium carbonate as fillers in pseudo-IPNs of PUR/epoxy, Wong\textsuperscript{67} found that the addition of both fillers shifted the peak of the PUR damping to higher temperatures and raised the loss factor. A particularly effective combination was a mica-filled PUR/Epoxy IPN in which the loss peaks were shifted from 258 to 281 K with significant broadening on the high temperature side of the peak. An earlier study\textsuperscript{64} showed that as the particle size of mica was decreased, the tan $\delta$ peak occurred at slightly higher temperatures, but the height was not affected. This agrees with the concept of greater adsorption on the larger surface area of the smaller particles which takes place with mica, but not to the same extent with calcium carbonate.

Polystyrene/poly(ethyl acrylate-co-n-butyl acrylate), PS/P(EA-nBA) latex IPNs were synthesised by a two-stage emulsion polymerisation technique\textsuperscript{95}. The effects of fillers on damping of these LIPNs have been investigated. The results indicated that inorganic fillers produced an increase in tan $\delta$ values and broadened the damping temperature range. Among the fillers, mica showed good results on damping properties. The large increase in damping values for filled LIPN indicated that mechanisms other than friction between particles or between particles and polymer contribute to energy dissipation. In mica-filled LIPNs, a mica platelet at one side of the LIPN damping layer can be considered as a vibrating substrate, while a platelet at the other side of damping layer acts as a constrained layer. When the specimen is vibrating, shear takes place in the polymer damping layer between the platelets, which increases the mechanical loss of energy, being converted to heat.
Klempner et al.\textsuperscript{(20,96)} investigated the IPNs composed of an elastomeric PUR and a glassy epoxy component. Several different fillers were incorporated into IPNs to determine their effects on \( \tan \delta \) and the rubbery modulus. The study based on the best formulation containing 60/40 PUR/Epoxy showed a maximum \( \tan \delta \) of 1.7. After the addition of 10% alumina trihydrate and untreated chopped glass fibres, a modest increase in the \( \tan \delta \) was observed (it increased to a maximum of 1.75 in the same temperature range of 25°C). Other fillers studied, such as 10% mica and wollastonite had no effect on \( \tan \delta \), while carbon black decreased the maximum \( \tan \delta \) value significantly to 1.0.

The influence of inorganic fillers on the dynamic mechanical properties of polystyrene/polyacrylate IPNs was undertaken by Li et al.\textsuperscript{(97)} 10% weight of fillers such as mica, graphite, TiO_2, CaCO_3 and wollastonite were introduced into the IPN system possessing PS/PA weight ratio of 50/50. The resulting dynamic mechanical spectra indicated that mica and graphite had good effects on the damping properties shown by the fairly high value of storage modulus over a broad transition temperature range. They attributed this to the fact that there are two important factors in connection with the influence of fillers on the damping value: one is the decrease in free volume, which limits the movement of some molecular chains so that the damping value decreases; the other is the internal friction between the fillers and polymer, and between the filler particles themselves over the Tg range which increases as the movement of molecule chains becomes greater so that the damping value increases. When the latter factor is predominant, the filler enhances the damping value of the IPN.

IPNs composed of acrylic/methacrylic polymers were examined by DMS for their damping capabilities\textsuperscript{(98)}. While homopolymers exhibited high damping properties only over a 20-30°C range, their IPNs could exhibit high damping properties over the temperature ranges as broad as approximately 100°C. Graphite was incorporated into some of IPNs to measure the changes in the damping properties. For important IPN compositions, graphite increased the damping properties indicated by the increase of \( \tan \delta \) values between 0.4 and 0.85 over a 75°C plus temperature range.
2.6 Polyurethane Networks

The original discovery leading to the world-wide interest in all classes of polyurethane was made by Bayer and his co-workers of I.G. Farben, Germany, in 1937 as a competitive response to the work by Carothers of Du Pont, USA, on the polyamides or nyons\(^{(99,100)}\). Polyurethane has received intense attention and become a very important class of material resulting in the syntheses of many specialized forms. Because of the wide variety of raw materials which form this polymer, polyurethane can be made as a soft elastomer, a hard solid or anything in between. It can be a fibre for clothing, a rubber for shoes and tyres, or a foam for thermal insulation or for mattresses and cushions\(^{(100)}\).

2.6.1 Polyurethane Chemistry

Polyurethane is synthesised by an addition reaction between diisocyanate, polyester or polyether polyol, and chain extender diol. The reaction is schematically represented by the equation below\(^{(99,101)}\). In the reaction, there is the advantage that, unlike polycondensation, the process normally gives rise to no by-products that require removal as the macromolecules are built up.

\[
\begin{align*}
\text{glycol} & \quad \text{diisocyanate} \\
\text{HO-[R-OCONH-R'-NH-OCO]_n-R'-OCO-NH-R'-NCO} & \quad (2.13)
\end{align*}
\]

Polyurethane

This simple reaction gives rise to the most complex and widely varied family of polymers known today. The reason for the complexity of this polymer is found in the wide variety of variables which affect the physical and chemical properties of the final polymer. A partial listing of these variables is as follows: polyol and diisocyanate functionality and molecular weight, utilisation of chain extenders to modify hard- and soft-segment content of the polymers, various catalysts, additives and fillers\(^{(102)}\). The manipulation of these variables gives rise to polymers that fall into one of several different classes which vary by chemical structure, density and hardness of the
polymers: thermoplastic and thermoset elastomers, engineering thermoplastics, rigid cellular plastics, and flexible cellular plastics.

Two main techniques are used in polyurethane production: the one shot (random melt polymerisation) and prepolymer technique. The both techniques are shown in general form in Figures 2.18 and 2.19.

**Figure 2.18** One shot process for polyurethane elastomer preparation\(^{(99)}\).

**Figure 2.19** Formation of polyurethane with urethane and urea linkages from polyester or polyether polyol, diisocyanate and diol or diamine chain extender\(^{(102)}\).
2.6.2 Further Isocyanate Reactions

Polymerisation of polyurethane is subjected to many side reactions due to the reactivity of isocyanate group, -NCO, which reacts exothermically with both active-hydrogen compounds and, under the right conditions, with itself. The speed of a NCO group reacting with its reactant depends not only on the NCO group, but also on the structure of the molecular radical to which it is bound\(^{(103)}\). The most important active-hydrogen compounds contain -OH or -NH\(_2\) functions. They are alcohols or amines\(^{(104)}\). Water has an essential role as OH component in the production of foams. When isocyanate is used as a source of carbon, gaseous carbon dioxide is formed and acts as a blowing agent. Carbon dioxide is also produced when the NCO group reacts with organic acids identified by the carboxyl group, -COOH\(^{(103)}\).

I) Primary reactions of isocyanate with hydrogen active compounds.

The NCO groups react generally with compounds containing active hydrogen atoms, as follows:

- With water

\[
\text{R-N=C=O} + \text{H}_2\text{O} \rightarrow \text{R-NH-CO-OH} \quad (2.14)
\]

(isocyanate) (carbamic acid (unstable))

\[
\text{R-NH-CO-OH} \rightarrow \text{R'NH}_2 + \text{CO}_2 \quad (2.15)
\]

(unstable) (amine)

The amine then reacts with the isocyanate group

- With amine

\[
\text{R-N=C=O} + \text{R'NH}_2 \rightarrow \text{R-NH-CO-NH-R'} \quad (2.16)
\]

(urea)

- With carboxylic acid

\[
\text{R-N=C=O} + \text{R'-COOH} \rightarrow \text{RNHCOR'} + \text{CO}_2 \quad (2.17)
\]

(amide)
Thus, if the reagents are di- or polyfunctional, polymer formation can take place. While these reactions normally occur at different rates, Equation 2.16 being the most rapid, they can be influenced appreciably and controlled by use of catalysts. Reactions 2.15 and 2.17 give rise also to carbon dioxide, a feature of value in forming foamed products, but introducing difficulty if bubble-free casting and continuous surface coating are required\(^{(99)}\).

II \ ) Secondary reactions of isocyanates with isocyanate adducts.

Unconsumed isocyanate in the reaction mixture can enter secondary reactions with the urea, urethane, and amide groups already introduced during the initial polymer formation. Other chemical structures which can permanently affect the properties of the finished polyurethane are also formed\(^{(103)}\). The secondary reactions of isocyanates can take place and introduce branching and crosslinking of the polyurethane due to the formation of allophanate, biuret, and acyl urea links onto the main chains:

\[
\begin{align*}
\text{R-NCO} + \text{R'-NH-CO-O-R''} & \rightarrow \text{R-NH-CO-N-CO-O-R''} \quad (2.18) \\
\text{urethane} & \quad \text{allophanate} \\
\text{R-NCO} + \text{R'-NH-CO-NH-R''} & \rightarrow \text{R-NH-CO-N-CO-NH-R''} \quad (2.19) \\
\text{urea} & \quad \text{biuret} \\
\text{R-NCO} + \text{R'-NH-CO-R''} & \rightarrow \text{R-NH-CO-N-CO-R''} \quad (2.20) \\
\text{amide} & \quad \text{acyl urea}
\end{align*}
\]

As several types of side reaction may be encountered during polymerisation, a slight excess of the diisocyanate is sometimes needed to produce high molecular weight polyurethane and to overcome the effect of side reactions.
III ) Autoaddition of isocyanates.
When isocyanates react with themselves, other structural elements are formed in the polymer and affect performance characteristics accordingly.\(^{99,100}\).

- Dimerisation to carbodiimide and uretidione.

\[
2 \text{R-NCO} \rightarrow \text{R-N=C=N-R} + \text{CO}_2 \tag{2.21}
\]

\[
\text{carbodiimide}
\]

\[
\begin{align*}
2 \text{R-NCO} & \quad \Rightarrow \\
\text{uretidione ring} & \quad \tag{2.22}
\end{align*}
\]

- Trimerisation
Isocyanates, under certain conditions, trimerise into a ring structure consisting of alternating nitrogen and carbon atoms.

\[
3 \text{R-NCO} \rightarrow \tag{2.23}
\]

\[
\text{isocyanurate}
\]

IV ) Thermal degradation of urethanes.
At higher temperature, dissociation into isocyanate and alcohol may take place as well as formation of primary amine, olefin and carbon dioxide\(^{101}\). Relatively low reaction temperatures, not higher than 120°C, are usually required. The degradation reactions of polyurethane are illustrated below\(^{100}\).
~ R-NH-OCO-CH₂-CH₂ ~ \rightarrow ~ R-NCO + HO-CH₂-CH₂ ~ (2.24)
~ R-NH-OCO-CH₂-CH₂ ~ \rightarrow ~ R-NH₂ + CH₂=CH ~ + CO₂ (2.25)
~ R-NH-OCO-CH₂-CH₂ ~ \rightarrow ~ R-NH-CH₂-CH₂ ~ + CO₂ (2.26)

Chemical crosslinking in polyurethane can also be produced by the use of branched polyester or polyether having hydroxyl functionality higher than two, or by the use of low molecular weight triol in the reactions. In addition to chemical crosslinking, physical crosslinking may be formed between ester carbonyl oxygen, urethane carbonyl oxygen or ether oxygen and the urethane NH group\(^{100}\). Figure 2.20. These hydrogen bonds influence the morphological structures of polymers which in turn determine the end use properties.

### 2.6.3 Basic Structure of Polyurethanes

A polyurethane elastomer can be regarded as a linear block copolymer of the type shown in Figure 2.21. This segmented polymer structure can vary its properties over a very wide range of strength and stiffness by modification of its three basic building blocks: the polyol, diisocyanate, and chain extender\(^{100}\).

Evidence from X-ray diffraction, thermal analysis, and birefringence supports the view that polyurethanes can be considered in terms of alternating glassy hard segments and soft rubbery segments which are chemically bonded together\(^{100}\). The hard segments consist of diisocyanate and chain extender, while the soft segments typically consist of polyester or polyether polyol. If the chain extender is a diol, a polyurethane with urethane linkages is formed, whereas if the chain extender is a diamine, urea linkages are formed\(^{105}\). Block structure of polyurethane containing polyol, diisocyanate and chain extender is shown in Figure 2.22. The molecular weight of the soft segment is believed to influence the segregation of hard segments. Segment mixing occurs at low molecular weights (about 1000), whereas above a certain limit (typically of the order of MW 2000) the phase separation is more or less complete\(^{104}\). The phase separation is also improved by the crystallisation and
hydrogen bonding of the hard segments. By contrast, crosslinking and hydrogen bonding between the hard and soft segments enhance phase penetration \(^{109}\).

\[\text{(a)}\]

\[\text{(b)}\]

\[\text{(c)}\]

*Figure 2.20* Hydrogen bonding in polyurethane a) ester-urethane, b) ether-urethane and c) urethane-urethane hydrogen bonding \(^{109}\).

\[\text{Isocyanate} \quad \text{Polyol} \quad \text{Mono- or} \quad \text{Chain}
\text{rigid block} \quad \text{flexible} \quad \text{polymeric} \quad \text{extender}
\text{block} \quad \text{isocyanate} \quad \text{rigid block}\]

*Figure 2.21* The basic unit in a urethane block copolymer.
2.6.4 Health Hazards and Precautions

Chemicals used in the manufacture of urethanes often have particular health hazard problems. Examples of such materials being nitro compounds, amines and some glycols. However, the primary emphasis in urethanes technology has always been given to the hazards associated with the isocyanates utilized for the manufacture of the final urethane polymers\(^{99,106}\). Isocyanates are strong irritants to the skin, eyes, gastrointestinal tract and are dangerous to the respiratory system according to their vapour pressure\(^{106}\). Some of them have very low vapour pressure while in others it is quite high. Increasing use is now being made of low volatility types of isocyanates, partly because they possess, through their low vapour pressure, less inhalation toxicity. Hence, skin absorption hazards are now also of particular concern.

Large air vents have to be installed in workplaces and foaming plant. Goggles with protective sides, water-proof gloves, impermeable overalls and solid shoes are prerequisites for the handling large amount of isocyanates. Spillage should be cleared up immediately and adequate supplies of suitable decontaminant liquid should be readily available for this purpose\(^{107}\).
2.7 Poly(ethyl methacrylate), PEMA

Poly(ethyl methacrylate) is a linear thermoplastic. It is amorphous because of its bulky side group and lack of stereoregularity. It has good optical clarity, mechanical and thermal properties. Ethyl methacrylate monomer has the chemical structure:

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2=\text{C} \\
\text{C}=\text{O} \\
\text{OCH}_2\text{CH}_3
\end{align*}
\]

This monomer can be polymerised by radical chain polymerisation consisting of a sequence of three steps: initiation, propagation and termination\(^{(101,108)}\).

- **Initiation**

The first step involves two reactions. First, the production of free radicals when an initiator undergoes thermal or photolytic scission to yield a pair of radicals, \( R^\cdot \). The second step is addition of these radicals to the monomer molecules to produce the chain initiating species.

\[
\begin{align*}
I & \overset{k_d}{\longrightarrow} 2R^\cdot \\
\text{CH}_3=\text{C} & \quad \text{CH}_2=\text{C} \\
\text{C}=\text{O} & \quad \text{C}=\text{O} \\
\text{OCH}_2\text{CH}_3 & \quad \text{OCH}_2\text{CH}_3
\end{align*}
\]

where \( I \) is the initiator and the rate constants of each reaction are indicated above the arrows.

\( k_d \) = the rate constant for the initiator dissociation, and

\( k_i \) = the rate constant for the initiation step
The initiator for this study was azobisisobutyronitrile (AIBN). Thermal dissociation of an azo compound is illustrated as follows.

\[
\begin{align*}
\text{C}_3\text{H}_5\text{N} = \text{N} \rightarrow 2 \text{C}_3\text{H}_5\cdot + \text{N}_2
\end{align*}
\] (2.29)

- **Propagation.**
  A chain radical formed in the initiation step is capable of adding successive monomers to propagate the chain. Each addition produces a new radical containing one more monomer unit.

\[
\begin{align*}
\text{RCH}_2\cdot + n \text{CH}_2=\text{C} \rightarrow \text{R} \left[ \begin{array}{c}
\text{CH}_3 \\
\text{C}=\text{O} \\
\text{OCH}_2\text{CH}_3
\end{array} \right]_n \\
\text{CH}_3
\end{align*}
\] (2.30)

\[k_p = \text{the rate constant for propagation}\]

- **Termination**
  The third step can take place in at least two ways. A radical chain reacts with another by combination and produces a dead polymer chain, or, more rarely, by disproportionation resulting in the formation of two polymer molecules, one saturated and one unsaturated.

\[
\begin{align*}
\text{CH}_2=\text{C} \cdot + \text{CH}_2=\text{C} \cdot \rightarrow \text{CH}_2=\text{C} \cdot + \text{CH}_2=\text{C} \cdot
\end{align*}
\] (2.31)
\[
\begin{align*}
\text{CH}_2\text{C}^\text{•} + \text{C}^\text{•} - \text{CH}_2\text{OCH}_2\text{CH}_3 & \xrightarrow{k_{td}} \text{CH}_2\text{CH}^\text{•} + \text{CH}_3\text{OCH}_2\text{CH}_3 \\
\end{align*}
\]

\[k_c = \text{the rate constant for termination by combination}\]
\[k_d = \text{the rate constant for termination by disproportionation}\]

Most termination reactions involve the combination of two polymer chain radicals. However, in many polymerisation systems the polymer molecular weight is observed to be lower than predicted on the basis of the experimentally observed extents of termination by coupling and disproportionation. This effect results from chain transfer reactions which may occur during the polymerisation. A chain transfer reaction is one in which polymer formation is achieved by the polymer chain radical reacting with another species in the polymerisation mixture, such as a solvent, initiator or monomer molecule. This results in a shorter chain length and hence lowers the molecular weight of polymer.
CHAPTER 3

EXPERIMENTAL
CHAPTER 3

EXPERIMENTAL

3.1 Materials

All raw materials used in this research were commercially available. They are listed in Table 3.1. The crosslinked polyurethane (PUR) component consisted of alternating glassy hard segments and soft rubbery segments. The hard segments were formed from the meta-tetramethylxylene diisocyanate (m-TMXDI) and the crosslinking agent trimethylol propane (TMP). The soft segment was polyoxypropylene glycol of a molar mass of 1025 (PPG1025). Stannous octoate was used as the PUR catalyst.

The glassy polymer component was polymerised from ethyl methacrylate monomers (EMA) which were crosslinked and initiated with tetraethyleneglycol dimethacrylate (TEGDM) and azoisobutyronitrile (AIBN), respectively. FTIR spectra of these materials are shown in Figure 3.1. In order to achieve better damping properties as well as higher rubbery modulus, a number of fillers of varying geometry were incorporated into some of the IPN formulations. The fillers used were silica, mica, calcium carbonate and talc.
3.2 Synthesis

All PUR/PEMA simultaneous IPNs in the present investigation were prepared in bulk in various proportions along with different types and amount of fillers according to the IPN formulae in Table 3.3

3.2.1 Purification of Monomers

The hygroscopic PPG 1025 was degassed at 80°C for 2 hours in a vacuum oven to remove traces of moisture and avoid the formation of air bubbles during polymerisation. After that it was kept in a desiccator over silica gel. In order to get rid of inhibitors, the EMA monomer and TEGDM crosslinking agent were passed through neutral aluminum oxide columns (alumina, Brockmann Activity I, Aldrich Chemical CO.,) and kept in a refrigerator until needed. All fillers were dried at 105°C for 6 hours in an open air oven and stored in a desiccator.
Figure 3.2 Chemical structures of the raw materials
### Table 3.1 Chemicals used in the research

<table>
<thead>
<tr>
<th>Materials</th>
<th>Abbreviation</th>
<th>Function</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polyurethane network</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1',3,3'-Tetramethylxylene diisocyanate</td>
<td>TMXDI</td>
<td>Diisocyanate</td>
<td>CyTec</td>
</tr>
<tr>
<td>Poly(oxypropylene)glycol (M.W.1025)</td>
<td>PPG 1025</td>
<td>Polyol</td>
<td>BDH</td>
</tr>
<tr>
<td>Trimethylol propane</td>
<td>TMP</td>
<td>Crosslinker</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Stannous octoate</td>
<td>SnOct</td>
<td>Catalyst</td>
<td>Sigma</td>
</tr>
<tr>
<td><strong>Poly(ethyl methacrylate) network</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl methacrylate</td>
<td>EMA</td>
<td>Monomer</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Tetraethyleneglycol dimethacrylate</td>
<td>TEGDM</td>
<td>Crosslinker</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Azobisisobutyronitrile</td>
<td>AIBN</td>
<td>Initiator</td>
<td>Degussa</td>
</tr>
</tbody>
</table>

### Table 3.2 Fillers used in the research

<table>
<thead>
<tr>
<th>Filler</th>
<th>Abbreviation</th>
<th>Average Particle Size</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>aerosil 380</td>
<td>5 nm</td>
<td>Degussa</td>
</tr>
<tr>
<td>Silica</td>
<td>VN 3</td>
<td>&lt; 50 μm</td>
<td>Degussa</td>
</tr>
<tr>
<td>Mica</td>
<td>SX 300</td>
<td>&lt; 53 μm</td>
<td>Microfine</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>RLO 6083</td>
<td>0.55 μm</td>
<td>ECC International</td>
</tr>
<tr>
<td>Talc</td>
<td>SF 10</td>
<td>&lt; 20 μm</td>
<td>Microfine</td>
</tr>
</tbody>
</table>

### Table 3.3 IPN Formulae

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ratio</th>
<th>(weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUR / PEMA</td>
<td>ratio</td>
<td>90/10, 70/30, 50/50, 30/70, 10/90</td>
</tr>
</tbody>
</table>

**PUR component**

- Isocyanate / hydroxyl: 1.1 / 1 (mole)
- Diol / triol: 2 / 1, 3 / 1, 4.5 / 1 (mole)
- PUR catalyst: 1.2 (PUR wt%)

**PEMA component**

- Initiator: 1 (PEMA mole%)
- Crosslinking agent: 2.5, 5, 7 (PEMA mole%)

**Filler**

- 0, 2.5, 5, 7.5, 10, 12.5 (IPN wt%)
3.2.2 Preparation of IPN Components

Ethyl methacrylate (EMA) monomer mix

The purified EMA monomer and TEGDM were mixed together with AIBN initiator in the desired proportions in a glass jar equipped with a mechanical stirrer. The components were then stirred at room temperature for 20 min to dissolve completely the initiator. During mixing, the mixture was flushed with nitrogen to remove the dissolved O₂.

Polyurethane monomer mix

In the case of filled IPNs, the filler was weighed and gradually added into the polyol, then homogeneously mixed for 30 minutes using a Silverson L2R mixing apparatus. After that TMP triol was added in desired mole ratio. The mixture was then kept under vacuum at 60°C for 30 min to dissolve completely the solid TMP (Tₘ = 58°C) into PPG. Next, the mixture was taken from the oven and allowed to cool to room temperature in a desiccator over silica gel. Finally, an addition of diisocyanate and catalyst in the desired amount was made.

Table 3.4 Calculation of IPN composition

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>70 PUR / 30PEMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPN weight ratio</td>
<td></td>
</tr>
<tr>
<td>Polyurethane component</td>
<td></td>
</tr>
<tr>
<td>Isocyanate / hydroxyl mole ratio:</td>
<td>1.1 : 1</td>
</tr>
<tr>
<td>Diol / triol mole ratio:</td>
<td>3 : 1</td>
</tr>
<tr>
<td>PUR catalyst (wt %)</td>
<td>1.2</td>
</tr>
<tr>
<td>PEMA component</td>
<td></td>
</tr>
<tr>
<td>Cross-linking agent (mole %)</td>
<td>5.0</td>
</tr>
<tr>
<td>Initiator (mole %)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Subst.</th>
<th>MW</th>
<th>Mole</th>
<th>Calculated weight(g)</th>
<th>Actual weight(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diisocyanate</td>
<td>TMXDI</td>
<td>244.3</td>
<td>1.10</td>
<td>268.77</td>
</tr>
<tr>
<td>Diol</td>
<td>PPG1025</td>
<td>1025.0</td>
<td>0.75</td>
<td>768.75</td>
</tr>
<tr>
<td>Triol</td>
<td>TMP</td>
<td>134.2</td>
<td>0.25</td>
<td>33.55</td>
</tr>
<tr>
<td>Catalyst</td>
<td>SnOct</td>
<td>405.1</td>
<td></td>
<td>0.29</td>
</tr>
</tbody>
</table>

| Monomer | EMA | 114.1 | 1.00 | 114.15 | 9.06 |
| Crosslinker | TEGDM | 330.4 | 0.05 | 16.52 | 1.31 |
| Initiator | AIBN | 164.2 | 0.01 | 1.64 | 0.13 |

PUR = 24.50
EMA = 10.50
Total = 35.00
3.2.3 Polymerisation
Immediately after the preparation of PUR and EMA monomer mixes, both of the IPN components were then combined together. Mixing was done at room temperature in a glass jar by vigorous agitation for 3 minutes. Then, a vacuum was applied to the mixture for 30-60 s to remove any air bubbles entrapped during the mixing process. After this, the mixture was carefully poured into the steel mould (Figure 3.3) where the polymerisation took place. Prior to filling the mixture, the mould was cleaned and sprayed with a silicone spray release agent (Cil Release 1711-Plus, Compounding Ingredients Limited). A nitrile rubber gasket of diameter 6 mm was place in between the steel plates that were held together using spring-loaded screws. Finally, the filled mould was placed for 24 hours in an air oven preheated at 60°C, then 24 hours at 80°C, and finally 24 hours at 90°C. The first low temperature period was applied in order to prevent the evaporation of volatile monomers and the occurrence of bubbles in the IPN samples.

Figure 3.3 Schematic of the steel mould used for IPN synthesis. 140 mm diameter.
### SYNTHESIS PROCEDURE

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler dispersion</td>
<td>Mixing (30 min)</td>
</tr>
<tr>
<td>IPN component</td>
<td>Diol混入，加热600°C (30 min) mixing (20 min)</td>
</tr>
<tr>
<td>preparation</td>
<td>Diisocyanate, Catalyst, Initiator, Monomer, Crosslinker</td>
</tr>
<tr>
<td>Mixing</td>
<td>PUR &amp; PEMA component</td>
</tr>
<tr>
<td></td>
<td>IPN mixture</td>
</tr>
<tr>
<td>Degassing</td>
<td>under vacuum 30-60 s</td>
</tr>
<tr>
<td>Moulding</td>
<td>O-ring mould</td>
</tr>
<tr>
<td>Curing</td>
<td>60°C, 24 hr, 80°C, 24 hr, 90°C, 24 hr</td>
</tr>
<tr>
<td>Demoulding</td>
<td>IPN sample</td>
</tr>
</tbody>
</table>

*Figure 3.4 Diagram of the IPN synthesis*
3.3 Characterisation Techniques

A number of characterisation techniques were used to investigate IPN morphology, dynamic mechanical and physical properties. Dynamic mechanical thermal analysis (DMTA), modulated-temperature differential scanning calorimetry (M-TDSC), and transmission electron microscopy (TEM) were the principal test methods used in this research to study glass transition behaviour and IPN morphology. The other techniques were scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and tensile testing. In the following section, these characterisation techniques, instrumentation and experimental conditions are briefly outlined.

3.3.1 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical testing method has become one of the most common techniques to determine polymer-polymer phase behaviour\(^\text{(7)}\). Measurement by DMTA refers to the method where a small amplitude cyclic stress is applied to a specimen, and two fundamental parameters are measured versus temperature: the storage modulus, \(E'\), a measure of the energy stored elastically, and the loss modulus, \(E''\), a measure of the energy dissipated\(^\text{(109)}\). Another parameter in wide use is \(\tan \delta\), the loss tangent, a measure of the ratio of energy lost to energy stored in a cyclic deformation. It is a dimensionless parameter\(^\text{(5,110)}\).

\[
\tan \delta = \frac{E''}{E'}
\]

(3.1)

In this work, the maximum in \(\tan \delta\) was used as the definition of the glass transition temperature with the error in results \(\pm 2^\circ\text{C}\).

Data obtained from DMTA are in the form of plots of \(\tan \delta\), \(E''\), or \(E'\) versus temperature. The degree of miscibility in multicomponent polymer systems can be inferred from the DMTA curve. If the two components are immiscible, or mixing is incomplete as when cross-linking occurs after phase separation, then two glass transitions at the locations of their respective homopolymers will be observed. Improved miscibility is indicated by inward shifts of the transition peaks and higher
tan δ values between the two transitions. A DMTA curve of a semi-miscible system with micro-heterogeneous morphology results in a broad glass transition region, indicating microheterogeneity in that a large number of phases of differing compositions exist, while a miscible system exhibits a single transition peak located between the two Tgs of the homopolymers\(^{4,17}\). Figure 3.5.

![Figure 3.5 DMTA curves for different degrees of miscibility. a) heterogeneous (solid line); b) limited miscibility (dashed line); c) micro-heterogeneous (dotted line); and d) miscible (dash dotted line)\(^{37}\).](image)

Dynamic mechanical measurements of various IPN samples were carried out by using a Polymer Laboratories dynamic mechanical thermal analyzer (Model MK II). Figure 3.6. The test temperature was varied from -60°C to 180°C at a heating rate of 3 °C/min. The strain amplitude was fixed at a value of × 4, while the frequency was 10Hz. Small rectangular bar specimens of approximately 35 mm × 10 mm × 3 mm were tested in the bending mode. The samples were subjected to constant cyclic stress by the clamping arrangement shown in Figure 3.7.
A central clamp holds the sample and was attached to a drive shaft linked to a mechanical oscillator. The resistance to the applied stress was recorded and converted by the built-in computer facilities, and dynamic modulii (both storage and loss modulii) and loss factor were calculated by the built-in software and plotted by a plotter.\(^{(111)}\)

**Figure 3.6** Schematic view of DMTA head\(^{(111)}\).

**Figure 3.7** IPN sample clamped in the DMTA prior to measurement\(^{(111)}\).
3.3.2 Modulated-Temperature Differential Scanning Calorimetry (M-TDSC).

Differential scanning calorimetry (DSC) is one of the thermal analysis techniques which has been widely used for decades to measure changes in the energy of the system under investigation\(^{(65)}\). DSC curves reflect the temperatures and heat flows associated with transitions in materials as a function of time and temperature. The measurement provides quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity\(^{(65)}\).

\[\text{Figure 3.8 Schematic for a typical heat flux DSC cell}^{(112)}\]

Recently, a new thermal analysis technique has been invented, known as modulated-temperature differential scanning calorimetry (M-TDSC)\(^{(113)}\). In this instrument, the same heat flux conventional DSC cell is used, but the linear heating programme is modulated sinusoidally. As a result, there are three heating-related experimental parameters involved: heating rate, amplitude of modulation, and frequency of modulation. The resultant signal is then analyzed using an appropriate mathematical procedure to deconvolute the response to the perturbation from the response to the underlying heating programme. Figure 3.9 shows a comparison of the same quenched PET sample between (a) the result from conventional DSC, and (b) the raw M-TDSC experimental curve\(^{(112)}\).
The normal response of a DSC is a combination of a signal that is dependent on the rate of change of temperature and one that is dependent on the value of the temperature. The former depends on the sample heat capacity and the latter on the rate of any kinetically-driven process. This response can be expressed as

\[
\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t, T)
\]  

(3.2)

where \( \frac{dQ}{dt} \) is the heat flow into the sample, \( C_p \) is the sample heat capacity (defined here as that due to the molecular motions in the sample), \( T \) is the absolute temperature, \( t \) is the time and \( f(t, T) \) is some function of time and temperature that governs the kinetic response of any physical or chemical transformation.
This equation shows that total heat flow is comprised of two contributions one of which is heating rate dependent and the other which is dependent only on absolute temperature. The relative amounts of these two contributions varies depending on the transition being evaluated\textsuperscript{112}.

The glass transition temperature is a parameter whose value is sensitive to many microstructure aspects of the material. Measurement of the T\textsubscript{g} is the most convenient and popular way of determination for miscibility or immiscibility of multicomponent polymer systems\textsuperscript{115}. This transition can be determined readily and accurately from the change in heat capacity of the polymer system by using the M-TDSC technique. Figure 3.10 shows M-TDSC data for polystyrene with the changes of heat flow, heat capacity, and \( C_p/dT \) with temperature\textsuperscript{116}.

![M-TDSC curves](image)

**Figure 3.10** M-TDSC curves shows changes of heat flow, heat capacity and \( dC_p/dT \) with temperature\textsuperscript{116}.

\[ \Delta C_p \text{ can be obtained from} \textsuperscript{116}: \]

\[ \Delta C_p = \int_{T_i}^{T_f} [dC_p/dT]dT \tag{3.3} \]

where \( T_i \) and \( T_f \) are the initial and final values of the temperature in the glass transition region.
Chapter 3

Experimental

For a miscible two-polymer system, $T_g$ depends on the composition ratio of the constituent polymers. In the case of immiscible polymer system, the total $\Delta C_p$ is the algebraic sum of the $\Delta C_p$ values of the two homopolymers\(^{116}\). 

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

(3.4)

$\omega_{10}$ and $\omega_{20}$ are the weight fractions of polymer 1 and polymer 2, respectively. $\Delta C_{p1}$ and $\Delta C_{p2}$ are the values of the increment of heat capacity at the corresponding $T_g$s.

For a partially miscible polymer blend, when the system exhibits an interface, the $\Delta C_p$ can be expressed by\(^{116}\):

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

(3.5)

\[
\Delta C_p = \omega_1 \Delta C_{p10} + \omega_2 \Delta C_{p20} + \Delta C_{pi}
\]

(3.6)

$\omega_1$ and $\omega_2$ are the weight fractions of components 1 and 2, respectively, in the mixed phases. $\Delta C_{pi}$ is the increment of heat capacity of the interface in its glass transition region.

A TA Instruments M-TDSC was used in this study. The samples were heated at 3°C/min with an oscillation amplitude of 0.8°C and oscillation period of 60s. A calibration of melting peak temperature and cell constant were carried out by using a standard indium sample and the baseline was calibrated by running an empty pan\(^{117}\).

3.3.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy of ultrathin specimens has become a prime technique for characterisation of samples with multiphase morphologies. This technique provides further insight into the level of mixing of block and graft copolymers, and polymer blends\(^{118}\). It has been generally known that phase separation of the two components takes place, and that is indeed important to the development of the mechanical characteristic of these materials. Information about the
extent of molecular mixing and morphology; the size and shape of the domains, can be based on TEM\(^{(118,119)}\). The diagram of image formation in a TEM is shown in Figure 3.11\(^{(120)}\). Basically, the electron gun, usually made of a tungsten filament, produces thermal electrons. These electrons are accelerated by applying high voltage to form an electron beam. The electron beam is then focused on and penetrates the specimen. Additional electrostatic and/or electromagnetic lenses are used in order to form the image which can be observed on a fluorescent screen or recorded photographically\(^{(119)}\).

**Figure 3.11** Diagram of image formation in transmission electron microscope\(^{(120)}\).

In order to improve the electron contrast unsaturated polymer (e.g. polydienes) can be stained by treating the specimens with osmium tetroxide (OsO\(_4\)). This method allows visualisation of the internal structure details of unsaturated polymers. The resulting image contains mass contrast that is derived from the distribution of staining material within the sample. The regions of the specimen that react readily with the stain easily appear dark, whilst the other regions appear light. Osmium tetroxide reacts with the unsaturated double bonds as the simplified reaction shown below. The sample preparations involve two steps. Generally, the staining reagent is allowed to diffuse into the sample. After the an appropriate period, the sample is then removed from the stain and a thin section is cut and examined by the TEM. Although in some cases the order of these two stages is reversed\(^{(128)}\).
Transmission electron micrographs were taken by direct observation of the prepared specimens employing a Joel 100 electron microscope. In order to harden the soft IPN sheets, the samples were trimmed and imbedded in epoxy resin, such that the long dimension of the section was perpendicular to the cutting direction of the microtome\(^{121,122}\). A LKA Bromma 8800 Ultratome III ultramicrotome equipped with a glass knife was used for sectioning samples of approximately 100 nm thickness. The ultrathin specimens were stained with \(\text{OsO}_4\) to get image contrast between phases\(^{121,122}\).

3.3.4 Scanning Electron Microscopy (SEM)
This technique is extensively used to examine the topographic features of specimen surfaces\(^{124}\). The scanning electron microscope is a device which forms images of microscopic surface region at magnifications normally in the range of \(\times 20\) to \(\times 100,000\) with the optimum useful magnification being \(\times 20,000\) to \(\times 50,000\) depending on the type of specimen and the construction of the instrument\(^{120}\).

A schematic diagram of a scanning electron microscope is shown in Figure 3.13\(^{120}\). The important features are: i) an electron gun and a means of focusing a beam of electrons on the specimen, ii) a system of electromagnetic lenses used to demagnify the electron beam diameter to 5-10 nm across the specimen, and iii) a means of detecting the response from the specimen and a display system.
Figure 3.13 Diagram of image formation in a scanning electron microscope. 

For some specimens preparation is very simple. The sample merely has to be attached to a stub by some adhesive and a conductive path provided from the specimen to the stub using conducting paint to bridge the thin adhesive layer. If the specimen is not a good conductor, it should be coated with a thin layer (100-500 Å) of conducting material (often gold, silver or palladium alloy). 

A Leica Cambridge Stereoscan S360 scanning electron microscope was used for this study. Samples were prepared from the fracture surfaces of the composite IPNs, broken after freezing in liquid nitrogen, and gold sputtered-coated.

3.3.5 Thermogravimetric Analysis (TGA)
Thermogravimetric analysis is a technique in which a known mass of sample is continuously weighed as it is exposed to heat. The resulting weight change is recorded as a function of temperature (or time) in a controlled atmosphere. The thermogram so obtained gives information concerning the thermal stability and compositions of the sample. For a polymer system, the effect of additives, blending, network structure etc. on the degradation process can be studied. However, to yield accurate and useful information, the individual decomposition weight loss must be well resolved. It
has been known that the most effective method of enhancing resolution in TGA is slowing the heating rate, which leads to a longer experimental time\(^{(134,135)}\). A relatively new technique, high resolution thermogravimetric analysis (Hi-Res TGA), has been introduced, which provides increased resolution without increasing the experimental time required\(^{(136-140)}\).

High resolution TGA, TGA 2950 was used to trace the thermal degradation of IPNs. This technique differs from the conventional TGA in the method of heating. While a constant heating rate is applied to the sample in conventional TGA, in high resolution TGA, the heating rate is varied, between a fixed minimum and a maximum, as a function of weight change in the sample (%/min). Dependent variables to this technique are two experimental parameters; i) resolution setting and ii) sensitivity setting. The resolution setting controls the temperature at which the transition will occur by selecting the reaction rate (%/min) and accordingly causes change in heating rate. The closer the reaction is to the isothermal decomposition temperature, the lower the reaction rate and the longer the reaction will take. The sensitivity setting controls the response of the system to changes in the rate of reaction (%/min). Larger sensitivity settings cause the system to be more reactive or sensitive to small changes in the rate of reaction. Lower sensitivity settings dampen this result. Generally, it is the best to adjust resolution first with sensitivity set to a low value. After a good result is obtained, then, an adjustment in sensitivity can be made to obtain a resolution improvement. Independent variables are the rate of weight change, time and temperature. The result is the ability to compute directly the appropriate heating rate of the current weight change condition\(^{(136)}\).

Samples of 8-12 mg were suspended from the balance by a long platinum wire in a furnace that can be heated at a given rate. Samples were examined in a nitrogen atmosphere from room temperature to 520 °C by the dynamic rate mode with an initial heating rate of 50 °C/min. The resolution setting 4 was chosen with sensitivity setting at 2\(^{(137)}\).
3.3.6 Tensile Study

The prime consideration in determining the general utility of a polymer is its mechanical behaviour, the deformation and flow characteristics under stress\(^{(101)}\). Tensile testing is a widely used basic measurement of the mechanical properties and also often considered as an indicator for quality control proposes. This test involves observing the behaviour of a polymer as tension is applied to it in order to elongate it to the point where it ruptures\(^{(7,141)}\).

Testing usually consists of securing a standard test sample between two sets of grips. One set of grips is fixed and the other is attached to a moving crosshead and load-cell arrangement. The sample used is usually of a dumb-bell shape so that breaking occurs in the central area away from the grips region. Crosshead speed depends on the nature of the polymer material. It should be noted that test speed will influence tensile behaviour dramatically. The general aim is to use a speed that allows all polymers to be tested in the same timescale.

The tensile testing results are usually shown as a plot of the stress versus the elongation (strain). See Figure 3.14.

The following tensile parameters were calculated\(^{(101,142)}\).

i) Tensile strength (\(\sigma\)) - the maximum tensile stress which the test piece is capable of supporting.

\[
\sigma = \frac{F}{A} \text{ (MPa)}
\]  

(3.7)

Where \(F\) = force, in N

\(A\) = initial cross-sectional area of the sample, in \(\text{mm}^2\)

ii) Elongation at break (\(\varepsilon\)) - the extent of elongation when the sample ruptures

\[
\varepsilon(\%) = \frac{L - L_o}{L_o} \times 100
\]  

(3.8)

Where \(L\) = length between reference marks at break, in mm

\(L_o\) = initial gauge length, in mm.
iii) Elastic modulus (modulus of elasticity or Young's modulus) - the ratio of applied stress to the strain it produces in the region where strain is proportional to the stress, i.e. in the initial straight-line portion of the stress-strain curve. Modulus is primarily a measurement of resistance to deformation or the stiffness of a material.

\[
\text{Modulus} = \frac{\Delta \sigma}{\Delta \varepsilon} \text{ (MPa)} \tag{3.9}
\]

where \(\Delta \sigma = \) the difference in stress between two points on the straight line
\(\Delta \varepsilon = \) the difference in strain between the same two points

The tensile testing was carried out by using a Lloyd model 2000R instrument equipped with a 500 N load cell, while the crosshead speed was maintained at 50 mm/min. Small dumbbell specimens were cut from the IPN sheets using a die punch cutter. Three to five specimens were tested at room temperature to obtain an average value for each sample of IPNs. The points for the calculation of elastic modulus were at \(\varepsilon_1 = 0.0\) and \(\varepsilon_2 = 0.1\).

\[\text{Stress (}\sigma\text{)}\]
\[\text{Strain (}\varepsilon\text{)}\]

\(\text{Figure 3.14 Stress-strain plots from tensile testing: (a) rigid plastic, (b) flexible plastic, (c) soft material.}\)
CHAPTER 4

STUDY OF PUR/PEMA IPNs
CHAPTER 4

STUDY OF PUR/PEMA IPNs

It has been reported\textsuperscript{(10-12,143-145)} that an enhancement of polymer properties may be achieved by the formation of micro-heterogeneous systems in which one component is glassy whilst another remains rubbery at room temperature. By using IPN technology together with varying the relative amounts of each constituent polymer, the properties of polymer systems can be altered to the required application. It is generally known\textsuperscript{(146)} that polymers form very useful damping materials near their glass transition temperature, T\textsubscript{g}, as a result of the onset of coordinated molecular motion, maximizing dissipation of the mechanical energy as heat. Application of such polymers to vibrating substrates leads to reduction of mechanical vibrations, which decreases emitted noise and reduces substrate fatigue. Among the different types of polymeric materials, IPNs are especially useful because of their broad glass transition regions\textsuperscript{(147)}.

In this study, a series of polyurethane/poly(ethyl methacrylate) interpenetrating polymer networks, PUR/PEMA IPNs, with different compositions and crosslink densities was investigated in terms of glass transition behaviour, morphology, phase continuity, mechanical and thermal properties. The crosslinked elastomeric PUR was intimately combined with a high glass transition plastic, PEMA, by the simultaneous IPN technique. Polymerisation of the constituent components involving step and radical chain reactions makes them suitable for non-interfering reactions required in simultaneous IPN preparation\textsuperscript{(20,145)}. The PUR and PEMA are considered\textsuperscript{(148)} as a semi-miscible polymer pair with solubility parameters, \(\delta\), of 20.5 (J/cm\textsuperscript{3})\textsuperscript{1/2} and 18.3 (J/cm\textsuperscript{3})\textsuperscript{1/2}, respectively.
4.1 PUR/PEMA IPN COMPOSITION STUDY

The present study investigated a series of different simultaneous PUR/PEMA IPN compositions. The PUR network was based on TMXDI, PPG1025, TMP, and SnOct, with PPG1025:TMP ratio of 3:1, whereas PEMA network was prepared containing 5 mol % TEGDM and initiated by AIBN (Chapter 3). The aim of this work was to elucidate the influences of IPN composition ratio on morphology and properties of IPNs. The samples were prepared and analysed by several characterisation techniques. The results are as follows.

4.1.1 Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis, DMTA, provides information about the extent of molecular mixing resulting in changes of transition temperature. The shifting and broadening of transitions are generally used as an indicator for the actual occurrence of mixing and interpenetration in IPNs.

Table 4.1 Dynamic mechanical properties of PUR/PEMA IPN compositions and their homopolymer networks

<table>
<thead>
<tr>
<th>IPN composition ratio</th>
<th>Tg (°C)</th>
<th>Tan δ value at Tg</th>
<th>Inter-transition tan δ value at 50 °C (°)</th>
<th>Peak width (°) for tan δ&gt;0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>from</td>
<td>PUR</td>
<td>PEMA</td>
<td></td>
</tr>
<tr>
<td>100 PUR</td>
<td>-5</td>
<td>1.21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90/10</td>
<td>-2</td>
<td>0.93</td>
<td>0.24</td>
<td>53 (-16/37)</td>
</tr>
<tr>
<td>70/30</td>
<td>2</td>
<td>0.42</td>
<td>0.38</td>
<td>132 (-8/124)</td>
</tr>
<tr>
<td>50/50</td>
<td>-13</td>
<td>0.14</td>
<td>0.38</td>
<td>90 (37/127)</td>
</tr>
<tr>
<td>30/70</td>
<td>-</td>
<td>0.14</td>
<td>0.50</td>
<td>74 (37/111)</td>
</tr>
<tr>
<td>10/90</td>
<td>-</td>
<td>0.14</td>
<td>0.20</td>
<td>63 (63/126)</td>
</tr>
<tr>
<td>100 PEMA</td>
<td>-</td>
<td>0.14</td>
<td>0.12</td>
<td>57 (76/134)</td>
</tr>
</tbody>
</table>

* Tan δ value at intermediate transition temperature, between Tgs of the two component polymers: -5°C and 105°C for polyurethane and poly(ethyl methacrylate), respectively. High tan δ values provide information about the degree of miscibility / component mixing in the polymer blend.
**Figure 4.1** Bending tan δ versus temperature plots for the PUR homopolymer and the PUR/PEMA IPNs of different composition: 90/10, 70/30 and 50/50.

**Figure 4.2** Bending tan δ versus temperature plots for the PUR/PEMA IPNs of different compositions: 50/50, 30/70, 10/90 IPNs and the PEMA homopolymer.
Figure 4.3 Storage modulus-temperature curves for PUR, PEMA and PUR/PEMA IPNs of different compositions.

Figure 4.4 Temperature range for PUR, PEMA and PUR/PEMA IPN compositions area which \( \tan \delta > 0.3 \).
The effect of PUR/PEMA composition ratios on dynamic mechanical properties of the IPNs are summarised in Table 4.1. The dynamic mechanical properties, storage modulus ($E'$) and loss factor ($\tan \delta$), over a range of temperature for different IPN compositions and individual homopolymer components are shown in Figures 4.1 to 4.3.

The literature\(^{(149-152)}\) indicates that only a miscible polymer pair produces an IPN with a single transition at intermediate temperature between the Tgs of the components. A semi-miscible polymer pair generally results in increased molecular mixing, then shifts or broadening of the component Tgs occur to a certain extent depending upon both the compatibility and the relative proportions of the constituent polymers. An immiscible polymer pair, on the other hand, exhibits two well-separated glass transitions.

DMTA plots of the PUR/PEMA IPNs (Figures 4.1 and 4.2) evidently show that the two polymers produced a semi-miscible system. As can be seen from the plots, single transition peaks were observed at both ends of the composition range, 90/10, 30/70, and 10/90 PUR/PEMA IPNs. Each composition produced an inward-shift of $\tan \delta$ glass transition together with a broader peak. Comparing the PUR homopolymer possessing a Tg at $-5°C$, a small shift to $-2°C$ was shown by the 90PUR/10PEMA IPN. At the other end of the composition range, the PEMA-rich transition inwardly shifted from $105°C$ for PEMA homopolymer to $97°C$ and $77°C$ for the 10/90 and 30/70 PUR/PEMA compositions, respectively.

A significant change in the shape of the $\tan \delta$ plot took place at the 70PUR/30PEMA composition where two prominent shoulders of PUR and PEMA-rich regions appeared at $2°C$ and $94°C$, respectively. The striking features of the $\tan \delta$ curve were an increase in intermediate plateau between the two transitions and a reduction in the $\tan \delta$ peaks. The curve was broad and almost rectangular in shape with a considerable high damping temperature interval. Glass transition broadening has been reported\(^{(118,153-155)}\) in IPNs prepared from semi-miscible polymers. Explanations of the broadening include micro-heterogeneity of the system with some extent of molecular
mixing and fine dispersion of the component domains. As the amount of PEMA component was increased to the mid-composition range, the 50PUR/50PEMA IPN, the tan δ curve revealed a dominant PEMA transition at 88°C, reflecting a change in IPN morphology, in which, perhaps, the PEMA phase became continuous. This was supported by the results from other characterisation techniques discussed in the following part of this chapter. At this composition, a fairly small shoulder of PUR-rich phase transition was observed at -13°C, which was even lower than the Tg of polyurethane homopolymer. This could be on account of incompletely formed PUR network containing defects such as loose chain ends.

Hourston et al. have employed the loss factor value at the inter-transition region as an indicator for degree of miscibility in polymer blends. This measurement is a convenient way of quantifying the level of mixing between the constituent polymers. As can be seen from Table 4.1, the inter-transition tan δ values, in other words, the extent of molecular mixing, increased with increasing of PEMA composition. The highest value of 0.50 was exhibited by the 30PUR/70PEMA IPN in which a single broad peak was obtained from the tan δ versus temperature plot. Further increase in PEMA content reduced the value to 0.20 as seen from the 10PUR/90PEMA IPN.

Figure 4.3 shows the storage moduli versus temperature for all IPN compositions. As demonstrated in this figure, there was no sign of gross phase separation morphology which would be noticed as sharp drops at the Tgs of both homopolymers. Compared with their homopolymers each IPN composition produced an inward shift and broadened the transition interval along with a concomitant increase in the modulus at the inter-transition region as the amount of the second network was increased. At room temperature, the PUR network showed the lowest modulus, whereas the crosslinked PEMA produced the highest value and the moduli of IPNs fell in between the values from their constituent polymers. With increasing PEMA content, the higher storage modulus reflected a gradual change in viscoelastic properties from elastic-like to a glassy material.
Corresponding with the data obtained from tan δ plots, single glass transitions were shown by the 90/10, 30/70 and 10/90 PUR/PEMA IPNs (Figure 4.3). It can be inferred that these IPN systems showed a great amount of molecular mixing as a result of the semi-miscibility of the constituent polymers. Therefore, there was no appreciable phase separation observed, or that the phase domains were so small that phase separation could not be detected. However, evidence of some degree of phase separation indicated by two-step broad modulus with slight changes of slope was found from the 70/30 and 50/50 PUR/PEMA IPN compositions. In the cases of both IPNs, it should be noted that the locations of Tgs were difficult to detect accurately, especially for the 70PUR/30PEMA composition, where a gradual decrease in storage modulus, almost a straight line over a certain range, was observed.

As already stated, polymers strongly damp noise and vibration over a limited temperature range around their glass transitions. The fundamental nature of damping in polymers arises from the onset of coordinated chain motion\(^\text{156}\). As a frozen segment obtains energy through mechanical deformation, the onset of molecular motion converts it to thermal energy\(^\text{70,157}\). Polymer blends with extensive, but incomplete, molecular mixing have a broad region of high damping extending over a temperature range between the two homopolymer transitions\(^\text{67,158-160}\). The broadening and increasing temperature range of damping have led to materials of interest in noise and vibration damping. Possessing tan δ values greater than 0.3 over a temperature range superior to 70°C, a polymeric material is considered to have good damping capability\(^\text{161}\).

A plot of temperature ranges for the IPN series exhibiting tan δ higher than 0.3 is shown in Figure 4.4. The crosslinked PUR displayed the shortest temperature range for potential damping, a range of 40°C, centred around -5°C, where the Tg was located. As the proportion of second network was increased, the range became broader and shifted to higher temperature. A dramatic increase in temperature range occurred at the 70PUR/30PEMA composition where the range spanned over 132°C from -8°C to 124°C. As a result, this material can be potentially useful in sound and vibration damping. Further incorporation of PEMA composition shortened the temperature
range, but still shifted it to higher temperature, closer to the transition of the PEMA network.

4.1.2 Modulated-Temperature Differential Scanning Calorimetry

In order to make a further investigation, IPNs of different compositions and their homopolymers were characterised by the relatively new technique, M-TDSC. The signals from differential heat capacity, dCp/dT, provide useful information as they are sensitive to glass transition temperature, miscibility and molecular mixing of the polymer blends(113).

M-TDSC curves, in the form of the differential of heat capacity versus temperature plots, for the PUR, PEMA, and IPNs of all compositions are shown in Figures 4.5 and 4.6, while in Figure 4.7 the glass transition temperatures are plotted versus IPN composition. Differential heat capacity signal, dCp/dT, for the PUR and PEMA homopolymers showed single peaks of values 0.027 and 0.011 J.g⁻¹°C⁻¹ where the transition temperatures centred at -38°C and 80°C, respectively.

Beside the PUR and PEMA homopolymers, a single glass transition was observed only from the 90PUR/10PEMA IPN (Figure 4.5). The other IPNs exhibited some degree of phase separation by possessing two separate Tgs. However, the spanning of transition spectra over wide temperature ranges between the transitions of pure PUR and PEMA implied that gross phase separation did not take place. Each morphology was related to a particular transition which together constitutes a transition spectrum(116). Addition of the second network into the IPN up to the 50PUR/50PEMA composition caused little change in the location of the PUR transition. Further addition of PEMA to 30PUR/70PEMA IPN shifted the transition to -15°C (Figure 4.7). For the 70/30 and 50/50 PUR/PEMA IPNs, PEMA transition spectra were very broad and it was difficult to identify the locations of Tgs. The same situation was observed from the 10PUR/90PEMA composition, where a broad shoulder appeared at the PUR transition.
**Figure 4.5** Plots of differential of heat capacity versus temperature for polyurethane, 90/10, 70/30, and 50/50 PUR/PEMA IPNs.

**Figure 4.6** Plots of differential of heat capacity versus temperature for 50/50, 30/70, 10/90 PUR/PEMA IPNs, and PEMA homopolymer.
Figure 4.7 Transition temperatures of PUR/PEMA IPN compositions from M-TDSC technique.

Figure 4.8 Transition temperatures of PUR/PEMA IPN compositions from DMTA technique
Figures 4.7 and 4.8 show the Tgs of the IPNs and homopolymers measured by M-TDSC and DMTA. As these techniques are based on different principles of measurement, different transition temperatures were produced. Transition temperatures obtained from M-TDSC were lower than those from DMTA. However, information observed from both techniques supported each other by a similar trend of changes in transition.

Most of the multi-component polymeric materials exhibit some degree of phase separation. Some of which show transitions spanning wide temperature ranges between the transitions of the homopolymers indicating large regions of interphase and mixed phases. These features play a major role in controlling the morphology, and the properties of the blends\(^{162,163}\). The ability to understand interphases and molecular mixing has been recognised as an important key in new material development. The study of interphase fractions has now been widely reported\(^{164,165}\) to be able to be estimated by means of thermal analysis techniques.

In this study, the M-TDSC was used as a quantitative thermal method to determine the the extent of molecular mixing in IPNs of different compositions\(^{116}\). The fact is that the glass transition temperature of a polymer system appears as a result of various chain segment motions. A polymer system can be considered as containing many sub-systems, 1, 2, ..., n, corresponding to different segmental chain lengths. Glass transition temperatures are \(T_g\) for sub-system 1, ..., \(T_g\) for sub-system n, and overall glass transition is a consequence of all different segmental motions\(^{115,116}\). The application of this thermal method assumes that a polymer blend comprises a number of individual phases. The interphase and the rest of the system can be modelled as a series of discrete fractions each with its own \(T_g\)\(^{116}\). By measuring the increment of heat capacity signal over a range of transition temperature, the extent of mixing and total interphase content in multicomponent polymer system can be studied\(^{115,116}\).

From TEM results (See 4.1.3), beside the black PUR-rich phase and the white PEMA-rich phases, the micrographs also showed different extents of interpenetration in mixed phase indicating by different shades of gray at the boundaries between the PUR and PEMA-rich phases. The mixed phases in IPNs are considered containing three
Chapter 4

PUR/PEMA IPNs

sub-systems representing the individual phases each with its own characteristic increment of heat capacity. These sub-systems are two miscible blend-like IPN phases where the transitions slightly shifted from the PUR and PEMA-rich phases and the diffuse interphase-like IPN phase. The latter exhibits highest degree of interpenetration showing its transition temperature in the middle of the dC/dT curve. In a further investigation, the areas under M-TDSC curves were resolved into five symmetrical peaks representing the individual phases. This process was computed on the basis of a Gaussian equation. The disintegration of area under dCp/dT curve for all IPN compositions can be inferred from the plots illustrated in Figures 4.9 to 4.13. In these plots, the original dCp/dT signals obtained from M-TDSC are shown by black diamonds. The symmetrically resolved peaks representing: PUR-rich (peak no.1), miscible blend-like IPN (peaks no.2 and 4), diffuse interphase-like IPN (peak no.3), and PEMA-rich phase (peak no.5), are presented by dashed lines while the solid curves are the overall dCp/dT calculated from the individual resolved peaks. Here, a perfect match between the original dCp/dT signal and the overall dCp/dT signal is required in order to reduce errors from the analysis.

![Graph](image)

**Figure 4.9** The differential heat capacity versus temperature plot for the 90/10 PUR/PEMA IPN.
Figure 4.10 The differential heat capacity versus temperature plot for the 70/30 PUR/PEMA IPN.

Figure 4.11 The differential heat capacity versus temperature plot for the 50/50 PUR/PEMA IPN.
Figure 4.12 The differential heat capacity versus temperature plot for the 30/70 PUR/PEMA IPN.

Figure 4.13 The differential heat capacity versus temperature plot for the 10/90 PUR/PEMA IPN.
Data obtained from peak resolution for each phase in the IPNs including the peak centre, the peak area and the percent peak area, are listed in Table 4.2.

**Table 4.2 Data from the integration of dCp/dT signal for all IPN compositions**

<table>
<thead>
<tr>
<th>IPN</th>
<th>Peak No.</th>
<th>Peak centre</th>
<th>Peak area</th>
<th>% Peak area</th>
<th>% Mixed phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>90/10 IPN</td>
<td>1</td>
<td>-35</td>
<td>0.522</td>
<td>83.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-15</td>
<td>0.021</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-3</td>
<td>0.030</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>41</td>
<td>0.046</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>77</td>
<td>0.006</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>70/30 IPN</td>
<td>1</td>
<td>-34</td>
<td>0.392</td>
<td>57.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-10</td>
<td>0.068</td>
<td>9.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>20</td>
<td>0.134</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>58</td>
<td>0.075</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>80</td>
<td>0.181</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>50/50 IPN</td>
<td>1</td>
<td>-35</td>
<td>0.271</td>
<td>43.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-13</td>
<td>0.029</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1</td>
<td>0.133</td>
<td>21.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>46</td>
<td>0.192</td>
<td>30.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>83</td>
<td>0.002</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>30/70 IPN</td>
<td>1</td>
<td>-40</td>
<td>0.027</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-20</td>
<td>0.101</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>0.181</td>
<td>38.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>42</td>
<td>0.145</td>
<td>31.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>82</td>
<td>0.013</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>10/90 IPN</td>
<td>1</td>
<td>-39</td>
<td>0.028</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-16</td>
<td>0.044</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15</td>
<td>0.137</td>
<td>27.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>53</td>
<td>0.251</td>
<td>51.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>72</td>
<td>0.032</td>
<td>6.5</td>
<td></td>
</tr>
</tbody>
</table>

*Peak No.1: PUR-rich phase,
Peaks No.2 and 4: miscible blend-like interpenetrating components,
Peak No.3: diffuse interphase-like interpenetrating component, and
Peak No.5: PEMA-rich phase.
The integration of differential heat capacity signal obviously showed that different patterns of morphology and molecular mixing were found in each IPN composition. The majority of the 90PUR/10PEMA composition (Figure 4.9) comprised a PUR-rich phase with the area under peak of 83.5% (Table 4.2). The peaks of PEMA-rich phase and mixed phases were much less pronounced due to the low content of PEMA network.

From the 70PUR/30PEMA IPN (Figure 4.10), it can be clearly seen that there existed a multi-phase structure. Five different phases were obtained from the integration of dCp/dT signal. Compared to the 90PUR/10PEMA IPN, the evidence of these phases implied a major change in morphology. This corresponds well with the earlier finding from DMTA in which a significant change in shape of tan δ plot took place, together with an increase in intermediate plateau between the two transitions. In this IPN, the area of PUR-rich phase was 57.1% while the miscible blend phases were 9.9% and 10.9% and the interphase was found to be 19.5% of the overall composition.

About the same amount of interphase, 21.2%, was calculated from the 50PUR/50PEMA IPN (Figure 4.11). However, a significant increase in peak area of the miscible blend-like IPN near the PEMA transition to 30.6% was observed. Another interesting point should be noted that the IPN comprised only 0.4% of PEMA-rich phase. It might be concluded that even though the two compositions produced about the same amount of interphase, the 50PUR/50PEMA IPN probably had more interpenetrating structure with finer PEMA-rich domains. More information about morphology will be discussed later in the following part of this chapter.

The 30PUR/70PEMA composition (Figure 4.12) exhibited not only the highest diffuse interphase-like IPN area value of 38.7%, but also a considerable amount of the miscible blend-like interpenetrating phases, with values of 21.6% and 31%. The tan δ plot from DMTA supported this information with a single broad peak in the region of PEMA homopolymer and a maximum value of inter-transition tan δ height, 0.50, reflecting high degree of molecular mixing. Considering the PUR-rich phase, only
5.8% of area under peak was found from this IPN. This could be an indication of a significant change in morphology, perhaps phase inversion.

M-TDSC signal of the 10PUR/90PEMA IPN (Figure 4.13) appeared to be PEMA-rich phase predominant with a broad spectrum at low temperature which was difficult to assign to the Tg of PUR. An indication about component mixing could be seen from the single curve peaking at 50°C which was 30°C inwardly shifted from the PEMA transition. Other supporting data about mixing was shown by the fairly high amount of interphase, 27.9%, and the miscible blend-like IPN peak values of 8.9% and 51% of the overall area under the curve.

4.1.3 Transmission Electron Microscopy

TEM investigation was conducted in order to study the effect of composition ratios on the IPN morphology. The image produced by this technique reveals information about molecular mixing and the size and shape of domains. Since the pictures are two-dimensional, the spherical domains observed in the study might be spheres, interconnected cylindrical or even rod-like structures. In order to gain better phase contrast in the micrographs, the PUR component in IPN samples was stained with OsO₄. Thus, the darker areas in the micrographs indicate PUR phases or contain high PUR content, while the lighter areas represent the PEMA phase. The micrographs of these IPN compositions are shown in Figures 4.14 and 4.15.

TEM micrographs confirmed the DMTA results that showed no discrete sharp glass transition for all IPN compositions indicating some extent of molecular mixing. There was no gross phase separation observed from the micrographs. At the outer composition ranges, 90/10, 30/70, and 10/90, the IPNs showed very fine morphology with the matrix of the major component and blurred domains of the other finely dispersed in it. In addition, single broad tan δ transition peaks were observed from these samples by the DMTA measurements.
Figure 4.14 TEM micrographs for PUR/PEMA IPN compositions: (a), (b) 90/10 IPN, and (c), (d) 70/30 IPN.
Figure 4.15 TEM micrographs for PUR/PEMA IPN compositions: (a), (b) 50/50IPN, (c), (d) 30/70 IPN, and (e), (f) 10/90 IPN
Although mixing took place at certain levels and network interpenetration was extensive, true solution between the constituent polymers apparently did not occur. The mid-range compositions, 70/30 and 50/50 PUR/PEMA IPNs, showed similar morphology with cellular structures suggesting lower a degree of component mixing. The micrographs corroborated the evidence of broad transitions stretching in between the Tgs of homopolymers as seen from DMTA.

At high magnification, micrographs of the 90PUR/10PEMA composition (Figures 4.14-a,b) displayed very fine white PEMA domains within a range of 10-50 nm dispersed in a dark PUR matrix. The morphology considerably changed as the amount of second network was increased to the 70PUR/30PEMA composition (Figures 4.14-c,d). For the 70PUR/30PEMA IPN, obviously two-phase morphology representing by white interconnected PEMA domains of 50-300 nm stretching through the matrix of PUR were observed. Beside the dark PUR matrix and white PEMA domains, TEM micrograph at 50k magnification revealed a high extent of interphase which can be seen by the different shades of gray dispersing in the PUR matrix and especially at the phase boundaries around PEMA domains. In other words, phases of distinct compositions did not exist in this IPN. The broad DMTA transition obtained from this composition may be considered as a result of interphase and miscible blend areas of varying compositions that could contribute independent transitions. Moreover, a similar pattern of morphology was observed from the micrograph of the 50PUR/50PEMA composition (Figures 4.15-a,b). With further increase of PEMA content, the white domains became bigger and more interconnected, while the PUR phases decreased in size. Interpenetration between the two networks can be noticed from the gray areas at the boundaries between domains and matrix indicating molecular mixing between the two components.

The 30PUR/70PEMA composition revealed a significant change in morphology (Figures 4.15-c,d). The domains became progressively smaller and less distinct. The cellular morphology was replaced by a much finer and more interpenetrating structure. This finding agreed well with the single transition curve illustrated by DMTA and the highest value of diffuse interphase-like IPN peak area obtained from
M-TDSC. At the 10PUR/90PEMA composition (Figures 4.15-e,f), as expected, the high amount PEMA appeared as a white matrix with very small gray domains of PUR dispersed in it.

4.1.4 Tensile Testing

The effect of composition ratio on tensile properties was studied. From the stress-strain curves, tensile stress at break, elongation at break and initial modulus were calculated. The results are summarised in Table 4.3. Plots of tensile properties versus PEMA composition are shown in Figure 4.16.

Literature\(^{(48,145,155,167,168)}\) has reported extensively on the multicomponent polymer systems based on elastomers and plastics. Tough plastics or reinforced elastomers are obtained depending upon the composition of the blends. In this work, considerable changes in mechanical properties were observed as the content of PEMA was increased in the IPNs. Tensile stress and modulus of elasticity exhibited similar trends. Both properties were improved when the plastic component was increased. On the other hand, elongation at break was found to decrease.

Tensile stress at break was very low for the elastic PUR at 1.2 MPa. The values gradually rose for the compositions with higher PEMA content. A sudden change in both tensile stress and modulus of elasticity was observed at the 10PUR/90PEMA IPN where the IPN behaved more like PEMA homopolymer. Tensile strength went up to 36.7 MPa, which was three times greater than the value of the 30PUR/70PEMA IPN. This could be an indication of a change in IPN morphology to be more predominant PEMA matrix with discontinuous PUR phases which agreed well with the TEM micrographs. A maximum tensile strength, 46.1 MPa, was measured from the crosslinked PEMA.

A corresponding pattern was observed from the measurement of modulus of elasticity. A gradual increase in modulus was noticed from PUR homopolymer up to 70PUR/30PEMA composition with values raising from 0.5 to 6.3 MPa. Further increase in PEMA component shifted the values up to 66.4 and 135 MPa for the 50/50
and 30PUR/70PEMA compositions, respectively. Again, evidence of a change in morphology exhibited through a significant increase of modulus was shown by the 10PUR/90PEMA IPN. Finally, the modulus reached a maximum at 353.8 MPa for the PEMA homopolymer.

Compared to the tensile stress, data obtained from elongation at break provided the opposite trend. Slight increase in elongation can be seen between the PUR homopolymer and the 70PUR/30PEMA IPN where elongation reached maximum value at 924%. Adding more PEMA component to the 50PUR/50PEMA composition led to a dramatic drop of elongation to 323%. Then, the value continually decreased to the value of 15% exhibited by PEMA homopolymer.

Table 4.3 Tensile properties of PUR/PEMA IPN composition and their homopolymer networks.

<table>
<thead>
<tr>
<th>IPN composition</th>
<th>Stress at break* (MPa)</th>
<th>Elongation at break* (%)</th>
<th>Modulus of elasticity* (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 PUR</td>
<td>1.2 (0.09)</td>
<td>815 (47.5)</td>
<td>0.5 (0.1)</td>
</tr>
<tr>
<td>90/10</td>
<td>1.3 (0.03)</td>
<td>850 (42.2)</td>
<td>1.0 (0.05)</td>
</tr>
<tr>
<td>70/30</td>
<td>4.6 (0.1)</td>
<td>924 (19.6)</td>
<td>6.3 (0.3)</td>
</tr>
<tr>
<td>50/50</td>
<td>8.7 (0.1)</td>
<td>323 (25.4)</td>
<td>66.4 (6.8)</td>
</tr>
<tr>
<td>30/70</td>
<td>11.7 (0.2)</td>
<td>98 (19.1)</td>
<td>135.0 (25.4)</td>
</tr>
<tr>
<td>10/90</td>
<td>36.7 (1.3)</td>
<td>21 (8.6)</td>
<td>294.1 (20.1)</td>
</tr>
<tr>
<td>100PEMA</td>
<td>46.1 (0.3)</td>
<td>15 (2.1)</td>
<td>353.8 (25.1)</td>
</tr>
</tbody>
</table>

*standard deviation values are shown in brackets
Figure 4.16 Tensile properties of PUR/PEMA IPNs versus % PEMA composition.
4.1.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) provides an important tool in the study of the complex thermal degradation pathways for polymer systems. The effects of additives, blending, network structure etc. on the degradation can be investigated by measuring the weight change as the temperature of the sample is increased.

Figures 4.17, 4.18 and 4.19 show the TGA thermograms and derivative weight loss plots for PUR, PEMA and the series of IPNs. Thermal stability of polyurethanes has been extensively studied\(^{169-172}\) because of the great importance of this material. It is generally known that polyurethanes are not very thermally stable polymers and the onset degradation temperature of the urethane bond depends on the type of isocyanate and alcohol involved\(^{113}\). The three basic thermal decomposition mechanisms of polyurethane are: dissociation of the urethane bond into its starting components, i.e., alcohol and isocyanate; breaking of the urethane bond with formation of primary amine, carbon dioxide, and an olefin; and, finally, splitting of the urethane bond into secondary amine and carbon dioxide\(^{166,173}\).

![Figure 4.17 TGA thermograms for PUR, PEMA, and different compositions of IPNs](image_url)
Figure 4.18 Derivative TGA curves for the PUR, 90/10, 70/30 and 50/50 PUR/PEMA IPNs.

Figure 4.19 Derivative TGA curves for the 50/50, 30/70, 10/90 PUR/PEMA IPNs and PEMA.
Chapter 4  

PUR/PEMA IPNs

The TGA curve for PUR (Figure 4.17) displayed two distinct regions of weight loss between 235°C and 400°C. A similar pattern of PUR degradation was reported earlier by Lee and Ko[174]. From their work, the initial degradation was shown to start with the hard segments and the second degradation process resulted from degradation of soft segments and the loss of all volatile materials. Degradation of PEMA homopolymer was shown by considerable weight loss initiating at 272°C and ending at 450°C (Figure 4.17). The thermal degradation of PEMA has been reported to be similar to that of PMMA[129,130]. Kashiwagi et al.[131] described the degradation of PMMA as proceeding in three steps: initially, scission of the head-to-head linkages, secondly, scissions initiated from vinylidene ends, and finally, random scissions within the polymer chains.

TGA analysis of a series of PUR/PMMA IPNs by Kim et al.[56] showed an increase in the weight retention with increasing PMMA content, and all the IPNs exhibited a greater heat stability than the individual components. They attributed this to the

Figure 4.20 Temperatures of derivative weight loss peaks for PUR, PEMA and composition IPNs.
presence of the unzipped PMMA monomer, which acted as a radical scavenger for the radicals produced by polyurethane degradation, thus delaying the degradation. However, different information was found here. From figure 4.17, it was apparent that none of the IPNs had greater thermal stability than either of the homopolymers.

Similar to the PUR, a two-step degradation was observed from derivative weight loss curve for the 90PUR/10PEMA IPN (Figure 4.18). However, the onset of the first step degradation shifted to higher temperature and peaked at 289°C which was very close to the first peak of PEMA degradation at 292°C (Figure 4.19). This could be due to the dispersion of very fine PEMA domains in the PUR matrix as seen from the TEM micrographs. See Figures 4.14. At higher PEMA content, the 70PUR/30PEMA IPN, two main degradation steps were also found at 263°C and 326°C, but the peaks became broader with three overlapping shoulders around 246°C, 300°C and 365°C (Figure 4.20) illustrating the several steps in the degradation mechanism which could arise from the more complicated morphology. The TEM micrograph and the DMTA results of this IPN clearly showed a considerable change in morphology with some extent of mixing and interphase between the two components.

In the 50PUR/50PEMA IPN, the overlapping shoulders became prominent with minor changes in position of the peaks (Figure 4.20). The degradation for this composition proceeded in a similar way as observed from the 70PUR/30PEMA IPN, except for the appearance of the last peak at 425°C which could be a result of the final step of the PEMA degradation. According to the TEM micrographs, one major difference in morphology between the two IPNs was the size of the phase domains in which the PEMA domains appeared to be larger and more interconnected in the 50PUR/50PEMA IPN. At the 30PUR/70PEMA composition, several steps of degradation were again detected. All the peaks centred around the same positions as those observed from the 50PUR/50PEMA IPN (Figure 4.19). The differential weight loss curve for the 10PUR/90PEMA IPN displayed a significant change. Like PEMA homopolymer, the IPN exhibited one major step of degradation in which 60% of sample weight was lost. The degradation then carried on with three small steps around 313°C, 370°C and 434°C.
4.2 70PUR/30PEMA IPN CROSSLINKING STUDY

Further study was concentrated on the 70PUR/30PEMA IPN as this composition was found to be potentially useful for damping. In the previous section, the IPNs were shown by DMTA to possess tan δ values greater than 0.3 covering a temperature range of 132°C, from -8°C to 124°C. Evidence of micro-heterogeneous morphology in this IPN was provided by the inter-transition tan δ value (Figure 4.1), as well as the continuously almost linear storage modulus curve (Figure 4.3), and most important, the co-continuous morphology seen from TEM micrographs (Figure 4.14). Moreover, M-TDSC showed high content of interphase and mixed phases between the two transitions of the constituent polymers.

Crosslink density\(^{(175)}\) is one of the crucial factors in determining the morphology and properties of simultaneous IPNs. It is the presence of chemical crosslinking that brings about the dominant features in IPNs compared to other multicomponent polymer systems. Although most IPNs are phase separated, the presence of crosslinks reduces the phase domain size and provides a method of controlling their properties. As in the previous study, the effects of crosslink density on damping properties, component mixing, thermal degradation and mechanical properties were characterized by DMTA, M-TDSC, TGA and tensile testing.

4.2.1 Dynamic Mechanical Thermal Analysis

An investigation of crosslink density in the PUR and PEMA homopolymers is also represented here as a basis of comparison for the study of crosslink density in the 70PUR/30PEMA IPN. In this research, the PURs were prepared at a fixed ratio of isocyanate/hydroxyl group (1.1/1). The amount of chemical crosslinking in the PUR component was varied by altering the ratio of difunctional polyol (PPG1025) to triol (TMP). Crosslinking in the PUR network could exert an important influence on the IPNs, since the gelation of PUR happens first. It is generally believed\(^{(176)}\) that the PUR network establishes the IPN properties to a great extent, since it very often represents the continuous phase and restricts the phase domain sizes of the second network.
Figure 4.21 Loss factor versus temperature data for PUR with different crosslink densities (PPG:TMP mole ratio).

Figure 4.22 Storage moduli versus temperature data for PUR with different crosslink densities (PPG:TMP mole ratio).
Figures 4.21 and 4.22 show the loss factor and storage modulus versus temperature for crosslinked PURs at varying diol/triol ratios while the plots for PEMA with different crosslinking levels (%TEGDM) are shown in Figure 4.23. It can be seen from DMTA that both PUR and PEMA networks were generally affected in the same manner by the variation of crosslink density. For highly crosslinked networks, the mobility of polymer chains is restricted, resulting in a shift of the glass transition to higher temperatures\(^{70}\). The PUR containing 4.5:1\ PPG:TMP exhibited a narrow transition peak at -8°C (Table 4.4), while the 3:1\ /\ PPG:TMP PUR showed the Tg at -5°C. Increasing the PPG:TMP ratio to 2:1 raised the transition to 2°C and broadened the peak.

A shift of Tg from 105°C to 112°C was observed from PEMA crosslinked with 5% and 7% TEGDM, respectively (Figure 4.23). The broadening of the tan δ peak could be explained\(^{99}\) by the heterogeneity of crosslink density, leading to a distribution of local transitions and a broad transition temperature. The plots of storage moduli versus temperature reflected the loss factor data. The modulus drop in Tg region
occurred at higher temperature as the crosslink density was increased. The modulus at the rubbery plateau region was also influenced\(^\text{70}\). As expected, the value increased with crosslink density.

**Table 4.4** DMTA data for the PUR and PEMA homopolymers and the 70PUR/30PEMA IPNs of different crosslink levels.

<table>
<thead>
<tr>
<th>Homopolymers</th>
<th>Crosslink levels</th>
<th>PUR Tg (°C)</th>
<th>Crosslink levels</th>
<th>PEMA Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 / PPG:TMP</td>
<td>2</td>
<td>5% TEGDM</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>3:1 / PPG:TMP</td>
<td>-5</td>
<td>7% TEGDM</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>4.5:1 / PPG:TMP</td>
<td>-8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**IPNs of different crosslink levels**

<table>
<thead>
<tr>
<th>70/30 IPN</th>
<th>IPN Tg (°C)</th>
<th>Tan δ at Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG:TMP/TEGDM</td>
<td>PUR PEMA PUR PEMA</td>
<td></td>
</tr>
<tr>
<td>2:1 / 5%</td>
<td>8</td>
<td>78</td>
</tr>
<tr>
<td>3:1 / 5%</td>
<td>2</td>
<td>94</td>
</tr>
<tr>
<td>4.5:1 / 5%</td>
<td>-9</td>
<td>75</td>
</tr>
<tr>
<td>3:1 / 2.5%</td>
<td>-2</td>
<td>75</td>
</tr>
<tr>
<td>3:1 / 7%</td>
<td>-1</td>
<td>98</td>
</tr>
</tbody>
</table>

Figures 4.24 and 4.25 show the loss factor and storage modulus versus temperature for the 70PUR/30PEMA IPNs at a fixed 5% TEGDM crosslink level in the PEMA and varied crosslink densities in the PUR networks (PPG:TMP ratio). The effect of crosslinking on dynamic mechanical properties of the 70PUR/30PEMA IPNs are given in Table 4.4, together with the transitions of the different crosslink density homopolymers.
Figure 4.24 Loss factor versus temperature data for the 70PUR/30PEMA IPNs with 5% TEGDM crosslinked PEMA and different crosslink densities (PPG:TMP mole ratio) in PUR networks.

Figure 4.25 Storage moduli versus temperature data for the 70PUR/30PEMA IPNs with 5% TEGDM crosslinked PEMA and different crosslink densities (PPG:TMP mole ratio) in PUR networks.
Figure 4.26 Loss factor versus temperature data for the 70PUR/30PEMA IPNs with 3:1/PPG:TMP crosslinked PUR and different crosslink densities (mole % TEGDM) in PEMA networks.

Figure 4.27 Storage moduli versus temperature data for the 70PUR/30PEMA IPNs with 3:1/PPG:TMP crosslinked PUR and different crosslink densities (mole % TEGDM) in PEMA networks.
The influence of PUR crosslink density can be seen by comparing the Tgs of the IPNs containing the same crosslink level in PEMA network. As expected, an increase in triol content limited the segmental mobility and shifted the location of loss factor peaks to higher temperature. The PUR transitions were -9°C, 2°C and 8°C for the crosslinked IPNs with PPG:TMP ratios of 4.5:1, 3:1 and 2:1, respectively. The variation of triol content affected the PEMA transition with a similar trend, as the Tgs shifted from 75°C to 94°C at the PPG:TMP ratios of 4.5:1 and 3:1. An exception from this was the highly crosslinked IPN containing 2:1/PPG:TMP in which an inward shift of PEMA transition appeared at 78°C. An obvious increase in loss factor was also detected from this IPN. This could be explained by the enforced component mixing of the tighter network which brought the transitions closer. Therefore, the transition in IPN might be a result of entrapped PUR in PEMA-rich phase. The latter can be confirmed by comparing the IPN transition to that of the homopolymer containing same crosslink density.

This series of IPNs was potentially useful for damping applications since the loss factor values were greater than 0.3 over wide range of temperatures: 123°C, 132°C and 133°C, for the IPNs with PPG:TMP ratios of 4.5:1, 3:1 and 2:1, respectively. Dual-phase continuity morphology in these IPNs was shown by the broad inter-transition plateau with high and approximately equal tan δ values indicating a high extent of component mixing. Evidence of mixing was noticed from the inward shifts of IPN transitions compared to those of homopolymers with the same crosslink density (Table 4.4). In the IPNs, the PEMA transitions were found to be between 11°C to 30°C lower than the corresponding homopolymers. This could have been because of the fact that the segmental movements of the rigid PEMA were less restricted when surrounded by the more flexible PUR networks, or more likely that the transition in IPN was not caused by the pure PEMA component, but by the PEMA-rich phase containing certain degree of mixed PUR. The storage moduli versus temperature plots (Figure 4.25) indicated the shifts of transition ranges to higher temperature as the crosslink density in PUR was increased.
Figures 4.26 and 4.27 show the effect of PEMA crosslinking levels on the DMTA properties of the IPNs, while the crosslinked PUR was fixed at a PPG:TMP ratio of 3:1. No significant effect on the PUR transition was observed from the increase of crosslinker content. The Tgs of PEMA in IPNs exhibited a corresponding trend to those of the homopolymers at the same crosslinking level such that higher crosslinking shifted the transition to higher temperature. The Tgs were 75°C, 94°C and 98°C for the IPNs containing 2.5%, 5% and 7%TEGDM, respectively. In addition, a decrease in PEMA loss factor at higher crosslink content was expected as a result of the restriction of molecular motion (Table 4.4).

4.2.2 Modulated-Temperature Differential Scanning Calorimetry

The effect of crosslinking on 70PUR/30PEMA IPNs was also investigated by M-TDSC. As PUR was the major component in the IPNs, M-TDSC study was done on the PUR homopolymers with three different PPG:TMP ratios: 2:1, 3:1, and 4.5:1 (Figure 4.28). Plots of the derivative heat capacity versus temperature for the 70PUR/30PEMA IPNs containing different crosslinking levels in PUR and PEMA are shown in Figures 4.29 and 4.30. Transition temperature data for the IPNs and PUR homopolymer are given in Table 4.5.

<table>
<thead>
<tr>
<th>Table 4.5 M-TDSC data for PUR and the 70PUR/30PEMA IPNs with varying crosslink densities.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUR homopolymer</td>
</tr>
<tr>
<td>2:1/PPG:TMP</td>
</tr>
<tr>
<td>3:1/PPG:TMP</td>
</tr>
<tr>
<td>4.5:1/PPG:TMP</td>
</tr>
<tr>
<td>3:1/PPG:TMP</td>
</tr>
<tr>
<td>3:1/PPG:TMP</td>
</tr>
</tbody>
</table>
Chapter 4  

Figure 4.28 Derivative heat capacity versus temperature for PUR homopolymers at varying PPG:TMP ratios.

The PUR containing 2:1/PPG:TMP exhibited the highest transition, at -36°C, as it was prepared containing highest crosslink density. The PURs made at lower crosslinking levels, PPG:TMP ratios of 3:1 and 4.5:1, showed lower transitions at -38°C and -39°C. A similar trend was observed in IPNs. With increasing crosslinking in the PUR network, the PUR transition in IPN shifted to higher temperatures (Figure 4.29). These Tgs were at -33°C, -34°C and -40°C for PPG:TMP crosslink ratios of 2:1, 3:1 and 4.5:1, respectively. Comparing the IPNs of varied PUR crosslink to their homopolymer networks, small degree shifts of PUR transition to higher temperature were observed in the IPNs. This could be due to the effect of molecular mixing between the PUR and PEMA networks, or another possibility could be differences in crosslink levels in homonetworks compared to those in IPNs.
Figure 4.29 Derivative heat capacity versus temperature plots for the 70PUR/30PEMA IPNs containing different PPG:TMP ratios and fixed 5%TEGDM.

Figure 4.30 Derivative heat capacity versus temperature plots for the 70PUR/30PEMA IPNs containing different % mole TEGDM and a PPG:TMP ratio of 3:1.
The influence of crosslinking in the PEMA network on the IPN transition is illustrated in Figure 4.30. Like the data obtained from DMTA, varying the amount of TEGDM crosslinker exerted small effect on the locations of PUR transitions in IPNs. A slight shift to lower temperature was found at -37°C from the IPN with 2.5% TEGDM crosslinker whereas a transition at -34°C was detected from the IPNs with 5% and 7% TEGDM. As expected, changes in the derivative heat capacity signals were more obvious at high temperature. Broader PEMA transitions shifting to higher temperature were noticed with an increase in PEMA crosslinker content. The highest transition of 62°C was shown by the IPN containing 7% TEGDM, while the Tgs at 61°C and 50°C were observed from the IPNs crosslinked with 5% and 2.5% TEGDM.

\[ \text{Figure 4.31 Derivative heat capacity versus temperature plot for the 70PUR/30PEMA IPN crosslinked with 2:1/PPG:TMP and 5\%TEGDM.} \]
Figure 4.32 Derivative heat capacity versus temperature plot for the 70PUR/30PEMA IPN crosslinked with 3:1/PPG:TMP and 5%TEGDM.

Figure 4.33 Derivative heat capacity versus temperature plot for the 70PUR/30PEMA IPN crosslinked with 4.5:1/PPG:TMP and 5%TEGDM.
**Figure 4.34** Derivative heat capacity versus temperature plot for the 70PUR/30PEMA IPN crosslinked with 3:1/PPG:TMP and 2.5%TEGDM.

**Figure 4.35** Derivative heat capacity versus temperature plot for the 70PUR/30PEMA IPN crosslinked with 3:1/PPG:TMP and 7%TEGDM.
Table 4.6 Data from the integration of dCp/dT signal for the 70/30 PUR/PEMA IPNs of different crosslink densities.

<table>
<thead>
<tr>
<th>70PUR/30PEMA IPN</th>
<th>Peak No.*</th>
<th>Peak centre</th>
<th>Peak area</th>
<th>% Peak area</th>
<th>% Mixed phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1/ PPG:TMP, 5% TEGDM</td>
<td>1</td>
<td>-32</td>
<td>0.442</td>
<td>61.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-8</td>
<td>0.051</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6</td>
<td>0.079</td>
<td>11.0</td>
<td>= 35.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>45</td>
<td>0.012</td>
<td>16.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>73</td>
<td>0.024</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>3:1/ PPG:TMP, 5% TEGDM</td>
<td>1</td>
<td>-34</td>
<td>0.392</td>
<td>57.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-10</td>
<td>0.068</td>
<td>9.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>20</td>
<td>0.134</td>
<td>19.5</td>
<td>= 40.3</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>58</td>
<td>0.075</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>80</td>
<td>0.181</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>4.5:1/PPG:TMP, 5% TEGDM</td>
<td>1</td>
<td>-40</td>
<td>0.342</td>
<td>54.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-20</td>
<td>0.050</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-4</td>
<td>0.106</td>
<td>17.0</td>
<td>= 39.9</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>46</td>
<td>0.093</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>65</td>
<td>0.032</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>3:1/PPG:TMP,2.5% TEGDM</td>
<td>1</td>
<td>-37</td>
<td>0.392</td>
<td>62.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-16</td>
<td>0.045</td>
<td>7.3</td>
<td>= 34.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-2</td>
<td>0.061</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>43</td>
<td>0.107</td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>71</td>
<td>0.019</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>3:1/ PPG:TMP, 7% TEGDM</td>
<td>1</td>
<td>-33</td>
<td>0.379</td>
<td>59.0</td>
<td></td>
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<tr>
<td></td>
<td>2</td>
<td>-10</td>
<td>0.043</td>
<td>6.7</td>
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<td>3</td>
<td>8</td>
<td>0.079</td>
<td>12.2</td>
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<td></td>
<td>4</td>
<td>53</td>
<td>0.104</td>
<td>16.2</td>
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</tr>
<tr>
<td></td>
<td>5</td>
<td>80</td>
<td>0.038</td>
<td>5.9</td>
<td></td>
</tr>
</tbody>
</table>

*Peak No.1 : PUR-rich phase,
Peaks No.2 and 4 : miscible blend-like interpenetrating components,
Peak No.3 : diffuse interphase-like interpenetrating component, and
Peak No.5 : PEMA-rich phase.
The extent of mixing and interphase content in the 70PUR/30PEMA IPNs with varied crosslink levels was examined by M-TDSC. The area under the dCP/dT versus temperature peaks were resolved into five symmetrical peaks representing the different phases: PUR-rich, miscible-blend like interpenetrating components, diffuse interphase-like interpenetrating component, and PEMA-rich phases. The resolved curves for each IPN are illustrated in Figures 4.31 to 4.35. The phase transitions and areas under peaks are summarised in Table 4.6.

Considering the IPNs containing PURs with varying crosslink level, it can be seen that the PUR-rich phase was located at higher temperature and became broader with increasing peak area as the extent of crosslinking was increased, corresponding to the finding observed from PUR homo-networks. The peak areas were 54.9% (at -40°C), 57.1% (at -34°C) and 61.7% (at -32°C) for PPG:TMP ratios of 4.5:1, 3:1 and 2:1, respectively. The broadening of these peaks resulted in the shifting of the second peaks, the miscible blend-like interpenetrating component, to higher temperatures. The peaks were centred at -20°C, -10°C and -8°C in the order of low to high extent of crosslinking. The location of other peaks were observed at different temperatures because of the different shapes of the dCP/dT signals. The mixed phase area values of 39.9%, 40.3% and 35% were calculated from the IPNs with PGG:TMP ratios of 4.5:1, 3:1 and 2:1, respectively. The fact that the peak areas from the ratios of 4.5:1 and 3:1 were particularly close, agreed with the findings from the DMTA curves. Both IPNs exhibited similar shape of tan δ signal. The only difference was that the shifting to higher temperature occurred in the IPN crosslinked with 3:1/PPG:TMP.

From the IPNs with varied PEMA crosslinking degrees, shifts of Tgs to higher temperature ranges were observed with an increase in TEGDM (Table 4.6). The highest range of transition was measured from the 7%TEGDM crosslinked IPN possessing transitions at -33°C and 80°C for the PUR-rich and PEMA-rich phases, while the lower crosslinked IPNs, 5% and 2.5%TEGDM, exhibited their phase transitions at -34°C, 80°C and -37°C, 71°C, respectively. Again, no significant trend was observed from the extent of mixed phase. The peak areas were 35.1%, 40.3% and 34.2% for the IPNs crosslinked with 7%, 5% and 2.5% TEGDM.
4.2.3 Thermogravimetric Analysis (TGA)

TGA studies were performed on three samples of IPNs prepared with different degrees of crosslinking. The plots are shown in Figures 4.36 and 4.37. In this study, it can be seen that the variation of IPN crosslinking had no effect on thermal stability, since the investigation revealed the same degradation pattern. The data of derivative weight loss versus temperature showed slight differences in terms of area under curves, whereas the locations of peaks stayed unchanged. A three-step reaction was observed from the plots where the onset of thermal degradation started around 225°C and was complete at about 440°C, with no residue.

Figure 4.36 TGA thermograms for the 70PUR/30PEMA IPNs of different crosslink densities.
**Figure 4.37** Derivative TGA curves for the 70PUR/30PEMA IPNs of different crosslink densities.
CHAPTER 5

SILICA-FILLED 70PUR/30PEMA IPNs
The use of fillers is one of several methods widely used to improve the properties of polymeric materials. Both basic scientific information and useful engineering data can be obtained from the introduction of an inorganic filler. In this chapter, a further investigation was undertaken on the 70PUR/30PEMA IPNs, because, in the previous chapter, the IPN showed a micro-heterogeneous morphology and a great potential for sound and mechanical energy absorption. The effects of silica filler on the IPN were examined in an effort to further broaden and heighten tan δ peak and, hence, improve the mechanical properties of the material.

The two grades of silica used as fillers in the study were products of Degussa Ltd. under the commercial names of Aerosil 380 and VN 3. Aerosil 380, a synthetic silica, is a fluffy, white amorphous powder. The product is widely used in industrial applications because of its extremely small particle size, spherical morphology, high surface area, unique surface chemistry and high purity. Aerosil 380 is manufactured under controlled reaction conditions to produce a product consisting of primary particle size approximately 5 nm which is relative to the product surface area having a range of 380 ± 30 m²/g. The latter grade of silica is called VN 3. This filler is also a white amorphous powder. However, it is composed of bigger average particle size approximately 50 μm. It was chemically prepared from sodium silicate by a reaction with sulphuric and hydrochloric acids. The filler properties can be varied by controlling some process variables such as reactant concentration, rate of addition of reactants, and reaction temperature (76,80).

Inorganic silica at 2.5%, 5%, 7.5% and 10% by weight was introduced into the 70PUR/30PEMA IPN system which had a PPG:TMP ratio of 3:1 and 5 mole% TEGDM crosslinker. The silica-filled samples were synthesised under the same
conditions as those unfilled IPN samples in the previous chapter. It was difficult to prepare an IPN sample when the filler content exceeded 10% by weight, especially with the very high surface area silica, Aerosil 380, because of the highly viscous IPN mixture prior to the polymerisation.

The special surface properties of synthetic silica, such as viscosity building, thickening and absorption, are related to the silanol group density of the silica surface and the extent of hydration\(^{(76)}\). There are three\(^{(76,80)}\) types of hydroxyl groups present on the surface of synthetic silicas, as shown in Figure 5.1: (1) isolated silanol groups, (2) vicinal (on adjacent silicon atoms) silanols or hydrogen bonded hydroxyls, and (3) geminal (two silanols on same silicon atom) silanols.

![Figure 5.1 Types of surface hydroxyl groups in synthetic silicas\(^{(80)}\).](image)

It is customary to add synthetic silicas to some polymer resins to make the material thixotropic, which prevents the draining or sagging of resin when applied to vertical surfaces\(^{(80)}\). The thixotropic behaviour of silica in resin can be further enhanced by using suitable hydroxyl-containing polar additives, such as ethylene glycol, as shown in Figure 5.2, thereby producing an overall increase in the viscosity of the system. A similar situation to this bridging effect was also present in this work involving the polyoxypropylene glycol used as one of the raw materials for the PUR network.
Characterisation of the silica-filled IPNs was undertaken using several techniques in order to examine the influences of both grades of silica on the glass transition behaviour, morphology, damping and mechanical properties. The results from these characterisations are as follows.

5.1 AEROSIL 380-FILLED 70PUR/30PEMA IPNs

5.1.1 Dynamic Mechanical Thermal Analysis
DMTA is widely used to study glass transition temperature behaviour and the morphology, i.e. the miscibility and phase continuity, of polymer blends as mentioned earlier. The data on the dynamic mechanical properties of Aerosil 380-filled 70PUR/30PEMA IPNs are listed in Table 5.1. The resulting bending loss factor and loss modulus spectra are illustrated in Figures 5.3 and 5.4.

In order to investigate the effect of Aerosil 380 on the 70PUR/30PEMA IPN, the behaviour of the bending loss factor was examined over a temperature range of -40°C to 140°C. See Figure 5.4. In this temperature range, despite being the major component, polyurethane did not exhibit a maximum value in tan δ, but instead the poly(ethyl methacrylate) did, at temperatures below the PEMA transition measured from the unfilled IPN.

![Ethylene glycol](image-url)
Figure 5.3 Bending loss factor versus temperature plots showing the effect of Aerosil 380 on the 70PUR/30PEMA IPN.

Figure 5.4 Bending loss modulus versus temperature plots showing the effect of Aerosil 380 on the 70PUR/30PEMA IPN.
Table 5.1 Effect of Aerosil 380 on the dynamic mechanical properties of the 70PUR/30PEMA IPN.

<table>
<thead>
<tr>
<th>% (wt) Aerosil</th>
<th>Tg, °C at tan δ max.</th>
<th>Tan δ value at Tg</th>
<th>Inter-transition tan δ height at 46 °C (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>380 PUR PEMA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>unfilled</td>
<td>2 94</td>
<td>0.42 0.44</td>
<td>0.38</td>
</tr>
<tr>
<td>2.5</td>
<td>-1 87</td>
<td>0.33 0.49</td>
<td>0.39</td>
</tr>
<tr>
<td>5.0</td>
<td>-2 83</td>
<td>0.30 0.60</td>
<td>0.45</td>
</tr>
<tr>
<td>7.5</td>
<td>-2 79</td>
<td>0.31 0.63</td>
<td>0.50</td>
</tr>
<tr>
<td>10.0</td>
<td>-5 79</td>
<td>0.31 0.72</td>
<td>0.54</td>
</tr>
</tbody>
</table>

* Tan δ value at intermediate transition temperature, between the two Tgs of unfilled 70PUR/30PEMA IPN, 29°C and 94°C, respectively.

The PEMA transition appeared at 94°C (tan δ 0.44) in the absence of filler. Incorporation of 2.5% Aerosil 380 shifted the transition down to 87°C (tan δ 0.49). Further increase in filler content brought down the transition to lower temperatures, giving an enhanced damping response at PEMA Tg and around the inter-transition temperature, 46°C. The 7.5% and 10% silica content IPNs exhibited the same transition at 79°C. However, the highest tan δ value of 0.72 was shown by the latter. In addition, there was a slight downward shift of the PUR transitions over the range of the filled system, in combination with a reduced tan δ value at Tg which was in contrast to the finding for the PEMA transition. As the filler was added, the PUR transitions decreased from 2°C (tan δ 0.42) shown by the unfilled to -5°C (tan δ 0.31) shown by the sample of 10% filler loading.

Similar reduced tan δ values in filled IPNs were reported by Lipatov and co-workers(91) in the study of reinforcing silica-filled sequential PUR/PS IPNs. On increasing the amount of silica, the loss factor height at the PUR transitions was seen to decrease. They attributed this to a restricted mobility of the chains in the PUR network where the filler was blended in before curing.
In another paper, an explanation of the influence of filler on the damping properties was proposed by Li et al.\textsuperscript{(97)}. They suggested two possible factors in connection with the damping ability for filled polymer systems. One is a decrease in free volume, which limits the mobility of molecular chains so that the damping value decreases. The other is an internal friction between the fillers and polymer chains, and between the filler particles themselves over the transition range, which increases as the movement of molecular chains becomes greater so that the damping ability increases. Beside the explanation in terms of molecular mobility, another possible answer for loss factor behaviour of the filled IPNs could be the difference in crosslink density between the unfilled and the filled IPNs. A small difference in crosslink densities of filled and unfilled PURs was found by Akay et al.\textsuperscript{(140)}. They attributed this to the presence of an active pigment, titanium dioxide, which may affect the distribution of crosslinking.

In this research, some chemical substances might have been adsorbed on the surface of silica particles, because of the high surface area and the hydrophobic nature of the filler. Consequently, in the presence of filler, IPNs of lower crosslink density could be formed. A clue may be seen from the loss factor spectra where the IPNs exhibited lower transitions as higher amounts of filler were incorporated in the systems. In the previous chapter, the DMTA curves for IPNs of varied crosslink densities exhibited corresponding changes in that reduced PUR crosslinking led to a slight downward shift of Tgs and a small drop of loss factor value, whereas a significant increase of loss factor together with the lower transitions was observed with decreasing PEMA crosslinker.

Figure 5.4 shows the loss modulus of the IPNs with added Aerosil 380 as a function of temperature. It can be seen that the use of filler resulted in an increase in loss modulus both at the glassy stage and also around room temperature, although the gradient of the curve did not increase as the filler weight fraction increased. Typical increases in modulus for the filled systems have been reported earlier\textsuperscript{(177,178)}. 
5.1.2 Modulated-Temperature Differential Scanning Calorimetry

Figure 5.5 shows the effect of Aerosil 380 on the differential of heat capacity of the IPNs. For convenience, the IPN glass transition temperatures measured by M-TDSC are collected in Table 5.2. The Tgs obtained from M-TDSC were found to be lower than those measured from dynamic measurement, though similar trends were observed from both techniques. Available literature\(^{177,179}\) also supports a variation of glass transition temperatures as high as 20°C for the same polymer depending on the method of measurement and on the thermal history of the sample.

<table>
<thead>
<tr>
<th>% (wt)</th>
<th>IPN Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosil 380</td>
<td>PUR</td>
</tr>
<tr>
<td>unfilled</td>
<td>-34</td>
</tr>
<tr>
<td>2.5</td>
<td>-36</td>
</tr>
<tr>
<td>5.0</td>
<td>-37</td>
</tr>
<tr>
<td>7.5</td>
<td>-37</td>
</tr>
<tr>
<td>10.0</td>
<td>-36</td>
</tr>
</tbody>
</table>

It is seen from Table 5.2 that the presence of filler resulted in a decrease of IPN transitions corresponding to the results from DMTA. In addition, the filler was found to have greater influence over PEMA than PUR in terms of transition temperatures. Glass transitions of the unfilled sample were detected at -34°C and 61°C. An addition of 10% wt Aerosil shifted the transitions down to -36°C and 53°C for PUR and PEMA-rich phases, respectively. Compared with the unfilled PEMA, transitions appeared to be more distinct for the filled samples of 2.5%, 5% and 7.5% filler content, in which the transitions were shown at 61°C, 57°C, and 54°C, respectively. Besides the shift of Tgs, increased filler loading also reduced the volume fraction of polymer in the composites, as a result the differential heat capacity values at Tgs were lower in filled samples.
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Figure 5.5 Differential heat capacity versus temperature plots showing the effect of Aerosil on 70PUR/30PEMA IPNs

5.1.3 Transmission Electron Microscopy

The TEM micrographs showing the effect of Aerosil 380 content are given in Figures 5.6-5.8. The morphologies of a series of PUR/PEMA IPNs were investigated in the previous chapter. TEM micrographs showed that the IPNs contained a two-phase structure, regardless of the proportion of network I to network II. The degree of phase separation and the domain size depended, however, on the proportion of the two compositions. In this section, the morphology of the Aerosil 380-filled 70PUR/30PEMA IPNs was observed using the same technique. TEM micrographs showing the effect of increase in filler content are given in Figures 5.6 to 5.8. A small sample of each IPN was stained by OsO₄, an effective staining agent for polyurethane(180). Thus, the dark areas on the micrograph are PUR phases or contain high PUR content, and the light areas are PEMA network.
Figure 5.6 TEM micrographs for 70PUR/30PEMA IPN: (a), (b) unfilled sample and (c), (d) 2.5% Aerosil 380-filled IPN.
Figure 5.7 TEM micrographs for 70PUR/30PEMA IPN compositions: (a), (b) 5% Aerosil 380-filled IPN, and (c), (d) 7.5% Aerosil 380-filled IPN.
As can be seen from the unfilled sample, Figures 5.6 (a and b), the dispersed domains were the PEMA-rich phase having an approximate size range of 50-300 nm. In an IPN, the phase separation between the networks is dependent on the miscibility of both constituent polymers and the polymerisation condition. The solubility parameters of polyurethane network and PEMA are fairly different\(^{(55)}\). Although the phase separation was obvious, there existed a great deal of diffuse area between the two phases as seen by the different shades of gray in the matrix and at the phase boundaries.

TEM micrographs of the 2.5% Aerosil-filled IPN are shown in Figures 5.6 (c and d). Like the unfilled sample, this IPN exhibited a two-phase structure with some degree of diffuse interpenetration between the two components. As reported by the supplier, the primary particle size of Aerosil 380 is approximately 5 nm\(^{(90,181)}\) which is too small to be seen at 10k magnification. However, a number of aggregates was noticed.
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Using higher magnification, 26k and 50k, primary particles can be seen as tiny black specks evenly dispersing in both phases throughout the entire system, Figures 5.6(c) and (d). Moreover, there were some small-sized aggregates that did not break down fully to primary particles. A range of Aerosil particle sizes was seen up to as big as 30 nm. It was unlikely that the filler had influence over the IPN morphology, since the micrographs revealed a similar morphology to the ones observed for the unfilled specimen.

Figures 5.7 (a) and (b) show the morphology of the 5% Aerosil-filled IPN. Denser and bigger aggregates were seen since the sample contained a higher amount of filler. The micrographs showed a large variation in the aggregate sizes ranging from 10 to 200 nm. Primary particles did not appear at this filler concentration. Only a small number of small-sized aggregates was observed. This behaviour of filler dispersion is commonly encountered in cases of synthetic fillers, especially those of very fine particles\(^7\). This is the case where quite strong and complex aggregates are present. Frequently, under normal processing conditions, they do not break down, but act as primary particles. However, in this study, a relatively uniform dispersion of the aggregates was formed.

The morphologies of the 7.5% and 10% Aerosil-filled IPNs are illustrated in Figures 5.7 and 5.8, respectively. At low magnification, Figure 5.7(c), a pattern of ripples observed in 7.5% filled IPN was caused by the direction of ultra-microtoming. Here, a variation in sizes of the aggregates could be noticed ranging from 10 nm up to 250 nm. Despite the difference in filler concentration, both IPNs exhibited a similar morphology. Estimation of PEMA-rich domain sizes was not straightforward because of the dispersion of aggregated filler. However, in the dominant dark PUR matrix, the light PEMA network domains still appeared to be interconnected. The thorough dispersion of filler in both PUR and PEMA networks were quite evident in the micrographs. No obvious changes in interpenetration of the networks could be observed, regarding the variation of filler content.
5.1.4 Scanning Electron Microscopy

Filler particle size and shape are important at all stages of composite production and use\(^{(79)}\). Particle shape strongly influences the stiffness, or rigidity of a composite, the tensile and impact strength, and the surface smoothness of a component, i.e. virtually all the important properties of a composite\(^{(183)}\). The particle size and shape of Aerosil 380 can be seen in the SEM micrograph in Figure 5.9.

![Figure 5.9](image)

**Figure 5.9** SEM micrograph of Aerosil 380.

From the electron micrograph of Aerosil 380, primary particles are not visible. Instead, sponge-like masses are seen. According to the literature\(^{(80)}\), primary particles, in practice, do not appear in synthetic silica powders, but are aggregated to exhibit the secondary particle structure of a few to perhaps a hundred particles. The secondary particles further aggregate during the collection process to form tertiary structures called agglomerates. The formation of these structures is reversible. They can be disintegrated on mixing during the processing of the formulated composite.
Figure 5.10 SEM micrographs of the fracture surfaces for: (a) unfilled sample, (b) 2.5% and (c) 5% Aerosil 380-filled IPNs
Figure 5.11 SEM micrographs of the fracture surfaces for: (a) 7.5% and (b) 10% Aerosil 380-filled IPNs.
Scanning electron micrographs of IPN fracture surfaces are given in Figures 5.10 and 5.11. In this study, the specimens were prepared by fracturing the IPN samples under liquid nitrogen, below the Tg of PUR, to ensure brittle failure of the elastomeric composition. Under such cryogenic conditions smooth fracture surfaces are expected from the IPNs with uniform and intimate mixing between the two component polymers. By contrast, an appearance of rough surfaces or separate phases can be expected on the fracture surfaces of less thorough and non-uniform IPN specimens. For the unfilled 70PUR/30PEMA IPN, a smooth fracture surface was found as shown in Figure 5.10(a).

It is widely known that the dispersion characteristics of filler particles strongly affects the mechanical properties of composites. Poor dispersion produces non-uniform zones of polymer matrix and results in a lessening of general mechanical properties. Relatively uniform dispersions of aggregates were clearly seen in all the filled samples. See Figures 5.10 (b, c) and 5.11(a, b). In the micrographs, as the filler content increased, more aggregates were seen on the IPN fracture surfaces. A variation in the aggregate sizes were observed with a predominant size of less than 200 nm, corresponding with the findings from TEM micrographs. As seen from the micrographs, all filled IPNs presented smooth surfaces, regardless of the filler content. No sign of changes in IPN morphology due to the incorporation of Aerosil 380 could be detected.

5.1.5 Thermogravimetric Analysis
Thermogravimetric analysis has been widely used as an important technique for the thermal stability investigations. In case of polymer composites, the information about the effect of additives on the degradation process can be provided. The TGA plots of percent sample weight loss and its derivative are shown in Figures 5.12 and 5.13, respectively.
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Figure 5.12 Weight loss versus temperature plots for Aerosil 380-filled 70PUR/30PEMA IPNs.

Figure 5.13 Derivative weight loss versus temperature plots for Aerosil 380-filled 70PUR/30PEMA IPNs.
According to the TGA results, there was a slight sign of thermal stability improvement obtained from the incorporation of Aerosil 380. All the IPN samples, both unfilled and filled, exhibited a rather similar pattern of degradation. Despite the filler content, the onsets of degradation for all samples appeared to start at about the same temperature. See Figure 5.12. At the end of degradation process, the amounts of residues were in relation to the filler concentration in IPNs, since the silica was stable at the experimental temperature.

5.1.6 Tensile Study

Fillers can modify the properties of polymer systems in a wide variety of ways. Some examples of properties readily modified by incorporation of fillers are mechanical properties such as stiffness, hardness and strength. These properties are influenced by the interacting effects between the polymer and filler and also the reinforcing characteristics of filler used in the formulation\(^{(182)}\).

Data on tensile properties of the Aerosil-filled 70PUR/30PEMA IPN are listed in Table 5.3. Figure 5.14 illustrates the tensile properties (modulus of elasticity, tensile stress and elongation at break) versus the filler content as histograms.

Table 5.3 Tensile properties of Aerosil 380-filled 70PUR/30PEMA IPN.

<table>
<thead>
<tr>
<th>Filler content (wt %)</th>
<th>Stress at break* (MPa)</th>
<th>Modulus of elasticity* (MPa)</th>
<th>Elongation at break* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.6 (0.1)</td>
<td>6.3 (0.3)</td>
<td>924 (19.6)</td>
</tr>
<tr>
<td>2.5</td>
<td>5.4 (0.2)</td>
<td>7.1 (0.4)</td>
<td>900 (20.2)</td>
</tr>
<tr>
<td>5.0</td>
<td>6.6 (0.2)</td>
<td>8.9 (1.3)</td>
<td>828 (18.1)</td>
</tr>
<tr>
<td>7.5</td>
<td>6.7 (0.1)</td>
<td>9.5 (1.3)</td>
<td>830 (20.5)</td>
</tr>
<tr>
<td>10.0</td>
<td>6.6 (0.3)</td>
<td>9.7 (0.7)</td>
<td>771 (29.3)</td>
</tr>
</tbody>
</table>

* standard deviation values are shown in brackets.

Increasing filler content in the IPN systems produced the expected trends in mechanical behaviour: an increase in the stress at break as well as the elastic modulus and a decrease in the percentage elongation to failure at ambient temperature. The behaviour of these properties highlights possibilities of improvement in the
mechanical performance by appropriate formulation. From the unfilled to the sample with 7.5% filler content, the stress at break values increased from 4.6 to 6.7 MPa, where the maximum strength occurred. The contribution of filler content to the stress at break was minimal at higher filler content. Literature\(^{(183)}\) shows that the ultimate in tensile reinforcement can be obtained from a system of very fine particle fillers having a good adhesion with polymer matrix. Under these conditions the particles are more likely to be displaced uniformly throughout the matrix so that a maximum benefit may derive from the improved adhesion when the composite is under stress.

As can be seen from Figure 5.14, there was a slight increase in elastic modulus as the amount of filler was increased. The values gradually rose from 6.3 MPa for the unfilled sample to the maximum value of 9.7 MPa measured for the sample with 10% filler loading. The introduction of rigid particulate filler into a polymer matrix has been generally known\(^{(183)}\) to result in an increase in modulus, as solid fillers are normally many times more rigid than polymers. The magnitude of this increase depends not only on the amount of filler, but also on the nature of polymer\(^{(76)}\). In addition, higher modulus or stiffening effect can be provided by the aggregates or flocculated particles because the portion of the matrix that is isolated in the aggregates is less free to react to stress and strain than the continuous phase under the measurement conditions\(^{(183)}\).

A decrease in elongation at break with filler content was observed from Figure 5.14. This could be attributed to the way in which the matrix was restricted in its ability to stretch between the packed filler particles, and as the stress was applied, the separation of polymer matrix from the particles caused the breakage which began at low elongation.
Figure 5.14 Tensile properties versus filler content for Aerosil 380-filled 70PUR/30PEMA IPNs.
5.2 VN 3-FILLED 70PUR/30PEMA IPNs

An industrial grade silica, reported in the second part of this chapter, was manufactured by the Degussa Corporation under the commercial name of VN 3\textsuperscript{(144)}. The diameter of the primary particles, as seen from scanning electron microscopy, ranged from 1 \textmu m to 50 \textmu m. See section 5.2.3.

In this study, VN 3 concentrations of 2.5\%, 5\%, 7.5\% and 10\% by weight were incorporated into the 70PUR/30PEMA IPN system crosslinked with PPG:TMP in the ratio of 3:1 and 5 mole\% TEGDM crosslinker was used. The effects of filler on glass transition temperatures, damping ability, tensile and thermal properties of the IPNs were investigated by the several techniques.

5.2.1 Dynamic Mechanical Thermal Analysis

The effects of VN 3 on the glass transition temperatures and dynamic mechanical properties of the IPNs were measured and the data are shown in Table 5.4 and Figures 5.15 and 5.16 below.

<table>
<thead>
<tr>
<th>% (wt)</th>
<th>Tg, °C</th>
<th>Tan δ value</th>
<th>Inter-transition tan δ value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at tan δ max.</td>
<td>at Tg</td>
<td>at 46°C (*)</td>
</tr>
<tr>
<td>VN 3</td>
<td>PUR</td>
<td>PEMA</td>
<td>PUR</td>
</tr>
<tr>
<td>unfilled</td>
<td>2</td>
<td>94</td>
<td>0.42</td>
</tr>
<tr>
<td>2.5</td>
<td>2</td>
<td>94</td>
<td>0.40</td>
</tr>
<tr>
<td>5.0</td>
<td>3</td>
<td>94</td>
<td>0.37</td>
</tr>
<tr>
<td>7.5</td>
<td>3</td>
<td>95</td>
<td>0.37</td>
</tr>
<tr>
<td>10.0</td>
<td>3</td>
<td>95</td>
<td>0.39</td>
</tr>
</tbody>
</table>

* Tan δ value at intermediate transition temperature, between the Tgs of unfilled 70PUR/30PEMA IPN, 20°C and 94°C, respectively.
Figure 5.15 Bending loss factor versus temperature plots showing the effect of VN 3 on the 70PUR/30PEMA IPN.

Figure 5.16 Bending loss moduli versus temperature plots showing the effect of VN 3 on the 70PUR/30PEMA IPN.
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The effect of VN 3 on tan δ peak and loss modulus can be observed here. There was a minimal change in glass transition temperatures as the VN 3 was incorporated. The transitions measured for the unfilled IPN were at 2°C and 94°C, whereas the transitions of the IPN containing the highest filler content, 10%, were at 3°C and 95°C. However, marked changes were noticed from the height of tan δ peak.

Similar to the DMTA results from Aerosil 380 filled IPNs, the presence of VN 3 in the IPNs caused a decreased tan δ height at PUR transitions. On the other hand, a gradual rise in tan δ was seen around the PEMA transitions resulting in a small increase in inter-transition tan δ height at 46°C. Tan δ values of 0.42 and 0.44 at the PUR and PEMA Tgs were exhibited by the unfilled IPN, and the values of 0.39 and 0.55 were shown by the sample of 10% VN 3 (Table 5.4). Loss moduli at room temperature for the filled IPNs were slightly higher than that of the unfilled system, (Figure 5.16). Two changes of slope in each modulus-temperature plot were seen in regard to the location of PUR and PEMA-rich phase transition temperatures. At 25°C, the *E*" values were at 1.38×10⁷, 1.41×10⁷, 1.62×10⁷, 1.51×10⁷ and 1.70×10⁷ for the unfilled and the 2.5%, 5%, 7.5% and 10% VN 3-filled IPNs, respectively.

At equivalent filler loading, the effect of VN 3 on the IPN glass transition temperatures and tan δ peak values were less significant than the results measured from Aerosil 380 filled samples. This can be explained with the help of differences in filler properties. Although both fillers have the same chemical composition, SiO₂, they were chemically produced by different methods and conditions of preparation⁹¹,¹³⁸). As a result, they possess dissimilar primary properties, such as particle size and shape, particle size distribution and surface area, (See SEM micrographs in Figures 5.7 and 5.18) which essentially affect properties of the composite. As mentioned in the previous section, the effect of filler on the damping properties can be explained by two factors. They are the free volume and the internal friction between fillers and polymer chains and between filler particles themselves⁹⁷. Compared with Aerosil 380, VN 3 particles are much bigger, with dramatically smaller surface area. As a result, the influences of VN 3 on the IPN system in terms of the internal friction at the filler surface and the free volume are much less.
5.2.2 Modulated-Temperature Differential Scanning Calorimetry

The effect of VN 3 content on the glass transition temperatures of the IPNs was also studied by M-TDSC. The results are shown in Figure 5.17 and Table 5.5.

*Table 5.5* Effect of VN 3 on glass transition temperatures of the 70PUR/30PEMA IPN.

<table>
<thead>
<tr>
<th>VN 3 content</th>
<th>PUR Tg, °C</th>
<th>PEMA Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>unfilled</td>
<td>-34</td>
<td>61</td>
</tr>
<tr>
<td>2.5</td>
<td>-35</td>
<td>61</td>
</tr>
<tr>
<td>5.0</td>
<td>-34</td>
<td>61</td>
</tr>
<tr>
<td>7.5</td>
<td>-34</td>
<td>62</td>
</tr>
<tr>
<td>10.0</td>
<td>-34</td>
<td>63</td>
</tr>
</tbody>
</table>

*Figure 5.17* Differential heat capacity versus temperature plots showing the effect of VN 3 on the 70PUR/30PEMA IPN.
Corresponding to the DMTA results, VN 3 was found to have only a very slight effect on transition temperatures. The sample of high filler concentration, 10 wt%, exhibited a small shift of transitions from -34°C and 61°C, measured at the absence of filler, to -36°C and 63°C. All the filled IPNs showed a similar pattern in dCp/dT versus temperature plots, in that, at the inter-transition temperature, a slightly lower area under curve was noticed as the filler content became higher indicating somewhat less interphase between the PUR and PEMA-rich phases. This was expected because of the replacement of a polymer fraction by the filler particles.

5.2.3 Scanning Electron Microscopy
Scanning electron microscopy technique is a valuable tool for the study of filler particle size and shape. A scanning electron micrograph of VN 3 powder is shown in Figure 5.18.

Figure 5.18 SEM micrograph of VN 3.
Figure 5.19 SEM micrographs of the fracture surfaces for: (a) 2.5% VN 3 and (b) 5% VN 3 filled 70PUR/30PEMA IPNs.
**Figure 5.20** SEM micrographs of the fracture surfaces for: (a) 7.5% VN 3 and (b) 10% VN 3 filled 70PUR/30PEMA IPNs.
Compared with the study in the previous section, SEM revealed a considerable difference between the two silica fillers used in this research, Aerosil 380 and VN 3. As can be seen from the micrograph (Figure 5.18), VN 3 particles are oval-like in shape, although, some of them are generally of irregular shape. Apart from the particle shape, a wide range of particle sizes was also seen. In comparison to Aerosil 380, VN 3 has a lot less surface area and a great deal wider particle size distribution ranging from a size of 50 \( \mu \text{m} \) to those which are smaller than 1 \( \mu \text{m} \).

From the micrograph of VN 3, another interesting feature noticed at the particle surfaces is a large number of very fine particles on top of the bigger ones. This condition is frequently very obvious in micrographs of filler powders\(^{185}\). During the manufacturing process when fillers are ordinarily ground, very small particles tend to adhere, sometimes tenaciously, to larger particles. It is a result of attractive energy between bodies, which is the summation of van der Waals intermolecular forces. Attractive energy is operative in masses of particles, causing agglomeration at points of contact. Larger particles, such as grains of sand, can be separated simply during mixing process. Small to very small particles, however, have little mass, and the forces of agglomeration are relatively greater between particles. They generally exist as loosely bound agglomerates having low bulk densities. Although this force is weak, it may be mechanically effective in composite systems.

SEM investigation of the fracture surfaces of VN3 filled IPNs is shown in Figures 5.19 and 5.20. At all filler contents, a relatively good dispersion of VN3, showing different sizes of particles, was seen throughout the IPN matrix. Unlike the study of Aerosil 380-filled IPNs, complementary data about the effect of VN3 on IPN morphology could not be examined by transmission electron microscopy, since the ultrathin specimens, approximately 100 nm thickness, are crucial for the technique. With the presence of VN 3 particles, ultra-microtome sectioning was not successful due to the size of filler particles.
5.2.4 Thermogravimetric Analysis

TGA studies were carried out on the samples of IPNs containing different amounts of VN 3. The thermograms, both % weight loss and derivative weight retention versus temperature, are shown in Figures 5.21 and 5.22.

Two major degradation steps were shown by the technique. Considering the weight loss plots (Figure 5.21), all samples, including the unfilled, started losing weight at around 225°C. The degradation carried on until the temperature reached 275°C where the samples lost approximately 30% of their original weights. During this first degradation step, a striking feature was observed from the VN 3-filled IPNs of all filler content. While a gradual loss of weight was exhibited by the unfilled, sharp drops in weight loss of the filled samples were noticed around 275°C, resulting in 20% weight loss. The sudden change of weight can be clearly seen from the plot of derivative weight in Figure 5.22. This type of degradation was not observed in the TGA studies of Aerosil 380-filled IPNs. Further investigation was carried out and discussed below.

After the loss of some weight in the first step, the second step degradation occurred and continuously proceeded with a similar pattern for all samples. The sample with high filler content tended to exhibit slightly better thermal stability within a certain temperature range. At the end of the degradation process, which was at about 450°C, different amounts of residue were seen, relating to the VN 3 content. The residual weights of 0.9%, 2.6%, 5.8%, 8.5% and 11.4% were left by the unfilled sample and the samples of 2.5%, 5%, 7.5% and 10% VN 3, respectively.

In order to make a further study of the thermal effect of VN 3, filler contents of 5% and 10%wt were incorporated into PUR samples containing the same crosslink density as in the 70PUR/30PEMA IPN. The samples were examined by TGA and the results are plotted in Figures 5.23-5.24. As the filler content was increased, better thermal stability with an increased onset of degradation temperature was observed. Comparing the TGA results obtained for the filled PURs and IPNs, the improved thermal stability at early stage of the IPNs was clearly to be exerted by the effect of VN 3 on the PUR network.
Figure 5.21 TGA thermograms for the VN 3-filled 70PUR/30PEMA IPNs.

Figure 5.22 Derivative TGA curves for the VN 3-filled 70PUR/30PEMA IPNs.
Figure 5.23 TGA thermograms for the polyurethane and VN 3-filled polyurethane samples.

Figure 5.24 Derivative TGA thermograms for the polyurethane and VN 3-filled polyurethane samples.
5.2.5 Tensile Study

The mechanical properties of the VN 3-filled composition series were also investigated by tensile testing. The results are plotted and listed in Figure 5.26 and Table 5.6, respectively.

Table 5.6 Tensile properties of the VN 3-filled 70PUR/30PEMA IPNs.

<table>
<thead>
<tr>
<th>Filler content (wt %)</th>
<th>Stress at break* (MPa)</th>
<th>Modulus of elasticity* (MPa)</th>
<th>Elongation at break* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.6 (0.1)</td>
<td>6.3 (0.3)</td>
<td>924 (19.6)</td>
</tr>
<tr>
<td>2.5</td>
<td>4.5 (0.1)</td>
<td>6.9 (0.2)</td>
<td>880 (40.1)</td>
</tr>
<tr>
<td>5.0</td>
<td>4.2 (0.3)</td>
<td>7.5 (0.7)</td>
<td>805 (28.1)</td>
</tr>
<tr>
<td>7.5</td>
<td>4.1 (0.2)</td>
<td>7.4 (0.5)</td>
<td>789 (22.3)</td>
</tr>
<tr>
<td>10.0</td>
<td>4.0 (0.4)</td>
<td>6.9 (1.5)</td>
<td>655 (25.8)</td>
</tr>
</tbody>
</table>

* standard deviation values are shown in brackets.

From Table 5.6, increasing the filler content resulted in a gradual decrease in tensile stress and elongation at break. For example, when the IPN was filled with 10% VN 3 loading, its tensile stress and elongation at break was decreased from values of 4.6 MPa and 924% for the unfilled to 4.0 MPa and 655%. On the other hand, the modulus of elasticity generally increased from 6.3 MPa, as measured from the unfilled, to the maximum value of 7.5 MPa at 5% filler concentration. Adding more filler into the IPN led to a reduction in that a modulus value of 6.9 MPa was exhibited by the sample of 10% VN 3 loading.

Two possible models of tensile fractures can be depicted as shown in Figure 5.25(76). In model A, the adhesion bond strength between polymer matrix and filler particles is stronger than the polymer matrix. As a result, the fracture occurs in the matrix. Model B presents a system in which the strength of matrix exceeds the polymer-filler adhesion. For this discussion, the latter model is relevant as the fracture was seen at the interface of filler particles and matrix. This was shown by the SEM micrographs. See section 5.2.3. Under a given set of test conditions, the tensile force applied to a sample is primarily concentrated in the vicinity of the filler particle surface. In this
region, the stress level may be considerably higher than the average so that it causes delamination of polymer from the particles\(^{76}\). As a consequence, a crack occurs close to the filler particle-matrix interface and propagates by peeling the polymer off the filler surfaces.

\[ \textit{Figure 5.25} \text{ Two possible fracture surfaces of the tensile specimen for filled composites.} \]

Compared with the IPNs filled with Aerosil 380, the system filled with VN 3 showed a poorer performance in tensile strength and elongation at break. This can be explained by the difference between particle size and shape of Aerosil 380 and VN 3. As confirmed by the SEM micrographs, VN 3 exhibited a wide variation in particle size and shape. According to the literature\(^{180}\), as a general rule, a high reinforcing silica would exhibit small particle size, high filler surface area and narrow particle size distribution. Conversely, a non-reinforcing filler would be significantly larger in particle size, lower in surface area and have a wider range of particle sizes than the reinforcing filler. Fillers affect tensile strengths of composites according to their packing characteristics, sizes and shapes\(^{183}\). The composite filled with a broad particle size distribution will have larger and less uniform zones of matrix between the particles, so that, when a stress is applied, the weakest links, consisting of smaller matrix zones, bear the strain and break most rapidly. More uniformly packed systems, more uniformly distribute the strain, and, therefore, result in higher strengths\(^{70}\).
For the lower elongation at break measured from VN 3-filled IPNs, explanation may be attributed to the filler particle size and shape. Many facets and irregular angles between faces of the particle prevent uniform strain patterns and cause filler particles to produce lower strengths\(^{(76)}\).
Figure 5.26 Tensile properties versus filler content for the VN 3-filled 70PUR/30PEMA IPNs.
CHAPTER 6

TALC-FILLED 70PUR/30PEMA IPNs
CHAPTER 6

TALC-FILLED 70PUR/30PEMA IPNs

The mineral talc is a hydrated magnesium silicate with a theoretical formula $3\text{MgO}\cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. There is usually a little variation in the chemical composition according to the locality in which the talc is mined. The filler used in this study was an industrial-grade talc with a product name of Microtal SF-10. A platy structure provides talc-filled materials with important properties\(^{(96)}\), such as low gas permeability because the diffusion path is so complicated. It is considered to be a semi-reinforcing filler in many plastics applications\(^{(76,80)}\).

In the literature, studies on talc-filled IPNs have been reported. Lipatov and co-workers\(^{(90)}\) carried out an investigation on a system of talc-filled semi-IPNs based on crosslinked PUR and linear poly(butyl methacrylate). It was found that introducing the filler into the reaction mixture resulted in microphase separation inhibition on account of a local increase in viscosity near the solid interface. In another study\(^{(95)}\), polystyrene/poly(ethyl acrylate-co-n-butyl acrylate) latex IPNs were synthesised by a two-stage emulsion polymerisation technique. The effect of 10 wt % talc on damping properties of the LIPNs was investigated. The results indicated that the filler produced an increase in tan $\delta$ values and broadened the damping temperature range.

In this study, the 70PUR/30PEMA IPN crosslinked with PPG:TMP ratio of 3:1 and 5% TEGDM was used as an unfilled sample. A series of PUR/PEMA IPNs filled with talc loadings of 2.5%, 7.5% and 12.5% by weight was prepared. The effects of talc on the IPN properties, glass transition temperature, damping and mechanical properties and thermal stability were characterised by several techniques mentioned earlier. The results of these investigations are shown as follows.
6.1 Dynamic Mechanical Thermal Analysis

The dynamic mechanical properties for the talc-filled 70PUR/30PEMA IPNs are given in Table 6.1. The effectiveness of the platey talc in increasing loss factor height of the IPNs at elevated temperatures and the loss modulus data are shown in Figures 6.1 and 6.2.

Table 6.1 Effect of talc on the dynamic mechanical properties of the
70PUR/30PEMA IPN.

<table>
<thead>
<tr>
<th>% (wt)</th>
<th>Tg, °C</th>
<th>Tan δ value</th>
<th>Inter-transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at tan δ max.</td>
<td>at Tg</td>
<td>tan δ value at 46°C (*)</td>
</tr>
<tr>
<td>Talc</td>
<td>PUR</td>
<td>PEMA</td>
<td>PUR</td>
</tr>
<tr>
<td>unfilled</td>
<td>2</td>
<td>94</td>
<td>0.42</td>
</tr>
<tr>
<td>2.5</td>
<td>-3</td>
<td>90</td>
<td>0.39</td>
</tr>
<tr>
<td>7.5</td>
<td>-4</td>
<td>91</td>
<td>0.41</td>
</tr>
<tr>
<td>12.5</td>
<td>-4</td>
<td>92</td>
<td>0.41</td>
</tr>
</tbody>
</table>

* Tan δ value at intermediate transition temperature, between the two Tgs of unfilled 70PUR/30PEMA IPN, 2°C and 94°C, respectively.

It can be seen from Table 6.1 that both the PUR and PEMA-rich phase transitions of the filled IPNs shifted slightly to lower temperatures in comparison to the unfilled sample which the transition temperatures were at 2°C (tan δ 0.42) and 94°C (tan δ 0.44). Tgs of the talc-filled IPNs and tan δ values at PUR transitions were practically unaffected by increasing filler weight fraction. At 12.5% talc concentration, the PUR transition was measured at -4°C with tan δ value of 0.41. On the other hand, introducing higher amount of filler resulted in increased tan δ values at PEMA transitions and the peaks became remarkably broad. At the filler loadings of 2.5%, 7.5% and 12.5%, the composites exhibited their PEMA-rich phase transitions at 90°C (tan δ 0.49), 91°C (tan δ 0.63) and 92°C (tan δ 0.67), respectively. In addition, increasing the filler content provided an improved damping response at inter-transition temperature, 46°C, in that, tan δ value of 0.51 was observed for the sample with 12.5% filler loading, while the value of 0.38 was recorded by the unfilled IPN.
Figure 6.1 Bending loss factor versus temperature plots showing the effect of talc on the 70PUR/30PEMA IPNs.

Figure 6.2 Bending loss modulus versus temperature plots showing the effect of talc on the 70PUR/30PEMA IPNs.
An explanation of the tan δ peak broadening and the increase in damping values has been proposed by Shucai et al.\textsuperscript{(95)} in terms of the particle shape of the filler. In filled polymer systems with a presence of thin platelet particles, the filler platelet at one side of the polymer damping layer could be considered as a vibration substrate, while the platelet at the other side of damping layer acts as a constraining layer. When the specimen is vibrating, the shear takes place in the polymer damping layer between the platelets, which increases the mechanical loss of energy being converted to heat. Moreover, they suggested\textsuperscript{(95)} that the broadened damping peak, tan δ versus temperature curve, of the filled IPNs could be due to the inhomogeneous distribution of filler particles in polymer matrix.

![Mechanism for constrained layer damping](image)

Figure 6.2 shows the effect of filler content on the PUR/PEMA IPNs in terms of the loss modulus, $E''$, at different temperatures. From Figure 6.2, the trend was found to be similar to that observed for the silica filled IPNs, in that each filled IPN exhibited curve with two transitions indicating by the changes of slope. At room temperature, 25°C, a gradual increase in loss modulus was observed from the filled samples, although the values did not proportionally increase with the increased filler content. The $E''$ values were $1.38 \times 10^7$, $1.51 \times 10^7$, $1.55 \times 10^7$ and $1.74 \times 10^7$ Pa for the unfilled, 2.5%, 7.5% and 12.5% talc-filled IPNs, respectively.

### 6.2 Modulated-Temperature Differential Scanning Calorimetry

The effect of filler content on the glass transition temperatures of the 70PUR/30PEMA IPNs measured by M-TDSC is presented in Figure 6.3 and the $T_g$ data for each composite is given in Table 6.2.
Figure 6.3 Differential heat capacity versus temperature plots showing the effect of talc on the 70PUR/30PEMA IPNs.

Table 6.2 Effect of talc on glass transitions of the 70PUR/30PEMA IPN

<table>
<thead>
<tr>
<th>Talc % (wt)</th>
<th>IPN Tg, °C</th>
<th>Area under curve (J.g⁻¹.°C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PUR</td>
<td>PEMA</td>
</tr>
<tr>
<td>unfilled</td>
<td>-34</td>
<td>61</td>
</tr>
<tr>
<td>2.5</td>
<td>-35</td>
<td>54</td>
</tr>
<tr>
<td>7.5</td>
<td>-37</td>
<td>51</td>
</tr>
<tr>
<td>12.5</td>
<td>-42</td>
<td>54</td>
</tr>
</tbody>
</table>

From the M-TDSC plot for the unfilled sample, two dCp/dT peaks were observed at -34°C and 61°C, for the PUR and PEMA-rich phase transitions suggesting microphase separation in the system. However, there existed some extent of molecular mixing as indicated by the dCp/dT signal continuously spanning over the intermediate
temperatures between the two Tgs. Because of the shape of the plot, it was difficult to point out where the Tg of PEMA-rich phase was.

As the filler was introduced into the IPN, some changes were observed in these plots. With a presence of 2.5% filler loading, the IPN exhibited decreased transitions at -35°C and 54°C compared with the unfilled IPN. It was seen that all the talc-filled IPNs were also two-phase materials suggesting by the two distinct peaks in the dCp/dT signal corresponding to individual polymer components. Unlike the plot for the unfilled sample, the transitions of the filled IPNs appeared to be more distinctive with lower signal at inter-transition temperatures. As the filler concentration was increased, the phase separated character of the system did not change. In fact, an introduction of 7.5% and 12.5 wt.% filler content resulted in more apparent phase separation in the dCp/dT curves, and shifted both transitions to even lower temperatures at -37°C, 51°C and -42°C, 54°C, respectively (Table 6.2). One reason which could be offered for the low dCp/dT signal over the inter-transition temperature range, and the reduced area under the curves of the filled IPNs is the reduction in weight fraction of polymer which was replaced by the filler fraction, as mentioned in previous section.

6.3 Scanning Electron Microscopy

Scanning electron microscopy at high magnification was used in order to examine the particle shape and size of the filler. A SEM micrograph of talc particles used in these studies is shown in Figure 6.4.

The commercial grade talc, under a product name of SF-10, is a pale gray powder. It has a characteristic of pearl-like lustre. High magnification SEM micrographs show a finely-ground product consisting of thin platelets with an average primary particle size smaller than 20 μm, corresponding to the information given by the supplier. In general, talc exhibits a large surface area in relation to its thin and plate-like particle structure. Because of this platy nature of talc, it is usually considered to be a (semi-) reinforcing filler to distinguish it from the other particulate mineral fillers(85).
Chapter 6

Talc filled IPNs

Figure 6.4 Scanning electron micrograph of the platy talc.

Figure 6.5 Scanning electron micrograph of the 2.5% talc-filled 70PUR/30PEMA IPN.
Figure 6.5 (continued) Scanning electron micrographs of the talc-filled 70PUR/30PEMA IPNs with filler contents of: (a) 7.5% and (b) 12.5%.
SEM is one of the current methods generally used to examine the dispersion of filler particles in polymer systems. The high magnification technique allows one to observe the breakdown of agglomerates, and, therefore, it is very useful. Like the study of VN3-filled IPNs, complementary information on morphology could not be provided by the use of transmission electron microscopy technique. It was the particle size and hardness of the filler that makes ultra-microtome sectioning practically impossible especially with the samples of high filler loading.

Mechanical properties of filled polymers depend, among other things, on the uniformity of filler dispersion in the polymer matrix and the adherence of filler surface and matrix\(^7\). Figure 6.5 shows the SEM micrographs of the fracture surfaces of the talc-filled 70PUR/30PEMA IPNs containing different filler contents. It can be seen that the platy talc particles arranged themselves in every direction all over the IPN surfaces and good dispersions were achieved in all IPNs. At 2.5% filler content, the specimen surface appeared to be rather smooth with various sizes of primary talc particles embedded in the polymer matrix. Unlike the system of Aerosil-filled IPNs, no filler aggregates were noticed. As the filler loading level was increased, see Figures 6.5 (a) and (b), the fracture surfaces became irregular and rugged as a result of the particle size and shape of talc. This type of surface was not observed in Aerosil-filled IPNs containing the same amount of filler.

**6.4 Thermogravimetric Analysis**

Thermogravimetric analysis was used to investigate the thermal stability and decomposition mechanism of the sample. For a polymer system, the effect of filler and additive on the degradation process can also be studied. In this research, all samples were examined in a nitrogen atmosphere from room temperature up to 520°C where there was no further weight loss detected. The TGA thermograms, percent weight loss and its derivative (%\(^\circ\)C) versus temperature plots, are shown in Figures 6.6 and 6.7.
Chapter 6  
Talc filled IPNs

Figure 6.6 Weight loss versus temperature plots for the talc-filled 70PUR/30PEMA IPNs.

Figure 6.7 Derivative weight loss versus temperature plots for the talc-filled 70PUR/30PEMA IPNs.
Talc filled IPNs

The TGA investigation revealed a similar degradation pattern for both filled and unfilled IPNs. A two-step mechanism in sample weight loss was observed for all the samples. The onset of degradation started at about 200°C and was followed by a rapid weight loss between 240°C and 290°C. This first step degradation resulted in slightly different %weight loss in each sample. At 290°C, the IPN with high talc loading, 12.5%, exhibited the highest weight retention with a remaining mass of 70.1%, whereas 68.3%, 65.5% and 63.8% of weight retention was measured for the samples with 7.5%, 2.5% talc and the unfilled IPN, respectively.

The second degradation step caused a major loss of sample weight and appeared to be a long and more complex process indicated by a few overlapping shoulders of the main peaks in the derivative weight plots. See Figure 6.7. In case of the unfilled sample, this step led to almost complete decomposition in which less than 1% residual weight was left at the end of the degradation at 450°C. An enhancement of the weight retention at elevated temperature was shown by the filled samples. At the final stage of decomposition, higher amount of residues, 3.7%, 8.8% and 14.3%, were left by the filled samples in corresponding to the amount of filler loading, 2.5%, 7.5% and 12.5%, respectively. This was expected, since talc is an inert filler and thermally stable toward heat up to temperature as high as 800°C[45].

6.5 Tensile Study

Under stress, the tensile stress, modulus and elongation at break are all important properties both commercially and theoretically. In order to study the effect of talc on 70PUR/30PEMA IPN, the tensile properties of the unfilled as well as the filled IPNs with different filler contents were evaluated. The data are given in Table 6.3 below.

Table 6.3 Tensile properties of the talc-filled 70PUR/30PEMA IPNs

<table>
<thead>
<tr>
<th>Filler content* (wt %)</th>
<th>Stress at break* (MPa)</th>
<th>Modulus of elasticity* (MPa)</th>
<th>Elongation at break* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.6 (0.1)</td>
<td>6.3 (0.3)</td>
<td>924 (19.6)</td>
</tr>
<tr>
<td>2.5</td>
<td>4.8 (0.2)</td>
<td>6.4 (0.5)</td>
<td>879 (8.9)</td>
</tr>
<tr>
<td>7.5</td>
<td>4.1 (0.2)</td>
<td>7.2 (0.4)</td>
<td>811 (19.1)</td>
</tr>
<tr>
<td>12.5</td>
<td>3.8 (0.4)</td>
<td>7.8 (1.1)</td>
<td>700 (27.1)</td>
</tr>
</tbody>
</table>

* standard deviation values are shown in brackets.
Figure 6.8 Tensile properties versus filler content graph for the talc-filled 70PUR/30PEMA IPNs.
Figure 6.8 shows the effect of filler content on the tensile properties of the PUR/PEMA IPNs. At 2.5% filler loading, tensile strength at break showed a slight increase from 4.6 MPa observed for the unfilled to a value of 4.8 MPa. Adding more filler resulted in a gradual reduction of tensile strength. The strength of 12.5% talc-filled IPN was 3.8 MPa. It can be seen that the presence of filler caused reinforcement up to a certain critical value. Further addition of filler resulted in a decrease in the force needed to rupture the samples.

By contrast, the modulus of elasticity exhibited the expected trend. The values increased with increasing filler concentration. This is because inorganic fillers are, compared to most polymers, much stiffer and less extensible materials. Incorporation of filler into a polymer usually produces a composite material of a reduced strain to failure and increased stiffness relative to the unfilled sample, i.e. the composite will be less elastomeric or less ductile. The highest modulus with the value of 7.8 MPa was shown by the IPN with 12.5% filler. From the plots, there was a relatively slight drop in elongation at break as the amount of filler was increased, which pointed to a restricted ability of polymer chains to stretch and, possibly, reduced interfacial bonding between the polymer matrix and the filler.
CHAPTER 7

CALCIUM CARBONATE-FILLED 70PUR/30PEMA IPNs
CHAPTER 7

CALCIUM CARBONATE-FILLED 70PUR/30PEMA IPNs

Calcium carbonate is one of the earth's most abundant minerals, found in various forms all over the world. It is also the most widely used filler or extender pigment in the plastic industry. This broad usage can be attributed to both economic and performance considerations. This filler is available at favorable pound-volume costs and is produced in a broad range of particle size distributions.

Investigations on the use of calcium carbonate as a filler in IPN systems have been reported. Li et al. studied the damping performance of a system of polystyrene/polyacrylate LIPNs. Ten wt. percent calcium carbonate was introduced into the IPN possessing a PS/PA ratio of 50/50. The resulting dynamic mechanical spectra showed that the filler had no effect in broadening the loss tangent curve. However, the curve was heightened over a certain temperature range. Another study was conducted on a 30/70 PS/P(EA-nBA) LIPN. Like the previous study, 10 wt % of calcium carbonate was incorporated into the LIPN. From the dynamic mechanical properties data, it was seen that the filler produced increase in tan δ values and slightly broaden the damping temperature range.

For this research, the 70PUR/30PEMA IPN crosslinked with PPG:TMP ratio of 3:1 and 5% TEGDM was again used as the unfilled reference sample. The effects of CaCO₃ (RLO 6083, ECC International) concentration were monitored from a series of 70PUR/30PEMA IPNs filled with 2.5%, 7.5% and 12.5% filler loadings.

7.1 Dynamic Mechanical Thermal Analysis

The dynamic mechanical performance has been determined for these 70PUR/30PEMA IPNs. The DMTA spectra of loss factor and storage modulus versus temperature are shown in Figures 7.1 and 7.2.
Chapter 7

CaCO₃ filled IPNs

Figure 7.1 Bending loss factor versus temperature plots showing the effect of CaCO₃ on the 70PUR/30PEMA IPNs.

Figure 7.2 Bending loss modulus versus temperature plots showing the effect of CaCO₃ on the 70PUR/30PEMA IPNs.
Table 7.1 Effect of CaCO$_3$ on the dynamic mechanical properties of the 70PUR/30PEMA IPNs.

<table>
<thead>
<tr>
<th>% (wt) CaCO$_3$</th>
<th>Tg, °C at tan δ max.</th>
<th>Tan δ value at Tg</th>
<th>Inter-transition tan δ value at 46°C (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PUR</td>
<td>PEMA</td>
<td>PUR</td>
</tr>
<tr>
<td>unfilled</td>
<td>2</td>
<td>94</td>
<td>0.42</td>
</tr>
<tr>
<td>2.5</td>
<td>-2</td>
<td>90</td>
<td>0.42</td>
</tr>
<tr>
<td>7.5</td>
<td>-6</td>
<td>86</td>
<td>0.38</td>
</tr>
<tr>
<td>12.5</td>
<td>-7</td>
<td>86</td>
<td>0.35</td>
</tr>
</tbody>
</table>

* Tan δ value at intermediate transition temperature, between the two Tgs of the unfilled 70PUR/30PEMA IPN, 20°C and 94°C, respectively.

From Figure 7.1, it can be seen that CaCO$_3$ had a good effect on the damping ability of the PUR/PEMA IPN, especially over the elevated temperature range. Compared with the unfilled IPN, a general trend exhibited by the filled samples was a broadening of the tan δ peak around both the PUR and the PEMA transitions, as well as an increase of the loss factor at the intermediate transition temperature, 46°C, and over the PEMA-rich phase transition. See Table 7.1. This can be explained in terms of an increase in internal friction between the filler particles and polymer and between the fillers themselves$^{67}$, as mentioned earlier in Chapter 5. Furthermore, all of the CaCO$_3$-filled IPNs exhibited a wider range of temperatures where the loss factor values were higher than 0.3. However, the enhanced damping capability seemed to reach maximum with the 7.5% filler loading, as a slight decrease in tan δ values was measured from the sample with 12.5% CaCO$_3$ content.

Similar to the finding observed from Aerosil 380-filled IPN, the incorporation of CaCO$_3$ generally lowered the IPN transition temperatures. When 12.5% weight of CaCO$_3$ was introduced into the IPN, the Tgs shifted down from 2°C (tan δ = 0.42) and 94°C (tan δ = 0.44), which was observed for the unfilled IPN, to -7°C (tan δ = 0.35) and 86°C (tan δ = 0.63). The decrease in IPN transition temperatures could be an
indication that the introduction of filler might lead to a difference in crosslink density between the unfilled and the filled samples\(^{90}\).

Evaluation of the influence of CaCO\(_3\) on the loss modulus, Figure 7.2, showed the same trend as those results from the silica and talc filled samples. The IPN composites became stiffer with the added CaCO\(_3\). Evidence of a two-phase blend system with a fine dispersion between the polymer components can be seen from the gradual changes of the \(E''\)-temperature slope. Again, at room temperature, 25°C, an increase in \(E''\) was seen from the plots. The values were 1.38×10\(^7\), 1.38×10\(^7\), 1.82×10\(^7\) and 1.99×10\(^7\) for the unfilled, and the IPNs with 2.5%, 7.5% and 12.5% filler contents.

### 7.2 Modulated-Temperature Differential Scanning Calorimetry.

Glass transition behaviour of CaCO\(_3\)-filled IPNs was also evaluated by M-TDSC. The technique offered corresponding data to those obtained from DMTA in that adding CaCO\(_3\) into the PUR/PEMA IPN brought the glass transitions to lower temperatures. Glass transitions of the unfilled IPN were detected at -34°C and 61°C, while the Tgs at -37°C and 56°C were exhibited by the IPN with 12.5% CaCO\(_3\). Like the other filled IPN systems, a decrease in area under \(dCp/dT\)-temperature plots was noticed with the increased filler content. This could be an indication of a reduced extent of segment mixing between the PUR and PEMA networks.

**Table 7.2** Effect of CaCO\(_3\) contents on glass transitions of the 70PUR/30PEMA IPNs.

<table>
<thead>
<tr>
<th>CaCO(_3) % (wt)</th>
<th>IPN Tg (°C)</th>
<th>Area under curve (J.g(^{-1}.°C(^{-1}))</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>unfilled</td>
<td>-34</td>
<td>61</td>
<td>0.70</td>
</tr>
<tr>
<td>2.5</td>
<td>-37</td>
<td>60</td>
<td>0.69</td>
</tr>
<tr>
<td>7.5</td>
<td>-38</td>
<td>62</td>
<td>0.66</td>
</tr>
<tr>
<td>12.5</td>
<td>-37</td>
<td>56</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Chapter 7

CaCO₃ filled IPNs

Figure 7.3 M-TDSC plots for the CaCO₃-filled 70PUR/30PEMA IPNs.

7.3 Scanning Electron Microscopy

CaCO₃ is produced in a broad range of particle sizes, shapes and distributions. Owing to the varied geological history of CaCO₃ deposits, many different forms of this mineral filler are recognized. SEM micrograph of the filler powders with an average primary particle size of 0.55 μm is illustrated in Figure 7.4. Aggregations of a few to perhaps a hundred primary particles were seen from the micrograph. Formation of the aggregates is reversible. They can be the broken down during the mixing process.

Examination by SEM of the sample fracture surfaces is shown in Figures 7.5 (a to c). At all filler contents, the micrographs revealed smooth fracture surfaces of the IPN matrices and a good distribution of different sizes of filler aggregates throughout the matrices. A denser number of aggregates was observed as the amount of filler increased.
**Figure 7.4** Scanning electron micrograph of CaCO$_3$.

**Figure 7.5** Scanning electron micrographs at the fracture surface of the 2.5%CaCO$_3$-filled IPN.
Figure 7.5 (continued) Scanning electron micrographs at the fracture surfaces of CaCO$_3$-filled IPNs with filler weight contents of: (b) 7.5% and (c) 12.5%.
7.4 Thermogravimetric Analysis

All the CaCO₃-filled samples were examined by TGA in a nitrogen atmosphere. Results are shown in Figures 7.6 and 7.7 as plots of weight loss (%) and derivative weight versus temperature. Both the unfilled and filled samples decomposed in a two-step degradation mechanism. The first step was between 210°C and 290°C, then followed by the second step where more than 65% of the samples were decomposed. Except for the small overlapping shoulders in the derivative weight plots, Figure 7.7, the filler did not produce any drastic change in the IPN degradation pattern. At the end of the degradation, different weights of residue left were related to the concentration of CaCO₃ in the IPNs.

![Figure 7.6](image-url)

**Figure 7.6** Weight loss versus temperature plots for the CaCO₃-filled 70PUR/30PEMA IPNs
Chapter 7  

2.5 6 unfilled 0 2.5% CaCO₃ 0 7.5% CaCO₃ 0 12.5% CaCO₃

Figure 7.7 Derivative weight loss versus temperature plots for the CaCO₃-filled 70PUR/30PEMA IPNs.

7.5 Tensile Study

In order to investigate the effect of CaCO₃ on the IPN mechanical behaviour, tensile properties of the filled PUR/PEMA IPNs were evaluated. The results of tensile stress, elongation at break and modulus of elasticity are shown in Table 7.3 and Figure 7.8.

As expected, the stress and elongation at break decreased with increasing filler content, whereas the contribution of the filler to the material stiffness can be seen from an increased elasticity modulus of the filled samples. Compared with other fillers at equivalent weight fraction, CaCO₃ exhibited less improvement in tensile strength. The tensile strength dropped steadily, as the filler content increased. With 12.5% filler content, the strength decreased from 4.6 MPa, for the unfilled sample, to a value of 2.9 MPa. Measurement of the elongation at break produced a typical trend for a filled polymer system where there was no interfacial bonding between the polymer and filler particles. The values of 924, 900, 877, and 725 were measured from the unfilled IPN and the IPNs with 2.5%, 7.5% and 12.5% CaCO₃ contents, respectively.
Figure 7.8 Tensile properties of the CaCO$_3$-filled 70PUR/30PEMA IPNs.
Table 7.3 Tensile properties of CaCO$_3$-filled 70PUR/30PEMA IPNs.

<table>
<thead>
<tr>
<th>Filler content (wt. %)</th>
<th>Stress at break* (MPa)</th>
<th>Modulus of elasticity* (MPa)</th>
<th>Elongation at break* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.6 (0.1)</td>
<td>6.3 (0.3)</td>
<td>924 (19.6)</td>
</tr>
<tr>
<td>2.5</td>
<td>4.2 (0.3)</td>
<td>6.5 (0.5)</td>
<td>900 (18.2)</td>
</tr>
<tr>
<td>7.5</td>
<td>3.7 (0.2)</td>
<td>7.4 (0.01)</td>
<td>877 (10.9)</td>
</tr>
<tr>
<td>12.5</td>
<td>2.9 (0.1)</td>
<td>8.1 (0.4)</td>
<td>725 (31.5)</td>
</tr>
</tbody>
</table>

* standard deviation values are shown in brackets.
CHAPTER 8

MICA-FILLED 70PUR/30PEMA IPNs
CHAPTER 8

MICA-FILLED PUR/PEMA IPNs

Mica is a plate-like crystalline aluminosilicate\(^{76}\). This filler has a rather low surface area, mostly in range of 2-5 m\(^2\)/g\(^{79}\) and excellent mechanical properties. The main advantage of mica is an increasing stiffness and dimensional stability; its disadvantage is poor impact strength. The mica grade used in this study was supplied by the Microfine Minerals Limited under the commercial name SX300. This mica was micronised using selected muscovite raw material. Compared with other fillers used in the previous chapters, this filler is composed of rather big particles.

According to the literature, a number of researches has been undertaken to study the effects of mica on IPN systems. Li et al.\(^{97}\) investigated damping performance of 10 wt% mica-filled polystyrene/polyacrylate LIPNs. It was shown by dynamic mechanical spectra that the filler had a good effect on the damping properties. Another study of a similar system was reported by Shucai et al.\(^{95}\). The dynamic mechanical data on mica-filled 35/65 polystyrene/poly(ethyl acrylate-co-n-butyl acrylate) IPNs indicated that the damping values and width of damping peak increased with increasing mica content. They reported difficulties in preparing the sample with filler contents higher than 20 wt. percent. However, it could be inferred that the damping properties decreased if the mica content was too high. Work done by Klempner et al.\(^{15}\), on the other hand, showed a contrasting finding. For instance, 10% mica was reported to have no effect in enhancement of tan \(\delta\) height or breadth in PUR/epoxy IPNs.

In this study, two mica-filled IPN systems were prepared. Firstly, the 70PUR/30PEMA IPNs crosslinked with PPG:TMP ratio of 2:1 and 5% TEGDM were prepared with 2.5% and 7.5% SX300 content. Secondly, mica-filled 75PUR/25PEMA IPNs of the same crosslink density were synthesised and characterised.
8.1 MICA-FILLED 70PUR/30PEMA IPNs

8.1.1 Dynamic Mechanical Thermal Analysis

In order to study the effect of mica content on this IPN system, the DMTA technique was used to determine damping behaviour. Glass transition temperatures were measured from the tan δ peak and listed in Table 8.1. The behaviour of tan δ and loss modulus over a range of temperature for the 2.5% and 7.5% mica-filled 70PUR/30PEMA IPNs are shown in Figure 8.1.

For the unfilled sample, the tan δ peak temperatures were at 8°C and 78°C for the PUR and PEMA rich phases, respectively. As mica was added into the IPN system, it could be seen that the PEMA Tgs were shifted upwards and the tan δ peaks became broader, while the PUR Tg was unaffected. The transitions were 8°C, 90°C and 8°C, 91°C for the IPNs with 2.5% and 7.5% mica weight contents, respectively. Incorporation of filler also resulted in broadening the range where tan δ ≥ 0.3. A range of 157°C was exhibited by the 7.5% mica-filled IPN, 22°C wider than the unfilled IPN. However, the tan δ height at inter-transition temperature, 46°C was not changed. No significant influence of filler content was shown in the loss modulus-temperature plots. An indication of extensive mixing between the two polymer components was seen by the gradual and continuous changes of the plot slopes.

Table 8.1 Effect of mica on the dynamic mechanical properties of the 70PUR/30PEMA IPN

<table>
<thead>
<tr>
<th>Mica content % (wt)</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ value at Tg</th>
<th>Temperature range of tan δ ≥ 0.3 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PUR</td>
<td>PEMA</td>
<td>PUR</td>
</tr>
<tr>
<td>unfilled</td>
<td>8</td>
<td>78</td>
<td>0.43</td>
</tr>
<tr>
<td>2.5</td>
<td>8</td>
<td>90</td>
<td>0.43</td>
</tr>
<tr>
<td>7.5</td>
<td>8</td>
<td>91</td>
<td>0.43</td>
</tr>
</tbody>
</table>
Chapter 8  Mica filled IPNs

Figure 8.1  Bending loss factor and loss modulus versus temperature plots showing the effect of mica on the 70PUR/30PEMA IPNs.

8.1.2 Modulated-Temperature Differential Scanning Calorimetry

The \( \frac{dC_p}{dT} \) signal-temperature plots of the mica-filled IPN are shown in Figure 8.2

Figure 8.2  M-TDSC plots for the mica-filled 70PUR/30PEMA IPNs
A corresponding result regarding changes of glass transition temperature was seen from M-TDSC plots. With increasing filler content, it was clearly seen that mica did not affect the Tg of PUR-rich phase and only a marginal shift of PEMA transition was observed. The unfilled sample showed Tgs at -33°C and 50°C for PUR- and PEMA-rich phases, respectively. There was no change of Tgs detected for the sample with 2.5% mica. Increasing filler content to 7.5% resulted in slight shifts of glass transitions which were seen at -33°C and 53°C.

8.1.3 Scanning Electron Microscopy

Figure 8.3 shows the plate-like structure for the mica filler at high magnification. It can be seen from the SEM micrograph that the filler particles have rather similar plate thickness. However, a wide range of plate shapes and size distribution was also evident. Like the micrograph of VN 3, a large number of very small particles was noticed adhering to larger particles. SEM investigation of the fracture surfaces for mica-filled samples is illustrated in Figures 8.4 (a) and (b). A relatively good dispersion of mica particles was observed at all filler contents.

![Scanning electron micrograph for the mica filler.](image)
Figure 8.4 Scanning electron micrographs for the mica-filled 70PUR/30PEMA IPNs with filler weight contents of (a) 2.5% and (b) 7.5%.
8.1.4 Tensile Study

Investigation of the tensile properties was carried out for both the unfilled and mica-filled samples. Figures 8.5 and 8.6 show the tensile stress at break, modulus of elasticity and elongation at break versus mica content. Improvement of the tensile properties can be seen from Figures 8.5. As the filler was added into the IPN matrix, the tensile strength and modulus increased without reducing the elongation at break. The stress at break and modulus of elasticity of the unfilled IPN were 4.6 and 4.9 MPa and the elongation at break was 741%. The values of stress and modulus generally increased to 5.4 and 7.2 MPa for the 7.5% mica-filled IPN, whereas a value of 744% was detected from the elongation at break.

![Graph showing tensile properties](image)

**Figure 8.5** Effect of mica on the tensile stress at break and modulus of elasticity for the mica-filled 70PUR/30PEMA IPNs
Figure 8.6 Effect of mica content on the elongation at break for the 70PUR/30PEMA IPN.

8.2 MICA-FILLED 75PUR/25PEMA IPNs

Incorporation of mica into the 75PUR/25PEMA IPNs was carried out in order to study the effect of mica on a different composition ratio IPN. The samples were prepared containing 2.5%, 5% and 10% mica contents.

8.2.1 Dynamic Mechanical Thermal Analysis

DMTA technique was again used to determine the influence of mica content on the 75PUR/25PEMA IPN damping behaviour. Tan δ and loss modulus values over a range of temperature for the 2.5%, 5% and 10% mica-filled 75PUR/25PEMA IPNs can be seen in Figure 8.7. Table 8.2 shows glass transition temperatures of the IPNs measured from the peaks of tan δ versus temperature plots.

Like the study of 70PUR/30PEMA IPN, it could be seen that mica had no striking effect on the glass transition temperatures of the 75PUR/25PEMA IPNs. The Tgs were 4°C and 80°C in case of the unfilled and 4°C and 81°C for the sample with 10% mica. However, the tan δ values at PUR-rich transition were decreased as mica was added into the IPNs and there were changes in temperature range of tan δ ≥ 0.3. The widest range of 134°C was exhibited by the IPN with 5% mica loading where as a range of 127°C was exhibited by the unfilled IPN.
Loss modulus of the filled samples was noticed to be higher than the unfilled. This was because the IPN became more tightly constrained when the filler was added. At 25°C, the $E''$ values were measured at $6.46 \times 10^6$, $7.24 \times 10^6$, $7.41 \times 10^6$ and $1.07 \times 10^7$ Pa for the unfilled IPN and the IPNs with 2.5%, 5% and 10% filler contents, respectively. This increase in loss modulus could be considered as indicating the better damping capability of the filled IPNs.

![Figure 8.7 Bending loss factor and loss modulus versus temperature plots showing the effect of mica on the 75PUR/25PEMA IPNs.](image)

**Table 8.2** Effect of mica on the dynamic mechanical properties of the 75PUR/25PEMA IPNs.

<table>
<thead>
<tr>
<th>% (wt)</th>
<th>Tg at tan δ max (°C)</th>
<th>Tan δ value at Tg</th>
<th>Temperature range of tan δ &gt; 0.3 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica</td>
<td>PUR</td>
<td>PEMA</td>
<td>PUR</td>
</tr>
<tr>
<td>unfilled</td>
<td>4</td>
<td>80</td>
<td>0.51</td>
</tr>
<tr>
<td>2.5</td>
<td>4</td>
<td>80</td>
<td>0.49</td>
</tr>
<tr>
<td>5.0</td>
<td>4</td>
<td>80</td>
<td>0.49</td>
</tr>
<tr>
<td>10.0</td>
<td>4</td>
<td>81</td>
<td>0.45</td>
</tr>
</tbody>
</table>
8.2.2 Modulated-Temperature Differential Scanning Calorimetry
The effect of mica on the glass transition temperatures of the 75PUR/25PEMA IPN was also again studied by the M-TDSC technique. Similar results to those obtained from DMTA were seen from the dCp/dT versus temperature signal. See Figure 8.8. There was no significant shifts of Tgs observed from the M-TDSC plots. Tgs for the unfilled sample were -38°C and 54°C. Adding 10% mica into the IPN system resulted in an IPN with PUR and PEMA rich phase Tgs of -37°C and 55°C, respectively.

![Figure 8.8 Differential heat capacity versus temperature plots for the mica-filled 75PUR/25PEMA IPNs.](image)

Figure 8.8 Differential heat capacity versus temperature plots for the mica-filled 75PUR/25PEMA IPNs.

8.2.3 Scanning Electron Microscopy
Figure 8.9 shows an SEM investigation of the fracture surfaces for mica-filled samples where good dispersion of filler was achieved at all filler contents.
Figure 8.9 Scanning electron micrographs for the mica-filled 75PUR/25PEMA IPNs with filler weight contents of (a) 2.5% and (b) 5%.
8.2.4 Tensile Study
The unfilled and mica-filled 75PUR/25PEMA IPN specimens were examined by the tensile test method. Figure 8.10 illustrates the tensile properties versus mica content for the 75PUR/25PEMA IPNs. A decreased in tensile stress and elongation was seen, as the filler was added into the IPN matrix. The values of stress at break, modulus of elasticity, and elongation at break of the unfilled IPN were 3.6 MPa, 3.3 MPa, and 713%, respectively. For the IPN with the 10% mica loading, the values of stress and elongation at break dropped to 2.3 MPa and 544% while the modulus of elasticity increased to 5.3 MPa.

8.2.5 Thermogravimetric Analysis
The influence of mica on the thermal properties of the 75PUR/25PEMA IPNs was also investigated under a nitrogen atmosphere using the high resolution mode TGA. The thermograms are illustrated in Figures 8.11 and 8.12. The TGA study showed the same pattern of degradation mechanism, a two-step reaction, for both unfilled and mica- filled samples. The onset of degradation started around 225°C and was complete around 430°C. Most of the sample weight was lost during the second degradation step.
which began after 285°C. At the end of the experiment, the amount of residue left corresponded to the amount of mica added in the IPNs.

![Graphs showing tensile properties for mica-filled 75PUR/25PEMA IPNs.](image)

**Figure 8.10** Tensile properties for the mica-filled 75PUR/25PEMA IPNs.
Figure 8.11 TGA plots for the mica-filled 75PUR/25PEMA IPNs.

Figure 8.12 Derivative TGA plots for the mica-filled 75PUR/25PEMA IPNs.
CHAPTER 9

CONCLUSIONS AND FUTURE WORK
CHAPTER 9

CONCLUSIONS AND FUTURE WORK

9.1 CONCLUSIONS

9.1.1 PUR/PEMA Simultaneous Interpenetrating Polymer Networks
Two-component IPNs consisting of polyurethane and poly(ethyl methacrylate) were prepared by the simultaneous technique. By varying the relative amount of each polymer in the IPN, the properties may be altered. Effects of the PUR/PEMA ratio on damping ability, thermal and mechanical characteristics were determined. The semi-miscible nature of PUR and PEMA was reflected in glass transition temperatures and dynamic mechanical properties of the IPNs.

The crosslinked PUR and PEMA homopolymers exhibited relatively high tan δ values and sharp Tgs at -5°C and 105°C, respectively. In comparison to the constituent polymers, each IPN produced an inward-shift of glass transitions with a broader tan δ peak indicating a certain degree of molecular mixing between the two networks. Single transition peaks were also observed at both ends of the composition range, -2°C, 77°C and 97°C for the 90/10, 30/70 and 10/90 PUR/PEMA IPNs, respectively. Significant changes in the DMTA plots took place at the mid-range composition, 70/30 and 50/50 IPNs, where there was exhibited two prominent shoulders of PUR and PEMA-rich phases, suggesting a higher degree of phase separation. The 70PUR/30PEMA showed its Tgs at 2°C and 94°C and a loss factor ≥ 0.3 spanned a range of 132°C. The striking features of this IPN, a broad tan δ peak with almost constant amplitude over a wide temperature range, was required for a potential material for damping applications.

Corresponding data on the morphology of the IPNs was confirmed by TEM together with complementary information on extent of component mixing from M-TDSC. At the 90PUR/10PEMA IPN composition, TEM micrographs revealed a predominantly PUR matrix containing dispersed PEMA phase domains smaller than 50 nm. A two-phase morphology with interconnected PEMA domains stretching throughout the
matrix of PUR was seen at the 70/30 and 50/50 PUR/PEMA IPNs. At the end of the composition range, the 30/70 and 10/90 PUR/PEMA IPNs showed a very fine morphology with the matrix of the PEMA major component and blurred domains of PUR finely dispersed in it. According to M-TDSC, the 30PUR/70PEMA composition exhibited the highest value of component mixing. For all IPNs, although mixing took place to a certain level and network interpenetration was extensive, true solution between the constituent polymers clearly did not occur.

The tensile behaviour of the IPNs highlighted the possibilities of improvements in mechanical performance with an appropriate formulation. As the PEMA content in the IPNs was increased, the tensile stress at break and the modulus of elasticity became higher. With PUR being the major component, adding PEMA ratio resulted in an increase in the elongation at break. The value went through maximum at the 70PUR/30PEMA composition. However, further increase in the PEMA content led to a deterioration of the properties.

9.1.2 70PUR/30PEMA Crosslink Density Study

Another method used to control the IPN properties and morphology was the variation of crosslink density in both the PUR and the PEMA networks. The effects of crosslink density was investigated for the 70PUR/30PEMA IPN. The crosslink densities of PUR networks was varied by altering the polyl (PPG) to triol (TMP) ratio, 2:1, 3:1 and 4.5:1, whereas in PEMA network, different TEGDM concentrations, 2.5%, 5% and 7% by mol, were added into the reaction mixture.

DMTA results showed that an increase in PUR crosslink density limited the segment mobility and shifted the IPN transitions, both of the PUR and the PEMA-rich phases, to higher temperatures. On the contrary, with tighter PEMA networks, no significant effect was observed for the PUR-rich transition. However, the PEMA-rich transition shifted considerably to higher temperature. Corresponding data were also obtained from the M-TDSC investigation.
9.1.3 Filled PUR/PEMA Interpenetrating Polymer Networks

Inorganic fillers of different geometry and weight fractions were introduced into the PUR/PEMA IPNs. The fillers were two types of silica, talc, calcium carbonate and mica. Dispersion of filler particles was examined by SEM and found to be rather uniform for all the filled systems. The effects of fillers on the dynamic mechanical properties and the material strength varied from type to type (See Table 9.1). The conclusions are as follows.

(1) Two grades of silica were used in the study: Aerosil 380 and VN 3. The first consisted of a very fine powder with an approximate diameter of 5 nm, while the latter contains a wide particle size distribution from nanometres up to 50 micrometres. The effects of fillers and filler contents were observed with levels of silica ranging from 0 to 10 wt. %. Addition of Aerosil 380 brought the IPN Tgs to lower temperatures. By contrast, this effect was not observed from the VN 3-filled IPNs. With an increased filler loading, both Aerosil 380 and VN 3, maximum tan δ value and broadening of the peak increased generally. However, at the equivalent filler loading, a better improvement in energy absorbing ability and also mechanical properties was possessed by the IPN containing Aerosil 380.

(2) Talc platelet powders at 2.5%, 7.5% and 12.5 wt % were incorporated into the 70PUR/30PEMA IPN. With the presence of talc, the Tgs shifted to slightly lower temperatures. This filler showed a significant increase in tan δ values at all temperatures and broadened the tan δ-temperature curves. The ultimate tensile strength showed a slight increase at only 2.5% filler loading. Further addition of filler resulted in a decrease of force needed to rupture the samples.

(3) Finely ground calcium carbonate at the same contents as talc was added into the IPNs. Like silica and talc, this filler changed the viscoelastic properties and slightly lowered the IPN transitions. In comparison to the unfilled IPN, the tan δ height at the PUR Tg was decreased with the filler loading. However, the filled samples showed wider ranges of temperatures where the loss factor was greater than 0.3. The enhanced damping ability seemed to reach a maximum at 7.5% filler.
loading, as a slight decrease in tan δ height was recorded for the 12.5% filled sample.

(4) The effects of mica on dynamic mechanical and other properties of the IPN were investigated on the 70/30 and 75/25 PUR/PEMA IPNs. At the 70/30 composition, the filler did not affect the tan δ height, only a broadening of the peak at high temperature was shown by DMTA. In the case of the 75PUR/25PEMA filled IPNs, a decreased tan δ height at PUR Tg accompanied by an insignificant change in the temperature range of tan δ ≥ 0.3 was observed with added filler.

(5) The effects of fillers on the PUR/PEMA IPNs are summarised in Table 9.1. Although not every filler affected glass transition temperatures, they all affected the dynamic mechanical properties of the samples. Incorporation of increasing amounts of Aerosil 380 shifted the transitions to lower temperatures and significantly enhanced the damping ability by increasing the loss factor values and broadening the curves. At the highest filler loading (10 wt%), the Tgs were measured at −5°C and 79°C (maximum tan δ = 0.72). Talc and calcium carbonate exhibited a similar trend, i.e. a downward shift of Tgs but only a moderate increase in the loss factor. An addition of 12.5 wt% talc reduced the Tgs to −4°C and 92°C (maximum tan δ = 0.67). The Tgs for calcium carbonate-filled IPN at the same filler content were −7°C and 86°C (maximum tan δ = 0.63). However, no significant improvement in damping ability and only minimal changes in Tgs were detected from the mica-filled IPNs.

In general, introducing the fillers resulted in a stiffening effect and increased the modulus of elasticity of the IPNs, but decreased the elongation at break. Improved tensile strength was only shown by the IPNs filled with the very fine silica particles of Aerosil 380. The 7.5% Aerosil 380-filled IPN showed the greatest tensile stress at break (6.7 MPa) with modulus of elasticity and elongation at break values of 9.5 MPa and 830%, respectively. For the same filler content, the presence of other fillers showed a deterioration of the tensile strength. The values
decreased from 4.6 MPa for the unfilled IPN to 4.1 MPa for the VN 3 and talc-filled IPNs, and 3.7 MPa for the calcium carbonate-filled IPN.

Table 9.1 Effects of filler on the PUR/PEMA IPNs

70PUR/30PEMA IPNs crosslinked with 3:1/PPG:TMP

<table>
<thead>
<tr>
<th>Silica, Aerosil 380</th>
<th>$T_g$ (°C)</th>
<th>Tensile properties*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMTA</td>
<td>M-TDSC</td>
</tr>
<tr>
<td></td>
<td>$\sigma_b$ (MPa)</td>
<td>E (MPa)</td>
</tr>
<tr>
<td>unfilled</td>
<td>2.94</td>
<td>-34, 61</td>
</tr>
<tr>
<td>2.5%</td>
<td>-1.87</td>
<td>-36, 61</td>
</tr>
<tr>
<td>5.0%</td>
<td>-2.83</td>
<td>-37, 57</td>
</tr>
<tr>
<td>7.5%</td>
<td>-2.79</td>
<td>-37, 54</td>
</tr>
<tr>
<td>10.0%</td>
<td>-5.79</td>
<td>-36, 53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Silica, VN 3</th>
<th>$T_g$ (°C)</th>
<th>Tensile properties*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMTA</td>
<td>M-TDSC</td>
</tr>
<tr>
<td></td>
<td>$\sigma_b$ (MPa)</td>
<td>E (MPa)</td>
</tr>
<tr>
<td>unfilled</td>
<td>2.94</td>
<td>-34, 61</td>
</tr>
<tr>
<td>2.5%</td>
<td>3.94</td>
<td>-35, 61</td>
</tr>
<tr>
<td>5.0%</td>
<td>3.95</td>
<td>-34, 62</td>
</tr>
<tr>
<td>7.5%</td>
<td>3.95</td>
<td>-34, 63</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Talc, SF-10</th>
<th>$T_g$ (°C)</th>
<th>Tensile properties*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMTA</td>
<td>M-TDSC</td>
</tr>
<tr>
<td></td>
<td>$\sigma_b$ (MPa)</td>
<td>E (MPa)</td>
</tr>
<tr>
<td>unfilled</td>
<td>2.94</td>
<td>-34, 61</td>
</tr>
<tr>
<td>2.5%</td>
<td>-3.90</td>
<td>-35, 54</td>
</tr>
<tr>
<td>7.5%</td>
<td>-4.91</td>
<td>-37, 51</td>
</tr>
<tr>
<td>12.5%</td>
<td>-4.92</td>
<td>-42, 54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CaCO\textsubscript{3}, RLO 6083</th>
<th>$T_g$ (°C)</th>
<th>Tensile properties*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMTA</td>
<td>M-TDSC</td>
</tr>
<tr>
<td></td>
<td>$\sigma_b$ (MPa)</td>
<td>E (MPa)</td>
</tr>
<tr>
<td>unfilled</td>
<td>2.94</td>
<td>-34, 61</td>
</tr>
<tr>
<td>2.5%</td>
<td>-2.90</td>
<td>-37, 60</td>
</tr>
<tr>
<td>7.5%</td>
<td>-6.86</td>
<td>-38, 62</td>
</tr>
<tr>
<td>12.5%</td>
<td>-7.86</td>
<td>-37, 56</td>
</tr>
</tbody>
</table>
filled samples is needed on this aspect. Work should be conducted on sound absorption measurements and also the use of the IPN materials in extension and constrained layer damping systems.

(3) Incorporation of other fillers into the PUR/PEMA IPNs should be examined in order to modify the damping and physical properties of the material and/or to reduce cost. For example, the use of short fibres (e.g. glass and carbon) is widely used for the stiffness and tensile strength improvement. Barium sulphate is another commonly encountered filler used in polyurethane foam to enhance sound absorption properties. It is usual to introduce filler as dispersions in the polyol component of the polyurethane reaction mixture. One should bear in mind that all fillers must be dried in order to prevent undesirable reaction with the isocyanate groups.

(4) In order to obtain improved properties in the filled IPNs, an attempt should be make to study the effect of filler surface modification. Improvement in mechanical properties and dispersion of the filler in polymer matrix could be expected from this investigation. A wide range of surface modifiers are offered and used commercially for this purpose. For example, fatty acids and organosilanes. Moreover, methods of characterising the surface and some effects of modification should also be considered.
REFERENCES


29) R.R. Roessler, Mod. Paint and Coat, April, 46 (1986).


36) D.J. Hourston, and Y. Zia, Polymer, 20, 1497 (1979).


57) D.J. Hourston, and F.U. Schafer, Polymer, 37, 16, 3521 (1996).
82) Calcium Carbonates from ECC., Bull. CC1, ECC International Ltd., Cornwall, England.


181) Aerosil 380 data sheet, Degussa Ltd.


184) VN data sheet, Degussa Ltd.
Appendix A : Product Definition For Micronised Mica SX300

Description
This mica grade is micronised using selected muscovite raw material to give a product with carefully controlled size distribution.

Typical Properties

<table>
<thead>
<tr>
<th>Chemical Analysis</th>
<th>Percentage by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>as SiO₂</td>
</tr>
<tr>
<td>Aluminium</td>
<td>as Al₂O₃</td>
</tr>
<tr>
<td>Potassium</td>
<td>as K₂O</td>
</tr>
<tr>
<td>Iron</td>
<td>as Fe₂O₃</td>
</tr>
<tr>
<td>Sodium</td>
<td>as Na₂O</td>
</tr>
<tr>
<td>Magnesium</td>
<td>as MgO</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td></td>
</tr>
</tbody>
</table>

Physical Properties

- Specific Gravity: 2.8
- Refractive Index: 1.58
- Hardness: Moh’s scale 2.5
- pH: BS 3483 8
- Water Soluble Matter: BS 1795 0.3%

Particle Size Distribution by Malvern Laser Diffraction

![Particle Size Distribution Graph](image)
Appendix B : Product Definition For Talc, Microtal SF-10

Description
This is a finely micronised high brightness grade of industrial talc, suitable for use in plastics and surface coating where colour is of prime importance.

Typical Properties

<table>
<thead>
<tr>
<th>Chemical Analysis</th>
<th>Percentage by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>as SiO₂</td>
</tr>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Aluminium</td>
<td>as Al₂O₃</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>Iron</td>
<td>as Fe₂O₃</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Calcium</td>
<td>as CaO</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>Magnesium</td>
<td>as MgO</td>
</tr>
<tr>
<td></td>
<td>31</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>(CO₂ + H₂O)</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
</tr>
</tbody>
</table>

Physical Properties
Specific Gravity       2.8
Refractive Index       1.62
Loose Bulk Density     kg/litre 0.22

Particle Size Distribution by Malvern Laser Diffraction
Appendix C : Stress/strain curve for the 70PUR/30PEMA IPN

Sample : Dumbbell specimen
Load cell : 500 N
Crosshead speed : 50 mm/min
Maximum load : 70.34 N
Maximum stress : 6.808 MPa
Extension at maximum load : 223.2 mm
Strain at maximum load : 892.9 %