



# Rubber modified acrylic polymers

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#### RUBBER MODIFIED ACRYLIC POLYMERS

A thesis

submitted for the Degree of

Master of Engineering

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INDUSTRIAL CHEMISTRY

at the

UNIVERSITY OF NEW SOUTH WALES

by

X. XIE, B.Sc.

MARCH, 1991

UNIVERSITY OF N.S.W.

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I hereby declare that the work described in this thesis is my own work and has not been submitted, in part or in full, to any other university or institution for any other degree or diploma whatsoever.

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#### ABSTRACT

Α toughened acrylic system based poly(methyl on methacrylate) (PMMA) with acrylic rubber (AR) was examined either as simple blends or interpenetrating polymer networks (IPNs). In the IPNs system the acrylic rubber served as network I, and the poly(methyl methacrylate) as network II. Two series of IPNs were prepared from two acrylic rubber networks, one being crosslinked with sodium stearate (with or without sulphur) and the other with acrylic acid anhydride (AAA). The AAA is a labile crosslinker and its hydrolysis leads to an extractable linear polymer. PMMA was crosslinked using TMPTMA in both series of full IPNs. The simple blends were prepared in two ways one being in mechanical mixing and the second by solution casting.

The systems were characterised on the basis of mechanical properties, dynamic mechanical behaviour and morphology. The results presented show that IPNs ( crosslinked with sodium stearate/sulphur ) possess better tensile properties than those of simple blends and the IPNs( crosslinked with AAA). Thermal analysis of simple blends, semi- and full IPNs reveals two glass transition temperatures, indicating an incompatible system. However, broadening and shifting of the glass transitions occurs, showing that the full IPNs have some limited missicibility compared with the other finer than in simple blends.

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#### CHAPTER ONE

#### INTRODUCTION

In the search for new materials people have polymerised new monomers, or made new random, block or graft copolymers from existing monomers. A third alternative has been to blend existing polymers to produce materials with new properties. An obvious advantage of this approach is that it usually requires little or no capital expenditure relative to the production of new polymers.

Rubber-plastic blends have been developed by polymer industry to improve the properties, balance processability and decrease cost. In general, rubber modification with plastics can improve the tensile strength, tear strength, modulus and wear resistance, whilst rubber modified plastics show improved impact resistance and associated toughness.

The toughening of brittle, glassy polymers is an important undertaking in the polymer industry. For example, high impact polystyrene is manufactured by the addition of rubbers having low glass transition temperatures. Transparent poly(methyl methacrylate) (PMMA) is a commercial polymer with excellent weathering resistance, but its high glass transition temperature results in the

polymer being very brittle at room temperature. Toughening PMMA with rubber is often necessary for many applications, where high impact strength and durability are needed. Since glass transition temperatures of rubbers are generally much lower than that of PMMA, blending the PMMA with rubber can reduce the glass transition temperatures of the mixture in compatible blending systems so as to achieve the toughening of the PMMA.

Acrylic rubber is expected to be compatible to PMMA due to the similar chemical structure as shown below scheme and has a similar excellent weathering resistance to PMMA. The expected similar refractive index and reasonable miscibility is desirable for good transparency.

$-(CH_2-CH)_n-$	CH <sub>3</sub>
C=O	$-(CH_2-CH)_n-$
	 C=0
 R	 0-CH <sub>3</sub>
(Where R is typically a long, linear alkyl or dialkyl ether group)	

Acrylic Rubber

PMMA

The aims of this work are to develop a tough transparent polymer based on acrylic rubber/PMMA. Mixture may be either simple blends or interpenetrating polymer networks (IPNs).

#### CHAPTER TWO

#### LITERATURE REVIEW

The literature reveals considerable interest in recent years concerning the morphology, phase relationships and mechanical properties of two phase, polyblend-like polymer and interpenetrating polymer networks (IPNs) systems The first component polymer system. appear as а discontinuous, dispersed phase in a continuous phase of the other polymer. The main effort has centred around high-impact plastics or rubber toughened plastics. Examples are high impact polystyrene(HIPS), acrylonitrile-butadienestyrene(ABS), toughened poly(vinyl chloride) (PVC), blends, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) toughened polypropylene (PP), nylon and epoxy resins[65].

Although similar acrylic rubber/poly(methyl methacrylate) blends have not been found in the open literature, a series of papers have discussed the semi- and full IPNs based on polyurethane/ polyacrylate (or polymethyl methacrylate) [1-15], poly(n-butylacrylate)/polystyrene [16-21] and IPNs based on polyacrylate polymers [22-27] systems. The polyacrylate polymers system of poly(ethyl acrylate)/poly(methyl methacrylate) is quite similar to acrylic rubber/PMMA. A variety of toughened acrylics are

now available, for example, in the coatings industry, a mixture of acrylic monomers are copolymerised to gave a desirable glass transition temperature (Tg)[92].

Some experimental methods and mechanisms mentioned in the literature can be applied to acrylic rubber/poly(methyl methacrylate) system and some experimental results in the literature can be compared with acrylic rubber/poly(methyl methacrylate) system.

#### 2.1 <u>TYPES OF POLYMER BLENDS AND NETWORKS</u>

#### 2.1.1 POLYMER BLENDS

#### 2.1.1.1 <u>Preparation of Polymer Blends</u>

A variety of experimental techniques are used to prepare and characterise polymer blends (see Section 2.2). Synthetic methods can be put into four categories (1) mechanical mixing (melt process); (2) mixing from ternary system (solution casting); (3) mixing via reaction[28]; (4) mixing by using surfactants[29].

The mechanical mixing and solution casting are simple blending systems and their preparations have been reviewed in the literature [30-31,66-69].

#### 2.1.1.1.1 Mechanical Mixing

Mechanical mixing is the most common commercial method for producing polymer blends. It offers the advantage of introducing no foreign components such as solvents. For this reason and because of simplicity and speed of melt mixing, it has economic advantages making it the primary commercial blending method. By using proper equipment (extruders or internal mixers), it is possible to obtain excellent dispersion and equilibration of the components. Temperature, time and environment for the mixing can be carefully controlled.

The primary disadvantage of mechanical mixing is that both the components must be in the molten state which can mean that temperatures may be high enough to cause degradation. The another disadvantage of mechanical mixing is the cost of equipment involved. Experimentally even a small internal mixer demands >50g of solid, which may be significantly large for exotic, research sub-grades.

The preferred industrial method for mechanical mixing is by use of a screw extruder which can be run continuously and produce polymer in a convenient form for further processing. Twin screws and other devices are often used to increase shear and improve mixing. Internal mixers may have "Banbury" rotors, or other configurations, and are widely used for rubbers and PVC. Many other types of mixers exist,

including two roll mill in which mixing takes place by repeatedly forcing the polymers through the gap between two rotating rollers (ie the "nip").

#### 2.1.1.1.2 Solution Casting

Solution casting in which two polymers are dissolved in a common solvent and the solvent allowed to evaporate to produce a film is the simplest mixing method available and is widely practiced. This is convenient way of making blends and it is often used in the laboratory since it requires little material and uncomplicated equipment. The resulting film is immediately useful for thermal analysis, dynamic mechanical analysis, mechanical testing, microscopic examination etc.. In many cases, temperature may not exceed ambient, so thermal degradation is reduced.

However, solution casting has obvious commercial disadvantages due to the cost and difficulty of solvent recovery as well as the potential environmental hazards associated with handing large volumes of often toxic chemicals. Furthermore, even when two polymers are miscible this method does not ensure homogenous blends since phase separation in the presence of the solvent. This occurs if there is a difference in the interactions between the solvent and each of the two polymers. This is called "A $\chi$ " effect[70,71]. Superficially, when one polymer interacts more strongly with the solvent, then it will force out the

other polymer from solution in order to maximise the number of favourable contacts. Thus a fractionation process occurs, which leads to microphase and possibly macro separation.

There are a number of methods for casting thin uniform films from polymer solution. One simple method is to spread the solution over a glass plate by rolling a rod wound with wire previously immersed in the mixed polymer solution in a puddle of the syrup. The simplest method is to cast dilute solution into dishes, which is commonly used in laboratory. Selection of solvent, initial concentrations, temperature and evaporation rate, and finial thickness may also be important. Advantage of method is that any cloud points etc can be observed visually.

#### 2.1.1.1.3 Mixing via Reaction

Mixing via reaction is a more complicated blending system, where a polymer is dissolved in a monomer, the monomer polymerised and a fine dispersion of two polymers produced. This blending system is often used both commercially and in the laboratory. There are many examples of the commercial application of this process for the production of rubbertoughened plastics, some of which have been described in detail[72]. This method is used to make HIPS, where polybutadiene, for example, is dissolved in styrene monomer. The subsequent polymerisation of styrene leads to

phase inversion with PBD as the dispersed phase. Some interfacial grafting doubtless occurs[74]. Other examples are given in the same reference.

Other forms of reactive mixing occur during extrusion, where for example in situ grafting of maleic anhydride onto polypropylene homo/copolymers by peroxides allows compatibilization with polyamides in the extruder barrels.

Another class of mixing via reaction products are the IPNs. These have been reviewed by Sperling [32,33]. and are described in detail elsewhere (Section 2.1.2).

#### 2.1.1.2 <u>Thermodynamics of Polymer Blends</u>

#### 2.1.1.2.1 <u>Basic Thermodynamics</u>

When two polymers are blended, by whatever methods, the most likely result is a two phase material. The reason why two polymers are usually not miscible can be considered on thermodynamic grounds. A necessary (but not sufficient) criterion for miscibility is that the free energy of mixing  $\Delta G_m$  shall be negative. That is given by

$$\Delta G_{m} = \Delta H_{m} - T\Delta S_{m}$$
 2.1

 $T\Delta S_m > \Delta H_m$ 

or

where  $\Delta H_m$  is the enthalpy of mixing;  $\Delta S_m$  is the entropy of mixing and T is the absolute temperature.

It is necessary to consider how both the  $\Delta H_m$  and  $\Delta S_s$  parts, are affected by composition and temperature. For miscibility[36,65,73]  $\Delta G_m$  must be negative and satisfy the additional requirement.

$$\left(\frac{\partial^{2}\Delta G_{\text{mix}}}{\partial \Phi_{i}^{2}}\right)_{T,P} > 0 \qquad 2.2$$

where P is the pressure,  $\phi$ i is the volume fraction of each component. If equation (2.2) is obeyed, then no phase segregation will occur.

Figure 2.1c shows the dependence on the free energy of a mixture on composition at three temperatures [58]. At  $T_1$  the above two conditions are fully satisfied and a miscible, single-phase mixture occurs for all compositions. At  $T_2$  equation (2.2) is not satisfied for all compositions and mixtures between the points B and B' separate into two phases. At these compositions the resulting total free energy falls on the dashed line which is lower than that of the homogenous phase (solid line). The curve for an intermediate temperature  $T_c$  has been drawn in a manner satisfying the conditions of a critical point at C. In Figure 2.1a  $T_1>T_2$  and Tc is an upper critical solution

temperature (UCST), whereas in Figure 2.1b,  $T_2>T_1$  and Tc is a low critical solution temperature (LCST).



Fig. 2.1 Phase diagram for mixtures: (a) UCST; (b) LCST; (c) composition dependence of the free energy of the mixture (on an arbitrary scale)[65].

The solid line (Fig. 2.1a and Fig.2.1b) is a curve of equilibrium phase separation called the binodal and on this curve,

$$\left(\frac{\partial \Delta G}{\partial \varphi}\right)_{\mathrm{T},\mathrm{P}} = 0$$

inside the binodal, there is a region of metastability, the

limit of which is shown by the dotted line, called the spinodal. On this curve,

$$\left(\frac{\partial^2 \Delta G}{\partial \varphi^2}\right)_{T,P} = 0$$

At the critical temperature, Tc, a homogeneous mixture is produced at all compositions, and at this point

$$\left(\frac{\partial^3 \Delta G}{\partial \phi^3}\right)_{T,P} = 0$$

It can be seen that temperature is very important for miscibility. Some mixtures are more compatible at higher temperatures, exhibit upper critical solution temperatures (UCST) and some others are more compatible at low temperatures and often exhibit lower critical solution temperatures (LCST).

#### 2.1.1.2.2 Flory and Huggins Theory

In term of the lattice theory developed by Flory and Huggins[75,76] the entropy of mixing is given by

$$\Delta S_m = -R \left( N_1 \ln p_1 + N_2 \ln p_2 \right)$$
 2.3

where  $N_1$  is the number of moles of component 1;  $N_2$  is the

number of moles of component 2;  $\varphi_1$  is the volume fraction of component 1;  $\varphi_2$  is the volume fraction of component 2; R is the gas constant. The enthalpy of mixing is given by

$$\Delta H_{m} = RT\chi_{12}N_{1}\varphi_{2} = BV_{1}\varphi_{2} = (v_{1}+v_{2}) B\varphi_{1}\varphi_{2} \qquad 2.4$$

where  $v_1$  and  $v_2$  are the actual volumes of components,  $V_1$  is the molar volume of component 1,  $\chi_{12}$  is the interaction parameter which can be expressed as

$$\chi_{12} = BV_1/RT \qquad 2.4A$$

B is an interaction energy density which can be expressed as

$$B = [(E_1/V_1)^{1/2} - (E_2/V_2)^{1/2}]^2 \qquad 2.4B$$

where  $(E_1/V_1)^{1/2} = \delta_1$  is the solubility parameter of component 1;  $(E_2/V_2)^{1/2} = \delta_2$  is the solubility parameter of component 2. The equation 2.4 can be written as

$$\Delta H_{m} = V (\hat{o}_{1} - \hat{o}_{2})^{2} \phi_{1} \phi_{2} \qquad 2.5$$

where  $v=(v_1 + v_2)$  is the total volume of mixture.

Some important conclusions can be gained from the above

equations. First,  $\Delta H_m$  does not depend on polymer molecular weight, whereas  $\Delta S_m$  does. Thus for a fixed mass or volume of a blend, the entropy of mixing becomes progressively smaller as the molecular weights of each component increase, the possibility of miscibility decreases. Endothermic mixing ( the case when  $\Delta H_m > 0$  ) does not favour miscibility. Thus for mixing the favourable entropic contribution must be large enough to yield a negative free energy of mixing, but as molecular weights are increased a point is reached where this fundamental requirement can no longer be satisfied and phase separation occurs. On the other hand, for exothermic mixing,  $\Delta H_m < 0$ , the Flory-Huggins theory predicts that all the conditions for miscibility are satisfied no matter how large the molecular weights. Thus as the most simple rule, miscibility of high molecular weight polymers is only assured when mixing is exothermic.

As the criterion of miscibility is  $\Delta G_m < 0$  or  $T\Delta S_m > \Delta H_m$ , the enthalpy of mixing  $\Delta$ Hm must be as low as possible. So when two polymers are blended, the value of  $(\delta_1 - \delta_2)$  shall be selected to be as small as possible. Normally the solubility parameter difference  $(\delta_1 - \delta_2)$  will be <1, and ideally<0.2 [29].

# 2.1.1.3 <u>Phase Separation Behaviour of Polymer-Polymer</u> Blends

#### 2.1.1.3.1 Phase Separation in Polymer Solution

Phase separation has already been studied for a wide range of polymers (including cellulose, vinyl, acrylic derivatives) dissolved in numerous solvents, during the 1940's[34]. The influence of solvent, concentration, molecular weight, and constitution of the macromolecules has been studied for 78 mixtures. The main results are

- (1) Incompatibility normally occurs;
- (2) The greater the concentration of the solution, the wider the range of separation;
- (3) When two high polymers are incompatible in one solvent, they are generally also incompatible in all other solvents;
- (4) The molecular weight of each polymer is of great importance, with higher molecular weight leading to lower compatibility;
- (5) The similarity of the principal chain is not sufficient to ensure the miscibility of the two polymers.

Ternary phase diagrams are normally used in the study of phase separation in polymer blends in homogeneous solutions. As the solvent is rapidly evaporated, the residual polymeric solution enters the two phase region. The process is best illustrated on a ternary phase diagram (Figure 2.2). This is a hypothetical phase diagram for two polymers, with a common solvent showing a two phase region. When the solvent is evaporated from a mixed solution at composition A it enters the two phase region at B. When it leaves at C the phase separated regions may have grown to such a size that remixing does not easily occur and the resultant blend at D is inhomogeneous.



Fig.2.2 A hypothetical phase diagram[28]

For mixing via reaction system, the ternary phase diagram can also be applied to study the phase separation. In the polystyrene/polybutadiene/styrene system which is a high impact polystyrene (HIPS), polybutadiene is dissolved in styrene monomer which is then polymerised by a free radical mechanism. When a small amount of styrene has polymerised, phase separation take place, the phase diagram being shown in Figure 2.3. Initially droplets of a polystyrene rich phase are formed within a polybutadiene rich phase at A. As the polymerisation proceeds the ratio of the two phases will change until the volume fraction of the polystyrene rich phase exceeds the volume fraction of the polybutadiene rich phase ( between B and C). The mixture will then phase invert so that the polystyrene phase becomes continuous. The actual point of phase inversion depends on the viscosities of phases and associated molecular weights of polymers, and stirring with the reactor[28].



Fig.2.3 The ternary phase diagram for mixtures of styrene/polystyrene/polybutadiene[28].

### 2.1.1.3.2 UCST and LCST Effect on Phase Separation

Many polymers show a variation in miscibility with temperature. Low molecular weight polymers are typically more miscible at higher temperature and many phase separate on cooling showing upper critical solution temperature behaviour (UCST). High molecular weight polymers which form homogeneous mixtures are typically less miscible at higher
temperatures and may phase separation on heating, showing lower critical solution temperature behaviour (LCST).

From a purely experimental viewpoint, the study of phase separation at low temperature may be impeded by kinetic reasons especially if the glass transition of the mixture is high. For these reasons, the UCST's reported in the literature are usually concerned with polymer of modest molecular weight for which macroscopic liquid phases, separated into distinct layers and the compositions of conjugated phases can be determined by standard analytical methods. Examples of blends examined in this way include, polyisobutene/poly(dimethyl siloxane) and polystyrene/polyisoprene[89].

Polystyrene/poly(vinyl methyl ether) was the first pair for which thermally induced phase separation was observed. Subsequently polycaprolactone/poly(styrene-coacrylonitrile) and poly(methyl methacrylate)/poly(styreneco-acrylonitrile) were also found to exhibit LCST behaviour[89]. The mixtures of PVC with poly(n-hexyl methacrylate), poly(n-butyl acrylate) and poly(n-propyl acrylate) phase separate when heated in the region between 100°C and 160°C indicating the existence of a lower critical solution temperature[43].

Thus it can be seen that homogeneous mixtures may occur phase separation at either lower temperatures or higher

temperature, exhibiting LCST or UCST behaviour.

#### 2.1.1.4 Effect of Composition on Properties

How properties are effected by varying compositions depends upon the particular property, the nature of the components (glass, rubbery, or semi crystalline), the thermodynamic state of the blend (miscible or immiscible) and its mechanical state. The amorphous portions of the blend components of a miscible pair form a single phase. The property dependence on compositions for such systems is different from that for immiscible mixtures, where each component in the blend is present as a separate phase.

## 2.1.1.4.1 <u>Miscible Blends</u>

Miscible binary blends of amorphous polymers have only one phase morphological phase and their properties are easily related to those of the blend components. Miscible blends show a single, composition-dependent glass transition which varies monotonically with composition reflecting the mixed environment of the blend on the property-composition diagram as shown in Figure 2.4. The Tg relation usually falls below the tie-line connecting the Tg's of the pure components in accordance with the Fox [35] and other glass transition temperature equations[36,37]. The miscible blends composition in has dependence on considerable commercial significance, because it largely determines the heat-distortion temperature (HDT) or the maximum-use temperature of the blend.



Fig. 2.4 Typical property vs composition relations for miscible blends of polymers A and B[65].

Miscible systems exhibit tensile strengths as a function of blend composition that are at least a weighted average of the values corresponding to the two components, for example, a near linear dependence. Often miscible blends have been reported to show a small maximum in tensile strength over certain blend compositions[90].

## 2.1.1.4.2 <u>Immiscible Blends</u>

An immiscible mixture of polymers shows multiple amorphous phases as determined, for example, by the presence of multiple glass transition temperatures. The property vs composition diagrams differ from those for miscible systems. For example, in amorphous immiscible binary mixtures, the stiffness, strength properties of principal component largely determine the properties of the blend[38,39] as illustrated in Figure 2.5.



Fig.2.5 Property vs composition profiles of immiscible(\_\_\_\_) and miscible(---) blends[65]

Poor elongation and impact-strength properties are related to poor stress transfer between the phases of the immiscible blend since low molecular attractive forces between the blend components are responsible for the immiscible-phases are to be expected. It is believed that this poor interfacial adhesion causes premature failure under stress as a result of the usual crack-opening mechanisms[93]. Immiscible blends have been reported to exhibit a broad minimum in tensile strength as a function of composition[90].

#### 1.2.1.5 Morphology

The large majority of polymer blends comprise multiphase systems, due to the positive free energy of mixing and differences in chain packing etc.. The morphology of such systems can be controlled to allow synergism of properties and also to produce commercially successful grades of polymers. These morphologies may consist of one phase dispersed in matrix of other polymers. The dispersed phase may take the form of simple spheres, fibrils or platelets as shown in Figure 2.6.

Another distinct morphology consists of both phases simultaneously having a continuous character[40] or an interpenetrating network exhibiting domain phase formation. (Figure 2.7). This is described in detail in Section 2.1.2.

The dimensions of the phases formed are important in all these morphologies. The featuresof the block which will effect the dimensions of phases can be classified as (1) The difference of viscosities of the two polymers. The larger the difference of the viscosities, The larger the size of the dispersed phase.



Fig. 2.6 Different types of dispersion of a polymer (dark regions) in the matrix of an immiscible polymer. (a) spherical droplets, (b) fibrils, (c) deformation[65].



Fig. 2.7 Conceptual illustration of an IPN of phases by showing the two interlocking materials separated from one another[95].

(2) Miscibility of polymers. The greater the difference between solubility parameters, the rough the blend domains.
(3) Constitution of polymers. Of these three features, the difference of viscosities of polymers is the most crucial in effecting the dimensions of phases for blends.

Novel microdispersions of one polymer in another in incompatible polymers have been created by solvent devolatilization[41]. Depending on the relative amounts of the two polymers and the rate of evaporation, polymer blends of widely differing morphologies can be formed. The larger particles can be made by slow evaporation and smaller particles by rapid evaporation, thus controlling dispersion partial size.

#### 2.1.1.5 <u>Acrylate-based Polymer Blends</u>

Some commercial blends with acrylic polymers are showed in Table 2.1[42], although it is expected that others also exist. Many compositions have not been revealed by the manufactures.

In recently developed new materials, PMMA is also blended with polybutadiene, acrylonitrile and poly(butyl acrylate). The materials exhibit higher impact strength, better chemical resistance, and reduced notch sensitivity[68]. Commercial high impact materials based on acrylate polymers include Diakon MX (ICI), Oroglas DR (Rohm and Haas) and Plex 8535-F (Rohm GmbH). In comparison with the better known ABS and ASA materials the high impact PMMA-type materials have generally lower values for mechanical properties such as tensile strength, impact strength and modulus. However long term weathering test shows the marked superiority of the toughened PMMA over ABS and even ASA materials to degradation[94].

Table 2.1	Acrylate-	based pol	Lymer bi	lends[42]
-----------	-----------	-----------	----------	-----------

Acrylate Polymer	Polymer Modifier	Phase Behavior	Property Modification	Applications
AMMA	PVF <sub>2</sub>	Miscible	Improved chemical resistance	Weatherable film
FMMA	PET	Immiscible	Lower cost, lower warpage	Electrical/electronic
FMMA and copolymers	Unsaturated polyesters	Immiscible	Lower shrinkage, low profile additive	Sheet molding compounds

Poly(methyl methacrylate)(PMMA)/PVC blends combine the heat resistance of the chemical PMMA and and flammability resistance of PVC into a material for injection moulding and extrusion applications. Commercial (PMMA) has been noted to be miscible with PVC[43]. However other studies have noted phase separation for these blends. The phase behaviour is considered to be only partially miscible at most and quite dependent upon composition of the PMMA and PVC constituents of the blend[44].

Blends of PMMA and poly(vinylidene fluoride)  $PVF_2$  have been also studied by many investigators(45-47) and found to be miscible when melt blended (Fig.2.8).



Fig. 2.8 Dynamic mechanical properties at 110 Hz for annealed 40% wt%  $PVF_2$  blend [46].

PVF<sub>2</sub> added in low amounts to PMMA acts as a polymeric plasticiser[48], whereas PMMA added in low amounts to  $PVF_2[49]$  yields improved processability. Since the Tq of  $PVF_2$  is much lower than that of PMMA, the  $PVF_2$  reduces the blend Tg and plasticises the PMMA component. This reduces strength and modulus and increases elongation at break with initial increase in PVF<sub>2</sub> content. Further addition of PVF<sub>2</sub> continues this trend until the Tg of the blend is reduced sufficiently and the  $PVF_2$  content is high enough (i.e. >40%) to allow it to crystallise. Continued addition of PVF<sub>2</sub> (60%) causes strength to increase and ductility to decrease as the crystalline portion of PVF, becomes the principal component[77]. Both components are resistant to UV degradation. Weatherable film applications have been suggested.

A blend of PMMA and Poly(ethylene terephthalate) was commercially available from Rohm and Haas under the trade name "Report"[50]. The blends were fibreglass reinforced and were offered for automotive and electrical markets where low warpage and fast moulding cycles are needed.

In a study of compatibility of polyacrylates and polymethacrylates with PVC[43], it has been found that all polymethacrylates up to (n-hexyl methacrylate), and poly(npropyl acrylate) and (n-butyl acrylate) are compatible with PVC. Higher chain polyacrylates are incompatible[43].

Poly(methyl acrylate) and poly(ethyl acrylate) are incompatible with PVC when prepared by solvent casting or mechanical mixing, but compatible when prepared by in situ polymerisation as shown in Figure 2.9.



Fig. 2.9 Tand -temperatures for mixtures of PMMA/PVC -solvent cast; 0-mechanical mixing; A-in situ polymerised[43]

The morphology of polystyrene/poly(methyl methacrylate) blends were studied by scanning electron microscopy (SEM) [78]. The pure PS (Figure 2.10) and pure PMMA (Figure 2.11) display characteristically different fracture surface displaying rather features, the PMMA one regular, recurrent, and intersecting parabolic structures. In the PS/PMMA system with PS (Mn = 19,650, W = 4.96 wt%) as the dispersed phase and PMMA as the continuous phase the morphology is found to be as shown in Figure 2.12. Clearly, successful use of SEM microscopy for this study depends on the ability to distinguish PS regions from PMMA regions.



Fig. 2.10 Pure, high-molecular-weight PS, 1150X[78].



Fig. 2.11 Pure, high-molecular weight PMMA. 1200X[78]



Fig. 2.12 PS/PMMA system with PS the dispersed and PMMA the continuous phase[78].

#### 2.1.2 INTERPENETRATING POLYMER NETWORKS

## 2.1.2.1 Definition of an Interpenetrating Polymer Network

An interpenetrating polymer network IPN has been defined as "a combination of two polymers in network form, at least one of which is synthesised and /or crosslinked in immediate presence of the other"[32]. Research in interpenetrating polymer networks (IPNs ) over the past ten years has been reviewed by Sperling[32,33,].

Depending on the method of synthesis, IPNs are generally

classified into three groups:

- Simultaneous IPNs, where both monomers are mixed together and polymerised by independent and noninterfering routs;
- (2) Sequential IPNs, where the networks are made sequential;
- (3) Thermoplastic IPNs, in which physical rather than chemical crosslinks are utilised.

In IPNs when only one of the polymers is crosslinked, the products will be called semi-IPNs. If polymer I is crosslinked and polymer II is linear, the product is called a semi-IPN of the first kind of or semi-1 IPN. If polymer I is linear and polymer II is crosslinked, a semi-IPN of the second kind or semi-2 IPN[61].

They are shown schematically in Figure 2.13, and compared with other polymers including blends and grafts.

## 2.1.2.2 <u>Acrylic Rubber Networks</u>

Acrylic elastomer, designated ACM by ASTM D1418-85[51], have no unsaturation in the polymer backbone. The backbone polymers are primarily copolymers of ethyl and butyl acrylate with a variety of monomers of a proprietary nature that provide cure sites and modify the balance between heat resistance, low temperature properties and oil resistance.



Fig. 2.13 Schematic diagram of two-polymer combinations; (a) a polymer blend; (b) a graft copolymer; (c) a block copolymer; (d) a semi-IPN; (e) an IPN; (f) an AB crosslinked copolymer. The solid line represents polymer I; dotted line represents polymer II. Enlarged intersections represent crosslink sites[96].

The basic chemistry and compounding of acrylic elastomers is summarised in several standard texts [51,63,97,] and in commercial literature [79].

#### 2.1.2.2.1 Chemistry of Acrylic Elastomer

Conventional acrylic elastomer are copolymers having two major components: the backbone, comprising 95 to 99 percent of the polymer; and the reactive cure site comprising 1 to 5 percent of the polymer. The copolymers have high molecular weights, a typical M<sub>v</sub> being around 100 000 amu.

The backbone is made from monomeric acid esters of primarily two types:

(1) Alkyl

$$-(CH_2-CH)_x -$$
  
|  
C=0  
|  
O-C\_nH2\_n+1

e.g. if n=2 ---ethyl acrylate e.g. if n=4 ---butyl acrylate

and (2) Alkoxy

$$(CH_2 - CH)_x -$$
  
|  
C=0  
|  
0 - CH\_nH\_{2n}O - C\_mH\_{2m} + 1

e.g. if n=2 and m=2 --- ethoxy ethyl acrylate

The reactive cure sites can be distinguished as [51]

(1) Unsaturated cure sites

(2) Chlorine cure sites

- (3) Epoxy cure sites
- (4) Hydroxyl cure sites
- (5) Multiple cure sites

Chlorine and epoxy types are most commonly used "Hycar" acrylic elastomers (B.F.Coodrich) contain chlorine type cure sites[79]. A typical monomer of this kind can be represented in the following general way:

where R is a group able to enhance the reactivity of the double bond and/or of the vicinal chlorine atom. The historical evolution of "R" can be summarised in Table 2.2 where some examples of monomers are reported[52].

Table 2.2	Histor	ical	evolution	of	"R"	[52]	l
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YEAR	COMMENT	R	MONOMERS
'50	Chlorine containing monomer		2-chloroethylvinylether(2)
'60	Monomer containing higher reactive chlorine		vinylchloroacetate (3)
'70	Monomer containing high. react. chlorine and activated double bound	(Q)	p-vinylbenzylchloriđe (4)

2.1.2.2.2. Vulcanisation of Chlorine Containing Elastomer

Many cure systems were developed to vulcanise acrylic elastomer containing chlorine cure site monomers. The most successfully commercial system is the soap-sulphur type in ratios 10 to 1 by weight. The curing mechanism is shown below:



According to this reaction, crosslinks are of the polysulphide type, probably quite short, and the soap acts as an acceptor of the released chlorine. As seen only one reactive monomer is involved for each crosslinking reaction.

This flexible system offers the ability to tailor

compounds to particular process requirements, yet still requires the traditional oven post-cure to achieve optimum physical properties.

#### 2.1.2.2.3 Advances in Acrylic Elastomer Cure Technology

In recent years, polymers based on epoxy and carboxyl functional monomers[53], have been introduced offering improvements in cure rate. However, these compounds sacrifice up to 25°C in heat resistance, and often are very scorchy or unstable in storage.

B.F.Goodrich developed polymers based on a dual chlorinecarboxyl cure-site system which offers superior heat and compression set resistance[54].

In 1987, a new cure technology, Non-Post-Cure" (NPC) [55,56], was discovered. Unique processing and cure behaviour results from curing chlorine-carboxyl cure-site polymer with a soap-quaternary salt system. The NPC system provides excellent cure rate, heat resistance and low compression set, while maintaining the excellent oil resistance inherent in acrylic elastomers. The NPC cure system mechanism is catalytic in nature, so that as each crosslink is formed, a new reactive site is generated with a very low activation energy requirement for forming the next crosslink. Therefore, the NPC system cures very quickly and completely with a stable chlorine crosslink.

#### 2.1.2.2.5. Synthesis of Acrylic Polymer Networks

A U.V. photochemical and chemical addition method has been developed for crosslinking poly(n-butyl acrylate)[16,20,22-24] networks. The crosslinkers used include acrylic acid anhydride (AAA) as the labile crosslinker, or tetrethylene glycol dimethacrylate(TEGDM) and divinybenzene (DVB) as the permanent crosslinkers.

Acrylic acid andydride is a labile crosslinker and can produce acrylate polymer networks which can be decrosslinked with base[17,20]. The mechanism is shown in below:



DECROSSLINK

The labile crosslinker (AAA) is very useful for the study of IPNs which can give semi IPNs. The reverted linear polymer is now extractable, so that morphology studies of the voided continuous (crosslinked) component can be made[16]. Further detail is given in Section 2.1.3.2

Experimental values of Mc estimated from swelling measurements and shear modulus at 10 seconds, are compared with the theoretical values calculated from the monomer/crosslink ratios shown in the Table 2.3. For AAA as crosslinker, the Mc values are much higher than expected, indicating lower crosslink formation[91].

Table 2.3 Homopolymer network characterisation data [91]

Polymer Network	Average molect	ular weight betwe	en crosslini	<u>(s. M</u> C			<u> </u>
	theoretical	from modulus		from sw	clling data	, solvent:	
		Cata	toluene	THF	benzene	MEK	acetone
PnBA (DVB)	13,000	14,400 <sup>(a)</sup>	12,200	12,700	12,600	13,200	12,800
PnBA (AAA)	13,000	38,100 <sup>(a)</sup>	36,200	35,900	37,400	41,300	42,600
PS (DVB)	10,500	10,800 <sup>(b)</sup>	8,300			11,000	
PS (AAA)	10,500	27,700 <sup>(b)</sup>	21,900			25,800	

(a) at room temperature

(b) at 160°C

2.1.2.3. <u>Interpenetrating Polymer Network with Acrylate</u> <u>Polymers</u>

## 2.1.2.3.1 Polyurethane/Polyacrylate IPNs

Those semi- and fully IPNs consist of polyurethane and polyacrylate systems have been described in some detail by

Hourston and Zia[1-7]. The glass transition behaviour of PU/PMMA IPNs was studied by dynamic mechanical spectroscopy (DMS). The study of the glass transition behaviour has established that phase separation occurs, but that the mutual misicibity of PU/PMMA is increased by combining them interpenetrated networks. However changing as IPN composition did not yield any unexpected behaviour[10] as shown in Figure 2.14. Other studies using DMA show more compatibility in PU/PMMA IPN system [12], as shown in Figure 2.15.

Some mechanical properties of PU/PMMA IPNs included stressstrain, impact resistance, elastic modulus, tensile strength and elongation to failure were measured. The increase in the PMMA content of IPNs produced the expected trends in mechanical behaviour: an increase in hardness, the elastic modulus and the tensile strength, and a decrease in impact strength [12] as shown Figure 2.16.

With increasing elastomer content, IPNs change from being rather brittle to quite ductile. Samples containing between 15 percent and 40 percent PU exhibit a yield point as shown in Figure 2.17b and behave like leathery materials[13]. The main mechanical properties are shown in Table 2.4.



Fig. 2.14 Tanô -temperature ▲ -PU network (K=1.07); △ -PMMA network; ■-34/66 PU/PMMA[13].



Fig.2.15 Tano-temperature for IPNs with PMMA/PU composition: A, 0/100; B, 29/71; C, 38/62; D, 52/48; E, 100/0 (%vol)[12].



Fig.2.16 Mechanical properties for IPNs PU/PMMA [12]

- (a). Elastic modulus vs % PMMA;
- (b). Percent elongation vs % PMMA;
- (c). Tensile strength vs & PMMA;
- (d). Impact energy at failure vs %PMMA.



Fig.2.17 Typical stress-strain curves for PU/PMMA IPNs containing (a) less than about 15% PU;

- (b) between 15% and 40% PU;
- (c) over 40% PU[13].

Table 2.4. Stress-strain and impact resistance for PU/PMMA

P	U/PMMA Samples	σ. (MPa)	€" (Percent)	E (MPa)	σ, (MPa)	€, (Percent)	Ŕ (−20°) (KJ/m²)
	15/85	_		338	56	22	11
	25/75	37	22	271	34	44	15
	34/66	26	20	210	26	184	24
	40/60	19	24	179	19	152	45
	~50/50	10	25	74	16	347	(86)*

IPNs with different compositions[13]

"Mean value from 5 samples only.

For a given composition, the main factor influencing the mechanical properties is the degree of crosslinking of each network. The crosslink density of polymer I is more important. The elongation at break decreases with increasing crosslink density of polymer I ( ie PU ) and the

IPN becames more brittle[13].

#### 2.1.2.3.2 Poly(n-butyl acrylate)/Polystyrene IPNs

Sequential poly(n-butyl acrylate)/polystyrene semi-2 and full IPNs of various compositions were made by UV photopolymerization[16-18]. The IPN morphology has been reviewed recently by Sperling[64]. The main areas of interest in sequential IPN morphology have been control and measurement of shapes and sizes of the phases, and other aspects concerning dual continuity. Phase domain diameters may be predicted for a full sequential IPN from the equations below[80]:

$$D_{1} = \frac{4\gamma}{RT(A\nu_{1} + B\nu_{2})}$$
(1)  

$$A = \frac{1}{2} \left(\frac{1}{\phi_{2}}\right) (3\phi_{1}^{1/3} - 3\phi_{1}^{4/3} - \phi_{1}\ln\phi_{1})$$
(2)  

$$B = \frac{1}{2} (\ln\phi_{2} - 3\phi_{2}^{2/3} + 3)$$
(3)

where  $D_1$  is the "sphere" diameters of polymer I,  $v_1$  and  $v_2$ are the crosslink density of networks I and II, r is the interfacial tension,  $\varphi_1$  and  $\varphi_2$  are the volume fractions of each phase component, T is the absolute temperature. Thus, the domain diameters of polymer II may be predicted solely on the knowledge of the networks and their interaction. Theoretical predictions are compared with experimental data for the IPN system poly(n-butyl acrylate)/polystyrene in Table 2.5 (21,80-82). The agreement between theory and experiment for this system, as well as others is excellent.

# Table 2.5. Domain diameter of poly(n-butyl acrylate)

D/oBA\/DC	Diameters in Ångstroms			
Volume Ratio	D <sub>2</sub> , Experiment	D <sub>2</sub> , Theory		
25/75	800	845		
40/60	650	644		
50/50	550	572		

polystyrene IPNs[80].

Molecular characteristics:  $r_1 = 3.7 \times 10^{-6} \text{ mole/cm}^3$   $r_2 = 21.8 \times 10^{-6} \text{ mole/cm}^3$  $\gamma = 3.65 \text{ dynes/cm}$ 

Widmaier and Sperling[16,17,83] approached the question of dual phase continuity through use of a decrosslinking and extraction route, using scanning electron microscopy techniques developed by Kresge[84]. The samples of poly(nbutyl acrylate) were crosslinked with a labile crosslinker, acrylic acid anhydride (AAA). Then, sequential IPNs were made with polystyrene with a permanent crosslinker, divinylbenzene (DVB). After IPN formation, AAA-containing network I was decrossinked and extracted. On soaking in aqueous ammonium hydroxide solution, the AAA hydrolysis, effectively decrosslinking the acrylic rubber. The resulting linear polymer was extracted from the other network in a soxhlet extractor using either toluene or Both suitable solvents acetone. for the acrylic phase[16,17]. The remaining DVB-crosslinked PS network II

was characterised by scanning electron microscopy. A porous

but continuous phase formed by aggregation of spherical polystyrene domains was observed (Figs. 2.18, 2.19).

The white portions represent the remaining PS phase, and the dark ones are voids where PnBA was previously located. It was also concluded that network I was continuous. Since it could be quantitatively and easily extracted. Hence, for compositions above about 20% by weight polymer II, dual phase continuity exist.



Fig. 2.18 Scanning electron micrograph of decrosslinked and extracted IPN[PnBA(AAA)/PS(DVB), 50/50], low magnification[16]



Fig. 2.19 Scanning electron micrograph of decrosslinked and extracted IPN[PnBA(AAA)/PS(DVB), 50/50], high magnification[16]

The dynamic mechanical properties of full IPNs, decrosslinked IPNs and semi-2 IPNs were also studied[17]. The extent of mixing of PnBA and PS phases is reflected, at least qualitatively, by the dynamic mechanical behaviour of the material. Phase-separated materials exhibit two glass transitions, one for each phase. Shifts and broadening are indicative of molecular mixing. The temperature dependence of the storage modulus G' and the loss tangent, tamb, of full IPNs, decrosslinked IPNs and semi-2 IPNs are shown in Figure 2.20.



Fig. 2.20 G'-temperature and Tano-temperature for (a) IPNs, (b) decrosslinked (c) semi-2 IPN with compositions; PnBA/PS, ▼-30/70; ■-40/60; ●-50/50; ●-60/40; ▲-70/30; △-PnBA; ▼-PS[17]

Decrosslinked IPNs and semi-2 IPNs give similar dynamic mechanical behaviour, and the main difference between the full IPNs and the decrosslinked IPNs is that the glass transitions of the respective polymers become more pronounced in the latter case, with a deeper valley between them. A significant level of molecular mixing was found for full IPNs of midrange compositions.

## 2.1.2.4 <u>Interpenetrating Polymer Networks based on Acrylate</u> Polymers

## 2.1.2.4.1 <u>Poly(ethyl acrylate)/Poly(methyl</u> <u>methacrylate) IPNs</u>

During the 1970's, IPNs based on poly(ethyl acrylate) and poly(styrene-co-methyl methacrylate) were studied by Huelck and Sperling[22,23]. Their morphology by electron microscopy and physical mechanical behaviour were reported. In the PEA/PMMA and PEA/PS systems it was found that the PEA/PS polymer pair is incompatible, whilst the PEA/PMMA pair can be better described as "semicompatible". After the morphology study of PEA/PMMA, butadiene (ca 1%) was added to the EA as a co-monomer before polymerisation, The butadiene was added to make available carbon-carbon double bond sites for osmium tetroxide staining of electron microscopy specimens. The electron micrographs of PEAB/PMMA are showed in Figure 2.21.

The dynamic mechanical spectroscopy measurement via vibron instrumentation show how compatibility increases as MMAmers replace s-mers in the IPN as shown in Figure 2.22. Principally two reasonably sharp glass transitions are replaced by one very broad continuous transition, which may be interpreted as a continuous range of transitions



Fig. 2.21 Electron micrograph of IPN: 47.1PEAB/52.9PMMA[22]

reflecting different local compositions. The mechanical behaviour revealed that the extent of molecular mixing increases with the percent MMA in PEA/P(S-co-MMA) IPN system. However a significant amount of phase separation remains even with the PEA-PMMA IPN system. Stress-strain and tensile date show that the work to break as well as the actual tensile values of the samples steadily increase as the amount of plastic component is increased in the elastomer-rich materials, as shown in Figure 2.23.





Fig.2.22 Dynamic mechanical properties for PEA/P(S-co-MMA) IPNs [23]



Fig.2.23 Stress-strain behaviour of several elastomeric IPNs [23]

In 1980's the extent of molecular demixing of poly[cross-(ethyl acrylate)]-inter-poly[cross-methyl methacrylate)] IPNs) of mid-range composition was (PEA/PMMA IPNs investigated by decrosslinking and/or annealing using dynamic mechanical spectroscopy. A single broad glass transition characteristic of extensive but incomplete molecular mixing was observed for the PEA/PMMA IPN[24]. The presence of crosslinking in both phases of an IPN enhances the mutual miscibility of the polymers as shown in the Figure 2.24(a). The corresponding semi-II IPN exhibits two distinct glass transitions, indicating a certain degree of phase separation Figure 2.24(b). Decrosslinking polymer I in an IPN through the use of a labile crosslinker results in a chemically blended semi-II IPN having transition behavior similar to the semi-II. Annealing IPNs at 120°C for four hours sharpen the transitions as a result of

molecular arrangements which is facilitated following decrosslinking as shown in Figure 2.24c.



(a) (b) (c)
 Fig.2.24 Dynamic mechanical properties for IPNs
 PEA/PMMA, (a) IPN, (b)semi-IPN, (c)decrosslinked,
 and annealed IPN[24].

### 2.2 METHODS of CHARACTERISING POLYMER BLENDS and NETWORKS

Polymer networks may be studied and characterised using electron microscopy[23,27], dynamic mechanical spectroscopy (DMS) or dynamic mechanical analyser (DMA)[23,27], differential scanning calorimetry (DSC)[62,63,] and mechanical testing equipment [60,12].

#### 2.2.1 Morphology

### 2.2.1.1 Electron Microscopy

Electron microscopy has become one of the most widely used techniques for characterising blend morphology[85].

Scanning electron microscope (SEM) offers the simplest procedure[86]. Since it only reveals surface feature, the internal structure of blends is investigated by viewing fracture surfaces created at ambient or cryogenic temperatures, photomicrographs of this type often give information about the extent of adhesion between phases.

In 1990, a new procedure of fracture surface preparation was described[94]. This is based on the specific property of polymer materials, namely up to a three-decade difference in the Young's modulus below and above the glass transition temperature. The fracture surface is prepared at a temperature at which the matrix is soft (sufficiently high above the glass transition temperature) and the inclusions are hard (below the glass transition temperature) at the same time. The method has been successfully tested for several systems, such as, silicon rubber/hard methacrylate copolymer, EPDM rubber/inorganic filler, EPDM rubber/polypropylene, liquid rubber/epoxy, and
ABS/inorganic filler ( ie. Figure 2.25 ).



Fig. 2.25 Fracture surface of a system silicon rubber/hard methacrylate copolymer, (a) lower and (b) higher copolymer content[99].

Transmission electron microscopy (TEM) requires viewing thin sections of materials. Normally, it is not useful directly for polymer blends because of insufficient contrast between most organic polymers in the electron beam, staining methods to enhance contrast are often used.

## 2.2.1.1.1 Decrosslinking and Extraction Techniques

To aid in the identification of phases and enhance morphological features, one of the phases may be selectively extracted by a solvent either in semi- IPNs or in full IPNs with labile crosslinker[17], leaving the other phase to be viewed in microscope as shown in Figure (18-19). This is especially useful when the two polymers form co-continuous phases. By solvent extraction, the matrix polymer can be selectively removed in materials such as HIPS, leaving the particular rubber phase for viewing by SEM[87] as shown in Figure 2.26.



Fig.2.26 Scanning electron photomicrographs of rubber particles extracted from HIPS[87].

## 2.2.1.1.2 Staining Techniques

Osmium tetroxide (OsO<sub>4</sub>) is a useful stain for rubber modified polymers[65]. The rubber phase, through its

unsaturation, reacts with OSO4, whereas the matrix phase does not. This can produce sufficient contrast between them owing to the high electron density of the OSO4 stained phase. The use of OSO4 is primarily limited to polymers with double bonds or other reactive sites. Examination of the morphology for IPNs based on acrylate polymers, where no carbon double bond exist, was completed with the addition of a third monomer, (such as butadiene[22], isoprene[26]), to one of phases for osmium tetroxide staining. This is previously shown in Figure 2.21. Reaction with OSO4 also causes hardening, which facilitates microtoming of ultrathin sections for viewing.

Since 1980, ruthenium tetroxide (RuO<sub>4</sub>) has been used for staining a number of heterophase polymers for TEM; it seems to be a more versatile staining agent than OsO<sub>4</sub>. For instance, in SAN modified with acrylate rubber, where the rubber phase is fully saturated, an excellent contrast between the rubber and the matrix has been achieved (65).

# 2.2.2 Thermal Analysis

Thermal analysis of polymer blends and networks can be carried out by dynamic mechanical spectroscopy (DMS) or dynamic mechanical analyser (DMA), differential scanning calorimetry (DSC) etc.

#### 2.2.2.1 DMS or DMA

From dynamic mechanical spectroscopy (DMS) or dynamic mechanical analyser (DMA), it is possible to determine the extent of molecular mixing of two phases based on the following observations from Tamb (loss factor) vs temperatures plots:

- (a) As mixing increases, the glass transition temperatures,
  Tg, of the individual transitions broaden and merge
  into a single transition.
- (b) For nearly homogeneous materials, an increase in the width of the glass transitions at half-peak height provides evidence of slight demixing.

The dynamic storage modulus E' vs temperature plots and the dynamic loss modulus vs temperature plots can also obtained from DMA or DMS for polymer blends or networks. Their relationship with loss factor (Tamb) is

$$Tanb = E''/E'$$

## 2.2.2.2 <u>DSC or DTA</u>

Differential scanning calorimetry (DSC) or differential thermal analysis (DTA), in which the sample is heated through a small temperature, and first and second order endo/exo therms are recorded, can be used for examination

of the thermal properties and transition behaviour of the samples. First order phenomena including melting and boiling points appear as endothermic peaks; heats of reaction as exotherms etc.. Second order phenomena including glass transitions (Tg's) are shown as changes in slope (inflections).

# 2.2.3 <u>Mechanical Properties</u>

Tensile testing, hardness testing, impact testing etc. mechanical testing can be carried out in accordance with ASTM methods using conventional mechanical testing equipment [12,13,60].

#### CHAPTER THREE

#### EXPERIMENTAL

#### 3.1 <u>Materials</u>

All polymers and chemicals used are described in Table 3.1 and Table 3.2. Methyl methacrylate (MMA) monomer was freed from inhibitor by washing first with 10% aqueous sodium hydroxide, then with distilled water through a separating funnel, followed by drying over anhydrous calcium chloride for a few days before use. All other raw materials were used as received.

#### 3.2 Equipment

## 3.2.1 Internal Mixer

Small quantities of acrylic rubber (AR) with curatives or mixtures based on poly(methyl methacrylate) ( PMMA ) and AR can be prepared in a "Haake" internal mixer with a 60 cm<sup>3</sup> chamber capacity and rotor blades. The instrument operates at constant rotor speed which can be set from 0 to 100 rpm. The mixing chamber is equipped with electrical heaters and air cooling which are controlled by

three "Pye Digi" temperature controllers as shown in Figure 3.1.

Table 3.1 Polymers

Polymer	TradeName	Description	Code
Poly(methyl		brittle,	PMMA
methacrylate)		transparent	
Poly(methyl		brittle,	GPMMA
methacrylate)		transparent	
grafted with		at room	
n-butyl acrylate		temperature	
Acrylic rubber	Hycar4051	off-white, slab	AR
	CG		
	Hycar4451	off-white, crumb	
	CG		

# 3.2.2 <u>Hydraulic Press</u>

All moulding and curing were carried out in a 50 tonne "Stacy" hydraulic press with steam heated platens and a four cavity mould. "Foxboro" pneumatic controllers were used to regulate the steam pressure, the maximum temperature achievable being 145°C. Due to the limit of

Table 3.2 Chemicals

Chemical	Comments	Code
Benzoyl peroxide	Interox 75% powder in $H_2O$	BP
Stearic acid		SA
Sulphur	Powder technical grade	S
Sodium stearate		SS
Methyl methacrylate		MMA
Acrylic anhydride acid	Labile crosslinker	ААА
Trimethylol propane trimethacrylate	Crosslinker	TMPTMA
Chloroform	$CHCl_3$ solvent	
Non-post-cure reagent	Crosslinker, B.F. Good Rich Co.	NPC
Acetone	Solvent	

temperature, the press was upgraded with electric heating platens instead of steam. The temperature can presently be controlled from room temperature to  $375^{\circ}$ C. The load of the press can be adjusted from 0 to 50 lb/in<sup>2</sup>, The system is shown in the Figure 3.2.



Fig.3.2 Hydraulic press

## 3.2.3. Mechanical Properties Testing Machine

Mechanical properties tests were carried out using an Instron 1115 Universal testing machine. The machine was configured with a 5KN load cell with sensitivities ranging from 100N to 5000N, the crosshead speed with ranging from 0.05 cm/min to 50 cm/min, chart speed with ranging from 0.2 cm/min to 50 cm/min can be selected to use for different samples which required different instrument settings. The instrument is shown in the Figure 3.3.



Fig.3.3 Instron 1115 universal testing machine

#### 3.2.4 Dynamic Mechanical Analyser

The Du Pont 983 dynamic mechanical analyser (DMA) was used with the Du Pont 2100 thermal analyser running version 6.0 software to examine dynamic mechanical properties. The 983 DMA has three major modules: the drive assembly where the sample is clamped and enclosed by oven, the oven where the temperature is controlled from -200 to 500°C, using a liquid nitrogen cooling accessory, and the DMA base where the system electronics are housed as shown in the Figure 3.4. There are four modes of operation: resonant frequency, fixed frequency, stress relaxation and creep can be selected.



Fig.3.4 Du Pont 983 Dynamic mechanical analyser

The dimensions of samples range in length range from 6 to 65 mm (horizontal), maximum thickness 12 mm (horizontal), and maximum width 15 mm (horizontal), and program heating rate from 0.01 to  $50^{\circ}$ C/min, cooling rate from 1 to  $5^{\circ}$ C/min and a resonant frequency range from 2 to 85 Hz can be used.

## 3.2.5. <u>Differential Scanning Calorimeter (DSC)</u>

The glass transition temperatures of polymers were obtained using a Du Pont 910 differential scanning calorimeter (DSC) with a Du Pont 2100 thermal analyser running at least version 6.0 software system. The temperature of the cell can be controlled from -150°C to 650°C, using a liquid nitrogen cooling accessory.

#### 3.2.6 <u>Microscope</u>

Electron micrographs were taken by using an JEOL JXA-840 scanning electron microscope which is a state of the art high resolution scanning electron microscope with all functions required of a scanning electron microscope as shown in the Figure 3.5.

The magnification can be used from 10X (at 39 mm working distance) to 30,000X, probe current from  $10^{-12}$  to  $10^{-5}$ A and accelerating voltage from 0.2 to 40 KV (linked with bias, lens currents, and coil currents); specimen movement ranges

at x,y,z-direction. In electron detector system, there are two electron detector systems: one is secondary electron detector for secondary electron images and high speed reflected electron images, the other one is backscattered "Robinson" electron detector for compositional and topographical images.



Fig.3.5 JXA-840 scanning electron microscope

# 3.3. Preparation of Simple Polymer Blends

# 3.3.1. Mechanical Mixing and Moulding

The internal mixer was used to mechanically blend various polymer and other additions. The "Haake" 600 mixing head

170°C and banbury mixtures with kept at total was massrotors maintained at a constant speed of 50 rpm. Various PMMA/AR compositions 65g of two polymers were mixed. The acrylic rubber was added to the mixing chamber first and allowed to melt over 1 minute and followed by the The mixing continued for 10 minutes to enhance PMMA. dispersion. The molten mixture was immediately removed and pressed using a platen press to form a slab about 5 mm suitable for sheet moulding. The thick slabs were compression moulded in a four cavity mould conforming to ASTM standard D3182. Each cavity was 150 mm square and 2 mm deep, and held about 65g of material. The slabs were placed in the preheated mould which was then compressed in the hydraulic press at a pressure of 40 lb/in<sup>2</sup>. Moulding time was 20-30 minutes at 165°C. The samples were allowed to cool down to room temperature whilst maintaining pressure, to reduce warpage.

# 3.3.2 Mixing from Ternary System (solution casting)

PMMA, graft PMMA (GPMMA) and AR were dissolved respectively in the chloroform solvent over 1 day. The chloroform is a good solvent for acrylic polymers due to the similar solubility parameter. According to

$$\delta = \frac{\rho \Sigma G}{M} \qquad 3.1$$

where G represents the group molar attraction constants,  $\rho$  the density and M the mer molecular weight[59], we can calculate, the solubility parameter of PMMA to be 9.35, the solubility parameter of poly(n-butyl acrylate) to be 9.35 and solubility parameter of chloroform to be 9.4.

The acrylic rubber solutions were added respectively to PMMA solutions to make up various compositions. The solution concentration of PMMA, graft PMMA, AR and the resulting PMMA/AR compositions (w/w) are described in the Table 3.3.

The mixed solutions were stirred with a magnetic stirrer for at least 5 minutes and then poured into glass petri dishes. The chloroform solvent was allowed to evaporate in a fume cupboard at room temperature over one day to form homogenous mixture films which are about 0.23 mm thick and transparent. The films was dried to constant weight in a vacuum oven at  $50^{\circ}$ C for 2 days. Pure PMMA and GPMMA films were formed by applying the same process as the mixture films of AR/PMMA.

Table 3.3 Solution concentration of PMMA, graft PMMA, AR and the resulting compositions of AR/PMMA.

PMMA solution	AR solution	AR/PMMA	Graft PMMA
5% (w/vol)	l% (w/vol)	composition	solution
(mls)	(mls)	(w/w)	5% (w/vol)
			(mls)
19	5	5/95	
18	10	10/90	
17	15	15/85	
16	20	20/80	
14	30	30/70	
20	0	0/100	
			20

# 3.4 Preparation of AR Networks

Acrylic rubber networks were formed by using three different crosslinkers and in different techniques.

# 3.4.1 Sodium Stearate as A Crosslinker

Various levels of sodium stearate (SS) with sulphur (S) (10:1) and without sulphur were dispersed into AR using an internal mixer which was operated at a rotor speed of 50

rpm. The mixing temperature set point was 70°C. The recipe was showed in Table 3.4. Sodium stearate and sulphur were added to the chamber followed by the acrylic rubber and then mixing continued for 7 minutes. The compound was then removed and pressed using a platen press to form a about 4mm thick sheet suitable for moulding and curing. The compounds were cured in a four cavity mould at 165°C and 40  $1b/in^2$  for 1 hour to produce acrylic rubber network[52]. The detail of curing mechanism was shown in Section 2.1.2.2.2. Then the pressure was released and the samples were allowed to cool to room temperature before removal. The sheets of acrylic rubber with sulphur were a light brown in colour and the sheets of acrylic rubber without sulphur were a pale white in colour.

#### 3.4.2 NPC System

AR was crosslinked with NPC system. The recipe was showed in Table 3.5. The technique was applied the same process as Section 3.4.1. NPC and other curatives were added to the chamber followed by the acrylic rubber and mixing continued for only 4 minutes at room temperature to keep from scorching of the compound. The compound was cured at 165°C for 12 minutes in the hot press.

Table 3.4 Compound recipes of sodium stearate with or without sulphur curing systems for AR crosslink

Paper designation without S	A	В	С	D
with S	(A)	(B)	(C)	(D)
Hycar 4451 (4051)	65	65	65	65
Sodium stearate (SS)	1.3	1.95	2.6	3.25
(Sulphur) (S)	0.065	0.13	0.195	0.26

Table 3.5 Compound recipe of NPC curing system for AR crosslink

Hycar 4451 (4051)	65
Stearic acid	1.3
Sodium stearate	2.6
Hycar NPC-50	1.3

# 3.4.3 Acrylic Acid Anhydride as A Labile Crosslinker

Acrylic rubber 5g was dissolved in acetone 20mls over 1 day in a sealed container. Then 0.05g acrylic acid anhydride (AAA) with 0.05g benzoin (photoinitiator) were added into acrylic rubber solution and mixed. The uncovered petri dish

with the mixture was exposed under a 125W ultraviolet lamp. The distance between lamp and sample is 9 cm and the mixture was allowed to crosslink at 35°C. After 72 hours of UV exposure, the mixture forms an approximately lmm thick network film which represent pale yellow in colour. Then the film (1%AAA) was removed from the petri dish. For comparison, various levels of AAA (1.5% w/w, 2% w/w) were used to crosslink acrylic rubber by applying the same process as the 1% AAA.

## 3.5 Preparation of Semi and Full IPNs based on AR/PMMA

Semi and full IPN were prepared by using two different crosslinking systems: The first was AR[SS(S)]/PMMA in which acrylic rubber was crosslinked using sodium stearate with or without sulphur. The second was AR[SS(S)]/PMMA in which acrylic rubber was crosslinked with a labile crosslinker, acrylic anhydride acid. When PMMA was linear (in both systems), products are semi-IPNs and when PMMA was crosslinked with a crosslinker, TMPTMA, the systems are designated as full-IPNs.

#### 3.5.1 IPNs with SS(S) Type Crosslinker

The sheets of acrylic rubber network, dimensions 80x40x2mm were weighed and then immersed in inhibitor free methyl methacrylate (MMA) monomer with and without 15%TMPTMA

(crosslinker) and with 0.5% benzoyl peroxide (as a initiator for MMA monomer polymerisation), Immersion times varied from 15 minutes to 2hrs at room temperature. The swollen sheets were removed and put into polyamide envelopes (to act both as a sheet mould release and sealing material) and clamped between steel-plates. Subsequently the sheets were heated to 80°C for 22 hours, followed by another 2 hours at 100°C for MMA monomer polymerisation. After cooling to room temperature samples were removed from the sealed bags and dried to constant weight in a vacuum oven at 50°C for 3 days, during which unreacted MMA monomer was removed.

The composition of each IPN was determined gravimetrically making allowance in the full IPN case for the 15%TMPTMA component in the PMMA.

# 3.5.2. IPNs with AAA Labile Crosslinker

Acrylic rubber films crosslinked with 1.5% acrylic acid anhydride (AAA) were weighed and then immersed in inhibitor free MMA with and without 15% TMPTMA (crosslinker) containing 0.5% benzoyl peroxide (initiator) for times varying from 5 to 30 minutes. The PMMA polymerisation and IPN's film preparation were completed as described in 3.5.1.

## 3.5.3. Decrosslinking of IPNs with A Crosslinker AAA

The full IPNs with labile crosslinker (AAA) were soaked in 28% aqueous ammonium hydroxide solution for a few days. Decrosslinking was effective[16,17]. After hydrolysing the AAA, the resulting linear acrylic rubber was soxhlet extracted with acetone, a good solvent for acrylic rubber, leaving the crosslinked PMMA as the solvent insoluble residue. The above process is shown as below scheme.



#### 3.6 Test Methods

# 3.6.1 <u>Determination of Crosslink Density and Interaction</u> Parameter

The extent of crosslinking can be easily measured from either equilibrium swelling measurements or from mechanical property data. For the equilibrium swelling measurements, the molecular weight between crosslinks(Mc) can be evaluated through application of the Flory-rehner equation[57]:

$$\frac{1}{M_c} = \frac{\ln(1-V_r) + V_r + X_{12}V_r^2}{pV_c(V_r^{1/3} - V_r/2)}$$
 3.2

where Vr = volume fraction of rubber in swollen rubber gel and can be calculated from:

WT dry rubberρ dry rubberWT dry rubberψT dry rubberρ dry rubberρ dry rubber

where weight of solvent can be found by weight difference, Vs is the molecular volume of solvent i.e molecular weight divided by density  $\rho$  (solvent),  $\chi_{12}$  is the polymer-solvent interaction parameter. According to Hildebrand and Scott solubility parameters  $\delta$  1 and  $\delta_2$ ,  $\chi_{12}$  can be calculated by below equation[16].

$$X_{12} = B + \frac{V_s}{RT} (\delta^2 - \delta^2)$$
 3.3

where the constant entropic term B was taken as 0.32. For poly(n-butyl acrylate) with various solvents, a value gives the best fit for self-consistent results for five different solvents. Hence  $\chi_{12}$  was equal to 0.327, 0.332, 0.344, 0.358 and 0.473 for toluene, THF, benzene, MEK, and acetone, respectively[16].

The quantity Mc can also be estimated from the shear modulus, measured well above Tg by the application of the statistical theory of rubber elasticity[58]

$$M_{c} = \frac{\rho RT}{G} \left( \frac{\overline{r}^{2}}{r_{o}^{2}} \right) \qquad 3.4$$

Usually,  $\left(\frac{\overline{r}^2}{r_*}\right)$  the ratio of mean-square end to end distance of a chain segment between crosslink sites to the equivalent free chain end to end distance, is assumed to be equal to unity[16]. Swelling experiments were conducted on small rectangular specimens in acetone solvent for a week to produce equilibrium swelling. For poly(n-butyl acrylate) with acetone solvent, the polymer-solvent interaction parameter  $\chi_{12} = 0.473[16]$ , the density of acrylic rubber = 1.1 and the density of acetone = 0.7899 were used through the calculation.

# 3.6.2 Tensile Testing

Tensile testing was performed at room temperature (20°C) in an Instron 1115 Universal testing machine in accordance with ASTM D1708. Serrated grips and an intergrip distance of 20mm were used. A crosshead speed of 0.5 cm/min and chart speed of 20 cm/min were used for the samples from simple blends, semi and full IPNs. The crosshead speed of 2 cm/min and chart speed of 2 cm/min were used for samples of acrylic rubber networks. Two or three microtensile dumbbells were punched for each sample from the sheet samples.

The tensile strength was calculated from tensile load, W, and original cross-section area of specimen using equation 3.5

$$\sigma = \frac{W}{A}$$
 3.5

where W = load

A = original cross-section area

The elongation at break was calculated from original distance between gage marks and distance between gage at break lengths of specimen, using equation 3.6

$$\varepsilon = \frac{1-1_0}{1_0} X100\%$$
 3.6

where  $l_0 = original$  distance between gage marks

1 = distance between gage marks at break

# 3.6.3 Dynamic Mechanical Analyser

Dynamic mechanical data of the samples were obtained by using a Du Pont 983 Dynamic mechanical Analyser (DMA) in the resonant frequency mode over a temperature from  $-60^{\circ}$ C to  $160^{\circ}$ C at a heating rate of  $5^{\circ}$ C per minute. The sample is clamped between two parallel arms and is deformed. When operating the DMA in the resonant mode, the sample and arms form a compound resonance system. The sample is displaced and set into oscillation. The frequency of oscillation is related to the stiffness or storage modulus while the energy needed to maintain constant oscillation amplitude is a measure of the damping within the samples. The curves of storage modulus, loss modulus and tand versus temperatures were obtained through a Du Pont 2100 thermal data analyser with version 6.0 software.

#### 3.6.4 Morphology

The morphological details of the samples were examined using a JXA-840 scanning microscope. The samples were cut and mounted on stubs. Samples for simple blends from mechanical mixing and IPNs from extraction were coated with a ~10nm thick layer of gold to provide a suitable surface , and the microscope was operated with a secondary electron detector, 39mm working distance. Typically a voltage of 10 KV and current of 6X10<sup>-9</sup>Å were employed, because low voltage and current gave less specimen damage. The magnifications of samples ranged from 500 to 9000X. The sample from mechanical mixing for composition 80/20 PMMA/AR was stained with ruthenium tetroxide for 30 minutes and washed with distilled water and dried. The sample was coated with carbon.

## 3.6.5 Tg Testing

The glass transition temperatures of samples were studied on a Du Pont 910 differential scanning calorimeter (DSC) with the Du Pont 2100 thermal analyser running version 6.0 software. The temperature set range from -60°C to 160°C. 15mg of each sample was tested. An empty pan was used as a reference and samples were run in nitrogen.

#### CHAPTER FOUR

## RESULTS AND DISCUSSION: SIMPLE PMMA/AR BLENDS

# 4.1 Tensile Properties

Tensile properties of simple mechanically mixed PMMA/AR blends of various compositions are given in Table 4.1, whilst those prepared from a ternary system ( ie. solution casting) are given in Table 4.2.

It is well known that the toughness of a material depends on a combination of tensile strength and elongation at break. The larger the tensile strength and elongation at break, the larger the toughness of the material.

The tensile strength of the simple blends derived from either mechanical mixing or solution casting increases as expected, with increasing PMMA contents, ( shown in Figure 4.1 ). This increase in tensile strength is because PMMA has much higher tensile strength than acrylic rubber. The tensile strength of the mixture depends on the compositions of PMMA/AR, however the relation is not linear. This may indicate that the simple PMMA/AR blends are incompatible[90] as a compatible system exhibits a near dependence between tensile strength linear with

polymer/polymer composition.

For an incompatible system of amorphous polymer blends, one polymer exists as a discontinuous, dispersed phase within a continuous phase of the other polymer. In general, when the thermoplastic is the continuous phase, the system exhibits high hardness, larger modulus, low recovery, moderate elongation at break (eb). However, when rubber is the continuous phase the system exhibits low hardness, small modulus, high elasticity and recovery, high elongation.

Table 4.1 Tensile properties of simple blend from mechanical mixing

Composition	Tensile	Elongation	5% Modulus
(%AR/%PMMA)	strength	eb	(MPa)
	( MPa )	( % )	
0/100	65.1	6.8	1005
1/99	60.6	8.0	1010
2/98	58.5	9.15	1039
5/95	55.9	9.2	977
10/90	54.7	9.75	885
20/80	46.2	10.13	677
30/70	21.8	13.5	430
35/65	15.5	14.25	288
50/50	8.4	19.5	126
100/0	0.83	725	1.05
	1		

Table 4.2 Tensile properties of simple blend from solution casting

Composition	Tensile	Elongation
( %AR/%PMMA )	strength	đe
	( MPa )	( % )
0/100	35	3.75
5/95	30	3.85
10/90	29	4.25
15/85	28	4.25
20/80	27	6.25
30/70	24	7.00
Graft PMMA	28	4.63

From Figure 4.1, It is seen that the tensile strength increases greatly as the PMMA contents exceed 70%. This is probably because the acrylic rubber phase becomes a dispersed phase surrounded by a continuous PMMA phase, and so in this case the material presents mainly properties of PMMA.



The behaviour of percentage elongation at break ( $\varepsilon$  b) (Figures 4.2 and 4.3) highlights the possibilities of improvements in mechanical performance with increasing acrylic rubber contents. However with acrylic rubber contents below 50%, the increase of  $\varepsilon$  b is slow with increasing acrylic rubber contents, compared with  $\varepsilon$  b of the pure acrylic rubber (Figure 4.3). The simple blends exhibit a low  $\varepsilon$  b showing the characteristic of immiscible blends[90].

The difference in tensile strength and eb between mechanical mixing and solution casting (Figure 4.1 and 4.2), may be due to following reasons:

(a). After mechanical mixing, although the system is incompatible, both polymers have significant viscosities which make molecular chain motion slow, with modest phases separation. For solution casting, the solvent is rapidly evaporated causing the residual polymeric solution to enter the two phase region. Other factors also exist. For example, traces of residual solvent might lower tensile strength, ( although in this case elongation at break is also low, the reverse of that expected if plasticising solvent remained ). In any event, rigorous exclusion of solvents was conducted. Secondly, the solubility of the two polymers in a given solvent is not identical due not only to chemical structure related solubility parameter changes ( as reflected by differing values of  $\delta$  or  $\chi$ , the polymer





Fig. 4.3 Elongation Vs % AR for simple blend system

solvent interaction parameter), but also by differences in molecular weight and initial concentration. Thus as solvent concentration decreases, the polymers fractionate, with the first fractions being of (microscopically) different composition to that subsequently laid down. Thus we do not expect that the blend will be homogeneous.

(b). When two polymers are mixed by mechanical work, due to the effect of high shearing force, the longer molecules are broken to form active free radicals some of which then react with oxygen to produce short chain polymers, and others forming new copolymers e.g. graft or block copolymers. Whilst phase separation is undeniably predicted during mechanical mixing, the formation of grafts will not only help to stabilise well dispersed fractions, but will also improve interfacial regions. This type of reaction does not proceed in the solvent casting case.

From the Table 4.2, the tensile properties of simple blends from solution casting at 15/85 AR/PMMA composition are almost the same as that graft PMMA in which PMMA was grafted with 15% poly(n-butyl acrylate).

#### 4.2 Dynamic Mechanical Properties

Samples of PMMA/AR mixtures from mechanical mixing in ratios 90/10, 80/20, 70/30, 50/50, pure AR and pure PMMA were examined on the Du Pont Dynamic mechanical analyser in resonant mode. A temperature shift is found in DMA. probably due to the frequency effect in which temperature axis is transposed. For example, pure PMMA shows a Tg of about 101°C by DSC (Figure 4.4), but by DMA the tam maximum is found at 117°C (Figure 4.5). Similarly the Tg's for the AR are also shifted upwards from typically -10  $-15^{\circ}$ C, to about  $5^{\circ}$ C as shown in Figure 4.6, (again a to shift of around 15-20°C). In general, where two polymers are mixed, the glass transition would be shifted or broadened[6]. In simple blend for which the component Tg's by DMA are 127°C for PMMA, at 12°C for AR are both shifted about 8°C, is seen in the DMA trace.

The behaviour of a dynamic mechanical property (tand) over a range of temperature from -60 to 160°C is shown in Figure 4.7. The simple AR/PMMA phase mixture shows two completely separated glass transitions which indicate a polymer/polymer incompatible system. The damping peak at low temperature corresponds to the Tg of AR and the damping peak at high temperature corresponds to the Tg of PMMA. The positions of the peaks are almost unchanged with



Fig. 4.4 DSC data for pure PMMA


Fig. 4.5 DMA data for pure PMMA



Fig. 4.6 DMA data for pure AR



Fig. 4.7 Tan<sup>3</sup>-temperature for simple blend from mechanical mixing with PMMA/AR(wt%) 1. 90/10, 2. 80/20, 3. 70/30, 4. 50/50.

varying composition of the two polymers, but the height of the peak increases with increasing component of corresponding peak, indicating little molecular mixing between both polymers in the simple blend. Thus the compositions of the two polymers can be evaluated from the height of peaks in this case. The peak of the PMMA is higher than that of AR at 50/50 (%PMMA/%AR), this is because damping of the PMMA is larger than that of the AR.

The behaviour of the dynamic storage modulus (E') over a range of temperatures from -60 to  $160^{\circ}$ C is shown in Figure 4.8. E' drops rapidly at the glass transition of the AR, but much less at the glass transition of the PMMA, even though the composition is 50/50. This is probably because the PMMA is dispersed as small particles in a rubbery AR matrix, that is the AR is a continuous phase at this composition. In this case, the material exhibits mainly the mechanical properties of the AR. It can be seen from Figure 4.8 that when the composition PMMA/AR is  $\geq$  70/30, The E' now shows an abrupt decline at glass transition of the PMMA, now suggesting that the PMMA is the continuous phase and AR is the dispersed phase. This correlates with the tensile data, where strength increases greatly with increasing PMMA contents over 70 percent.



Fig. 4.8 E'-temperature for simple blend from mechanical mixing with PMMA/AR 1. 90/10, 2. 80/20, 3. 70/30, 4. 50/50 (wt%).

4.3 Morphology

The surfaces of simple blends of PMMA/AR from solution casting in chloroform and from mechanical mixing were examined by SEM.

The surface of ( gold coated ) unmodified PMMA from solution casting is shown in Figure 4.9 and the crosssection cut with a blade in Figure 4.10. Similarly the surface of unmodified AR is shown in Figure 4.11 and the cross-section in Figure 4.12. From these pictures it is initially suggested that little difference between the two phases can be resolved both being relatively amorphous. However, the PMMA does not undergo beam damage to the same extent as the AR, the latter giving a closely knitted pattern of fissures. The lower Tg of this material may also lead to some distortion due to localised micromovement of the areas under the beam, although this seems to be low, as no blurring of the image occurs.

Thus the difference in sensitivity to the electron beam may be exploited when blends are observed, as AR-rich regions will appear as zones of increased surface crazing and microcracking. In Figure 4.13, the centre of this zone is relatively unaltered, but other zones ( marked with arrows ) are affected.



Fig.4.9 Surface of the PMMA from solvent casting (mag. 900X)



Fig. 4.10 Cross-section surface of the PMMA from solvent casting (mag.1000X)



Fig. 4.12 Cross-section surface of the AR from solvent casting (mag.1000X)



Fig. 4.13 Surface of the blend from solvent casting with PMMA/AR composition 70/30 (mag. 950X)

Thus from Figure 4.13 ( the 70/30 PMMA/AR mixture), it can be seen that AR looks like a continuous phase and PMMA is dispersed phase surrounded by AR. In most cases, if one component of a mixture exceed 70 vol.%, the component may become a continuous phase[98]. Thus when the PMMA content is > 70%, it is possible that phase inversion takes place.

The fracture surfaces of unmodified PMMA and acrylic rubber from mechanical mixing are shown in Figures 4.14 and 4.15. The PMMA displays surface characteristics of brittle fracture and exhibits rather regular hyperbolic or parabolic structures. The AR displays an irregular soft fracture surface. However it is not always possible from the visual appearance of the surfaces to specify the nature of a dispersed phase ( see Section 5.2.1.1).

In order to further analyse the dispersion and domain size of the two phases, one of the polymers (ie. acrylic rubber) was stained with ruthenium tetroxide, and this is shown in Figure 4.16. (The sample was coated with carbon.) The white regions should represent the stained acrylic rubber and dark regions should be the unstained PMMA due to a difference in reflectivity. It can be seen that the acrylic rubber exists as dispersed particles in the continuous PMMA phase, when PMMA content is 80%. The domain sizes of acrylic rubber are about 50nm (Fig.4.16).

A good correlation exists between morphology and initial tensile and dynamic mechanical data.

Figures (4.13, 4.16) show that the PMMA and AR phases are separated, indicating incompatibility. This correlates with the dynamic mechanical data, where AR/PMMA phase mixture shows two completely separated glass transitions.



Fig. 4.14a Electron micrograph of the fracture surface of the PMMA from mechanical mixing (mag. 150X)



Fig 4.14b Electron micrograph of the fracture surface of the PMMA from mechanical mixing (mag. 1000X)



Fig. 4.15a Electron micrograph of the fracture surface of the AR from mechanical mixing (mag. 150X)



Fig. 4.15b Electron micrograph of the fracture surface of the AR from mechanical mixing (mag. 1000X)



Fig. 4.16 Staining surface of the sample from mechanical mixing with PMMA/AR composition 80/20 (mag. 2000X).

The blend ratios were not uniformly spaced, so that data such as mechanical and thermal properties are not shown as a continuum. The reason for this is that we have concentrated on blends in which the AR content ranges only from 50 to 0% of the total. The main reason is that we are concentrating primarily on the blends behaving as thermoplastics, and levels of PMMA less than 50% would result in TPE or elastomeric behaviour.

Secondly, the tensile, dynamic mechanical and morphology data has shown that the level above which PMMA becomes the

continuous phase is 70%, thus our 65/35 and 50/50 blends are indications of behaviour beyond this point.

Thirdly, we are operating by analogy with other elastomer modified resins, such as HIPS and various toughened thermoplastics, where levels of  $\leq 20$ % elastomer has been shown to be optimal. Fourthly, these levels are appropriate for the electron microscope work. Finally it has been clear from attempts at solution casting that where the elastomer contents are high, particular care is required to manufacture defect-free samples. For example, removal of the strongly adhering, soft mixture is often impractical.

However, to place the mechanical and thermal data of the simple blends into a broad context, some data has also been included for the unmodified AR and PMMA. Thus in Figures ( 4.1 and 4.3 ) portraying strength and elongation behaviour, for example, we do not imply linear behaviour between 0 and 50% PMMA blends.

#### CHAPTER FIVE

#### RESULTS AND DISCUSSION: SEMI AND FULL IPNS

#### 5.1 Acrylic Rubber Network

#### 5.1.1 Molecular Weight between Crosslink Mc

The molecular weight between crosslink (Mc) of acrylic rubber crosslinked with SS(S) type, NPC system and labile crosslinker AAA, was measured by equilibrium swelling measurements through application of the Flory-Rehner equation ( Section 3.6.1.). The results of swelling tests are shown in Table 5.1 for SS(S) type, Table 5.2 for AAA type and Table 5.3 for NPC system.

The Mc values from SSS or SS type network decrease with increasing SSS or SS contents as expected. As the SSS type has sulphur, the Mc value of SSS type is little lower than that of SS type, at the same level of sodium stearate. However the former is coloured brown and is opaque whilst the latter is transparent ( off-white ). Table 5.1 Mc for AR crosslinked with SS and SSS. () indicates compounds with sulphur added.

Code	Мс		
( as previously given in	(g/mole)		
Section 3.4.1 )			
A	34,000		
В	27,500		
С	19,000		
D	16,000		
(A)	28,000		
(B)	21,500		
( C )	14,500		
(D)	12,500		

The Mc values from AAA type network decrease with increasing AAA content as well. However the Mc values are much higher than expected, indicating lower crosslink formation[91]. Never-the-less, the Mc values are lower than those obtained by Widmaier and Sperling[16,17]. The crosslink density are lower that those usefully employed, in black filled compounds used industrially. Table 5.2 Mc for the AR crosslinked with labile AAA

Content of crosslinker	Мс
( wt% )	( g/mole )
l (AAA)	31,630
1.5 (AAA)	30,390
2 (AAA)	23,820

Table 5.3 Mc for the AR crosslinked with NPC type

Crosslinker	Мс	
	(g/mole)	
NPC	14,000	

The Mc value from NPC system is the same as that from the (C) type of SSS ( 4% sodium stearate with 0.3% sulphur). Actually the NPC system also contains 4% sodium stearate.

#### 5.1.2 <u>Tensile Properties</u>

Tensile properties of acrylic rubber crosslinked with three type of crosslinkers:

(1). SS or SSS type

(2). AAA Type

(3). NPC system

are shown in Table 5.4.

## 5.1.2.1 Effect of Mc on Tensile Strength

The tensile strength values of SS or SSS type and NPC type networks are higher than that of AAA type network. Using theories relating crosslink density and methods to tensile strength, this result can be explained due to the AAA type network having a lower crosslink density. For many synthetic elastomers the tensile strength is extremely low in the absence of crosslinking, because the interactively high chain flexibility allows viscose flow to occur. ( Thus indeed all useful elastomers are crosslinked prior to being placed into service ). With the incorporation of a low level of crosslinker, a significant increase in stiffness and strength occurs, and generally this trend continues as crosslink density increases (ie as Mc decreases). Secondly, formation of AAA type network uses U.V. radiation which might reduce the mechanical behaviour.

Table 5.4 Tensile properties for AR crosslinked with three different crosslinkers. ( ) indicates compounds with S added.

Content of crosslinker	Elongation	Tensile strength	
in AR ( wt% ) or Code	( % )	(MPa)	
A. SS (A). (SSS)	725 (375)	0.89 (1.00)	
B. SS (B). (SSS)	380 (320)	1.15 (1.01)	
C. SS (C). (SSS)	510 (330)	1.32 (1.02)	
D. SS (D). (SSS)	340 (230)	1.08 (0.92)	
1.5% AAA	575	0.38	
NPC system without black	250	0.94	
NPC system with black	322	0.98	

However, it is also generally seen that when an excessively network is formed viscoelastic dense behaviour is restricted and the elastomer becomes more brittle. Thus although initial stiffness may continue to increase. ultimate properties including tensile strength fall. This trend appears to be found for the AR systems as seen in Figure 5.1 for the SS or SSS type network. Although more data points would be desirable, both types of crosslinking seem to cause a reduction in tensile strength at the highest level of addition. It is predicted that the weakening found for the SS cured rubber at lower crosslink density would be mirrored for the SSS at lower levels of addition. this, a minimum crosslink density is From necessary for tensile strength. The tensile strength increases and then goes through a maximum with increasing crosslinker content ( which is C or (C) type containing 4% sodium stearate ). When the crosslinker contents increase over 4%, the tensile strength decreases. It can be also thought that more active molecular chains in low crosslink density will benefit elongation, viscoelastic rearrangement and certain extent of crosslinking assists alignment of molecular chains, so the tensile strength increases. At excessive crosslink densities, the dense molecular network resists viscoelastic rearrangement and so the tensile strength decreases. This phenomena is quite typical of many elastomers, where optimum crosslinking levels can be prescribed.



From Table 5.4, the elongation at break of C and (C) in SS and SSS type networks shows also a higher value. We thus conclude that C and (C) SS or SSS type networks have better tensile properties.

### 5.1.3 Tg behaviour

The glass transition temperatures of linear and network acrylic rubber with various crosslinker contents are shown in Figures 5.2-5.7. It can be seen that when acrylic rubber was crosslinked, the glass transition temperature increases very slightly compared with linear acrylic rubber, but thence Tg was almost unchanged with increasing crosslinker content to 5%. This indicates that a low crosslink density has a negligible effect on the position of the glass transition, Tq. Because in general, the position of the Tg's reflects energy barriers to the relocation of relatively small segments, and SO at moderately low crosslinker densities little shift is expected. At very high crosslink densities ( where the polymer would harden to a resinous material ), a marked reduction in the amplitude of the transition is expected, and some shift to higher temperature may also occur.





Fig. 5.3 DSC Tg data for A type network



# Fig. 5.4 DSC Tg data for B type network



Fig. 5.5 DSC Tg data for C type network



Fig. 5.6 DSC Tg data for D type network



Fig. 5.7 DSC Tg data for AR(AAA) network

#### 5.2 Semi and Full IPNs based on PMMA/AR

In this part we examine decrosslinking and extraction of of the polymers prior to electron microscope one examination. Two PMMA/AR IPNs were studied, one being AR(SS or SSS)/PMMA system in which AR was crosslinked with SS ( sodium stearate ) or SSS ( sodium stearate with sulphur) by the curing method. The second was AR(AAA)/PMMA system in which AR was crosslinked with the labile crosslinker AAA ( acrylic acid anhydride ) by U.V. radiation. The former is expected to have better mechanical behaviour as reflected in tensile and dynamic mechanical properties. The latter IPN is of interest as scanning electron microscopy after decrosslinking and extraction may reveal structural features. In both systems, when PMMA is linear, the product is called a semi-IPN and if PMMA is crosslinked with a crosslinker ( TMPTMA, 15% ), the product is called full IPN. These designated а are as AR(SS(S)/PMMA(TMPTMA) or AR(AAA)/PMMA(TMPTMA).

### 5.2.1 Physical and Mechanical Behaviour

Generally, the properties of IPNs depend mainly on the properties of the component polymers, the phase morphology and interactions between the phases.

#### 5.2.1.1 Effect of Components on Tensile Properties

The tensile behaviour for semi-l IPNs based on AR(SS)/PMMA system or AR(SSS)/PMMA system have been examined with varying SS or SSS contents and also with increasing PMMA content. The corresponding data of tensile properties appear in Tables 5.5 and 5.6. The tensile strength of the IPNs increases, as expected, with increasing PMMA and crosslinker contents. The elongations at break decrease with increasing PMMA and crosslinker contents. The Young's modulus increases, as expected, with increasing PMMA content. Crosslinker content has little effect on Young's modulus. The main influence of crosslinking degree is upon tensile strength and elongation at break.

exhibit considerable of compositions Α number IPN toughness, as measured by stress-strain curves. Figure 5.8 shows the stress-strain curves of D-type semi-IPN. It can be seen that the IPNs change from being rather brittle to being rather ductile as acrylic rubber content increases. However, even at relatively high AR levels, strengths are those of a ductile plastic (i.e. comparable with LDPE, say) rather than the very weak tensile strength associated with non filled pure AR. However it is also note-worthy that breaking strains are very high, being typically more than 100%. Even the very

Table 5.5 Tensile properties for semi-1 IPNs based on AR(SS)/PMMA compositions with varying SS (A,B,C,D) contents.

Code	Composition	Elongation	Tensile	5%Modulus
	(%PMMA/%AR)	(%)	strength	(MPa)
			(MPa)	
	30/70	466	6.5	5
	40/60	276	7.2	12.5
AIPNS	55/45	83	7.7	51.3
	25/75	325	5.5	3.5
	40/60	276	7.4	24
BIPNS	50/50	83	8.8	37
	20/80	355	5.3	3.9
	30/70	315	7.6	5.9
CIPNS	60/40	38	9.0	169
	40/60	266	9.4	22
	60/40	50	10.8	133
DIPNS	65/35	23	15.7	283

Table 5.6 The tensile properties of semi-1 IPNs based on AR(SSS)/PMMA with varying SSS [(A),(B),(C),(D)] contents.

Code	Composition	Elongation	Tensile	5%Modulus
	(%PMMA/%AR)	(%)	strength	(MPa)
			(MPa)	
	25/75	300	6.5	18
	45/55	177	10.9	46
(A) IPNs	67/33	33	17.2	315
	35/65	247	12.1	38
	50/50	114	13.0	86
(B) IPNs	60/40	73	18.6	367
	10/90	240	1.5	1.8
	60/40	83	17.4	210
(C)IPNs	65/35	70	18.3	218
	40/60	158	11.2	56
	45/55	132	16.9	224
(D) IPNS	55/45	105	18.8	234



high PMMA content (60%) IPNs have a useful elongation at break, ranging from about 50% to 100% ( the elongation at break of pure PMMA is generally around 5% ). In all the stress-strain curves, no obvious yield points are exhibited, excepting the specimens with very high PMMA content (over 65%) where the test specimens break without necking. Stress whitening is observed for some IPNs containing more PMMA component ( over 50% ). These are usually ascribed to multiple crazing under stress. Thus, it seems that in the present materials, there exists a satisfactory rubber-matrix adhesion due to the physical entanglement of two phases which prevents interfacial decohesion. Hence one concludes that some interpenetration may be occurring.

The morphology of fracture surfaces also change with increasing PMMA content. Generally, when yield strength exceeds ultimate strength, the brittle fracture takes place. This indicates that all IPNs in Table 5.5 and Table 5.6 are rather tough materials. Figures 5.9-5.13 show scanning electron micrographs of the fracture surfaces of A and (B) types. With increasing PMMA content, the roughness of each fracture surface increases. As PMMA content increases so does the roughness of the fracture topography ( Figures 5.9 and 5.10), At higher A contents the fracture surfaces are smoother ( Figures 5.12 and 5.13 ).



Fig. 5.9a Electron micrograph of the fracture surface of (B) type for composition 60/40 PMMA/AR (mag.500X)



Fig. 5.9b Electron micrograph of the fracture surface of (B) type for composition 60/40 PMMA/AR (mag.100X)



Fig. 5.10 Electron micrograph of the fracture surface of A type for composition 55/45 PMMA/AR (mag.500X)



Fig.5.11 Electron micrograph of the fracture surface of (B) type for composition PMMA/AR 50/50 (mag.250X)


Fig.5.12 Electron micrograph of the fracture surface of A type for composition 40/60 PMMA/AR (mag.100X)



Fig. 5.13a Electron micrograph of the fracture surface of A type For composition 30/70 PMMA/AR (mag.500X)



Fig.5.13b Electron micrograph of the fracture surface of A type for composition 30/70 PMMA/AR (mag.100X)

When semi-1 IPN systems, one is without sulphur and the other with sulphur ( as additional crosslinker ) are compared, the tensile strength of the system without sulphur is lower than that of the system with sulphur. The elongation at break (eb) of the former is higher with less PMMA and eb is lower in more PMMA case than that of the latter. The elastic modulus of the former is lower than that of latter. In conclusion, the semi-IPN with sulphur has better tensile properties, but have a pale brown opaque appearance, whilst those without sulphur are transparent and virtually colourless.

The tensile behaviour of full IPNs based on AR[(C)SSS]/PMMA(TMPTMA) have been examined ( Table 5.7 ). The tensile strength of the IPNs increases and the elongation at break decreases, expected, with as increasing PMMA content. Compared with the semi-1 IPNs, the tensile strength scarcely changes, but the elongation at break decreases. This is probably due to both polymers being in network form, thus lowering molecular chain flexibility.

The semi and full IPNs with the labile crosslinker system shows the same trend in tensile properties. The elongation at break of semi-IPNs is much higher than that of full IPNs and tensile strength from semi to full IPNs changes little, as shown in Table 5.8.

The semi and full IPNs with sodium stearate and sulphur as crosslinker have better tensile properties due to the different crosslinker and crosslinking technique employed.

# Table 5.7 The tensile properties for full IPNs based on AR[(C)SSS]/PMMA(TMPTMA)

	Composition	Elongation	Tensile
Code	[%PMMA(15%TMPTMA	(%)	strength
IPN	/%AR(SSS)]		(MPa)
	35/65	71	11.4
<u>(</u> C)	45/55	69	12.9
Full	60/40	38	15.4
	65/35	14	19.1
	10/90	240	1.5
(C)	60/40	83	17.4
Semi	65/35	70	18.3

Table 5.8 Tensi		ile p	le properties			semi-	and	full	
		IPNs 1	based	on	AR (AAA	)/PM	MA (TME	PTMA)	

IPNs	Composition	Elongation	Tensile	
	(%AR/%PMMA)	(%)	Strength	
			(MPa)	
	100/0	575	0.38	
	55/45	26	11.4	
Full IPNs	40/60	15	20.3	
(15%TMPTMA)	30/70	9.8	44.3	
	20/80	6.6	36.5*	
	100/0	575	0.38	
	50/50	40	17.1	
Semi-IPNs	30/70	16	38.0	
	20/80	13	56.7	
	0/100	6.8	65.1	

\* This result is unexpected and unexplained. Further work with more replicates might reveal preparation difficulties.

# 5.2.2 Dynamic Mechanical Properties

## 5.2.2.1 Tg and Tam' Behaviour of Semi and Full IPNs

When two polymers form a phase-separated mixture, each retains its glass transition. In general, the transitions may be broadened or shifted by mixing. The behaviour of a dynamic mechanical property tam over а range of temperature is shown in Figures 5.14-5.17 for semi-1 IPNs. The A, B, C and D types vary in composition and crosslinker content. The semi-l IPNs show two glass transitions except at very low PMMA contents. The positions of the peaks for the IPNs were shifted, depending upon compositions, in contrast to simple blends, where little change occurred (Fig.4.4). The two glass transitions of the constituent polymers (-16,+100) were shifted inwards suggesting some segmental molecular mixing of two components. The shapes of the DMA traces also change with the AR/PMMA ratio. A prominent low temperature tam occurs for the high AR blend, and a poorly resolved tand for the corresponding PMMA, as shown in Figure 5.17. In contrast, the IPNs with high PMMA contents show prominent high temperature tand and barely resolved ARK traces, also as expected. Selected dynamic mechanical properties of these IPNs are presented in Table 5.9. The glass transition temperature increases



Fig. 5.14 Tand-temperature for A type semi-1 IPNs with AR/PMMA composition 1. 70/30, 2. 60/40, 3. 45/55 (%wt).



Fig. 5.15 Tand -temperature for B type semi-1 IPNs with AR/PMMA composition 1. 75/25, 2. 60/40, 3. 50/50 (%wt).



Fig. 5.16 Tamb-temperature for C type semi-1 IPNs with AR/PMMA composition 1. 80/20, 2. 70/30, 3. 40/60 (%wt).



Fig. 5.17 Tand-temperature for D type semi-1 IPNs with AR/PMMA composition 1. 60/40, 2. 45/55, 3. 35/65 (%wt).

Table 5.9 Glass transition data for semi- IPNs based on AR(SS)/PMMA.

Code	Com- position %PMMA/%AR	Tg⁰C AR	Tanð peak value (AR)	Tran- sition width at half peak( <sup>0</sup> C)	Tg⁰C PMMA	Tanð peak value PMMA
	30/70	7.2	0.87	32	-	-
A	37/64	12	0.53	42	98	-
	54/46	19	0.42	59	137	0.28
	25/75	14	0.83	33	-	-
В	37/63	17	0.53	44	100	-
	50/50	22	0.3	71	140	0.38
	23/77	12	0.65	40	-	-
С	25/75	15	0.58	71	-	-
	65/35	27	0.27	102	137	0.39
		· ·				
	38/62	17	0.45	57	100	-
D	62/38	21	0.31	88	133	0.45
	64/36	24	0.21	90	143	0.64

with increasing PMMA content at both transition peaks. The magnitude of the tand corresponding to the lower glass transition decreased, and the maximum value of tand increased at the second glass transition, as PMMA content

and crosslinker content increased. Thus not only the position of the glass transition, but also the maximum value of tam's of each polymer changes in networks. The crosslinker content is only important for the maximum value of tam's. When the PMMA content is small, broadening of acrylic rubber transition peak indicates some stiffening of the soft AR phase.

The higher extent of molecular mixing of the phases in full IPNs based on AR[(C)SSS]/PMMA(TMPTMA) is shown in Figure 5.18. This is due to trapping of the polymers into limited domains with some enforced molecular mixing in the networks. Compared to the previous glass transition shapes ( ie, of simple blends and semi- IPNs ) those of the full IPNs show a significant broadening of the transition peak and there is also an inward shift of the Tg. This is greatest at the 55/45 AR/PMMA ratio. The maximum value of Tand for each peak is much lower ( tand < 0.3 ).

The full IPNs based on AR(AAA)/PMMA(TMPTMA) (Figure 5.19) also shows the same trends as the Figure 5.18. but in this system, the maximum value of tand at the PMMA transition is higher than that at the AR transition. this is most obvious for the 55/45 AR/PMMA IPN. This may occur during the crosslinking process (ie Mc of AR in this system is much higher). The crosslink density of polymer I is very important for the domain size of polymer II and the



Fig. 5.18 Tamb-temperature for full IPNs with AR[(C)SSS]/PMMA(15%TMPTMA) 1. 65/35, 2. 55/45, 3. 40/60, 4. 35/65 (%wt).



Fig. 5.19 Tand -temperature for full IPNs with AR(AAA)/PMMA(15%TMPTMA) 1. 55/45, 2. 40/60, 3. 70/30, 4. 80/20 (%wt).

domain size may influence the mechanical properties of IPNs.

## 5.2.2.2 The Storage Modulus, E', Behaviour

The behaviour of another dynamic mechanical property (storage modulus E') over a range of temperatures is presented in Figures 5.20-5.23 for semi-1 IPNs A, B, C and D types. The transitions are broad and that at the lower temperature, associated with the predominantly AR, is as before shifted to a higher temperature relative to the AR network. When PMMA content is increased to a higher level, the corresponding curve is shifted to a much lower temperature relative to the pure PMMA (Figure 4.5). This may indicates that the IPNs are rather tough materials, correlating with the previous tensile data.

For the full IPNs, the glass transition is very broad, as shown in Figure 5.24 and Figure 5.25. With increasing PMMA content, the position of curves shift to higher temperature.

From these dynamic mechanical analyses, we can conclude the following: (i) the AR/PMMA phase mixture shows two glass transitions indicating an incompatibility in our semi- and full IPNs. (ii) a certain amount of molecular mixing occurs in semi- IPNs, shown by glass transition shifting and broadening and (iii) that higher molecular mixing is



AR/PMMA composition 1. 70/30, 2. 60/40, 3. 45/55 (%wt).



AR/PMMA composition 1. 75/25, 2. 60/40, 3. 50/50 (%wt).



Fig. 5.22 E'-temperature for C type semi-1 IPNs with AR/PMMA composition 1. 80/20, 2. 70/30, 3. 40/60 (%wt).



Fig. 5.23 E'-temperature for D type semi-1 IPNs with AR/PMMMA composition 1. 60/40, 2. 45/55, 3. 35/65 (%wt).



Fig. 5.24 E'-temperature for full IPNs with AR[(C)SSS]/PMMA(15%TMPTMA) 1. 65/35, 2. 55/45, 3. 40/60, 4. 35/65 (%wt).





indicated by broadening and large shift in glass transitions is found in the full IPN.

## 5.2.3 Morphology

One approach to the study of dual phase continuity in sequential IPNs is through the decrosslinking and subsequent dissolution ( or leaching ) of one polymer or the other. The morphological details of sequential IPNs based on AR(AAA)/PMMA(TMPTMA) were studied. Figure 5.26 shows the micrographs of the full IPNs (undecrosslinked). It is difficult to observe the dispersion of two phases AR/PMMA. The use of selective chemical degradation of the crosslinkers in one polymer followed by the extraction of the decrosslinked material, ( for example, the use of the labile crosslinker AAA allows subsequent alkaline hydrolysis, leading to a linear, extractable polymer ) offered a new dimension in analysis of IPN morphology by means of scanning electron microscope.

As previously indicated, this concept was first revealed by Sperling et al [16,17] for PS/poly(n-butyl acrylate) blends.

In general, all scanning electron micrographs of decrosslinked and extracted IPNs revealed a spongy interior having pores from 50nm to  $\mu$ m in diameter. Figures 5.27 and

5.28 show micrographs for the midrange composition. In these figures the lighter regions represent the remaining polymer which is PMMA and the dark zones are voids where network I was previously located. Undoubtedly the PMMA phase is continuous. The voids appear to be continuous too, and hence the AR phase must have been continuous before extraction. Figure 5.29 shows the porous structure of the 80/20 AR/PMMA IPN. For the 80/20 ratio, many voids are interlinked or semicontinuous. It is valuable to examine the morphology of the remaining phase (PMMA) particularly where obvious macroscopic discontinuity exists ( ie in IPNs with less than 20% PMMA ). The micrograph from a 20/80 AR/PMMA IPN is shown in Figure 5.30. Here the PMMA phase is continuous, although the AR phase is difficult to observe. We expect it to be continuous however, as previously reported for related IPNs[16], polymer I generally forms the more continuous phase in IPNs, and this tends to control the two phase interpenetrating morphology. An extracted PMMA structure from а semi-l IPN with AR(AAA)/PMMA composition 55/45 (%wt) is shown in Figure 5.31, and the remaining AR phase is more continuous. Thus the morphology of midrange compositions have dual phase continuity, and mirror those examined by Sperling[16].

The IPN composition reflects the relative amounts of the two phases present after polymerisation. Increasing amounts of polymer II generally lead to increasing domain sizes. For the sequential IPNs based on PMMA/AR only slight

increases in domain size occur as the composition range changes from 80/20 (380Å), 48/52 (440Å) to 42/58 (450Å). The domain size appears to be smaller than those measured by Sperling[16]. This is probably due to the Mc value of the AR being smaller than that of Sperling's (Table 2.3). Further, the composition of the blends differ, with differences in solubility parameter for our two components possibly being smaller than for the previous system.



Fig. 5.26a SEM surface of full IPN with AR(AAA)/PMMA(TMPTMA) composition 47/53 (mag.500X)



Fig. 5.26b SEM surface of full IPN with AR(AAA)/PMMMA(TMPTMA) composition 47/53 (mag.2000X)



Fig. 5.27a SEM surface for decrosslinked and extracted IPN with AR/PMMA composition 48/52 (mag. 5000X)



Fig. 5.27b SEM surface for decrosslinked and extracted IPN with AR/PMMA composition 48/52 (mag. 9000X)



Fig. 5.28a SEM surface for decrosslinked and extracted IPN with AR/PMMA composition 42/58 (mag.2000X).



Fig. 5.28b SEM surface of decrosslinked and extracted IPN with AR/PMMA composition 42/58 (mag. 3000X).



Fig. 5.29 SEM surface for decrosslinked and extracted IPN with AR/PMMA composition 80/20 (mag.1300X).



Fig. 5.30 SEM surface for decrosslinked and extracted IPN with AR/PMMA composition 20/80 (mag. 3700X)



Fig. 5.31 SEM cross section surface for extracted PMMA from semi-1 IPN AR(AAA)/PMMA 55/45 (mag.3000X).

#### CHAPTER SIX

### CONCLUSIONS

Increases in acrylic rubber content in both simple blends, semi- and full IPNs produced increases in elongation at break and a decrease in tensile strength and Young's modulus. The IPNs with AR(SSS)/PMMA(TMPTMA) possess better tensile properties, as expected, compared with simple blends and IPNs with AR(AAA)/PMMA(TMPTMA). A number of IPN compositions exhibit considerable toughness, at relatively high PMMA content (65%). Semi- IPNs are tougher than the corresponding full IPNs.

The SS or SSS type and NPC type networks revealed optimal mechanical behaviour, and SS and NPC networks and SS type IPNs are transparent.

The crosslink density of the AR controls the mechanical properties of the acrylic rubber network. As crosslinker content increases, the tensile strength and elongation at break also increase to a maximum (for example in C and (C) type networks). This trend is also found in associated IPNs. At very high crosslink levels, elongation at break decreases and the glass transition shifts to slightly higher temperatures for a fixed polymer composition.

Simple blends, as well as semi- and full IPNs have two glass transitions, consistent with phase separation. Little molecular mixing occurs in simple blends, as reflected by two completely separated glass transitions. Some segmental molecular mixing occurs in semi- IPNs as reflected by shifting and broadening the glass transitions. The higher extent of molecular mixing reflected by significant broadening and shifting glass transitions in full IPNs.

The morphology of midrange compositions have dual phase continuity, as shown by decrosslinking and extraction experiments. Here the labile crosslinker AAA was used in the acrylic rubber, which is then converted to IPNs designated as AR(AAA)/PMMA(TMPTMA). Above 20% of polymer II (PMMA), the phase domains were continuous and over the composition range studied, polymer I was continuous. For simple blends, phase conversion takes place over the 70/30 PMMA/AR composition. AR is a more continuous phase, not only in the IPNs but also in the simple blend.

In the sequential IPNs only a slight increase in domain size of phase is observed with increasing polymer II contents and the domain size is finer, this being typically 50nm in diameter.

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