Chapter 2

PU / PMMA

Interpenetrating Polymer Networks

INDEX

Interpenetrating Polymer Networks (IPNs) are blends of crosslinked polymers that are unique in properties among the polymer alloys. They can display more or less synergistic behaviour depending upon the level of mixing of component networks. IPNs are prepared to improve the properties of individual polymers. The IPNs are usually heterogeneous systems, in which one polymer exists above its glass transition temperature (Tg), which has a glassy microstructure whereas the other polymer exists below its Tg, which shows a rubbery microstructure. By altering the relative amounts of each polymer in the IPNs, the individual polymer properties may be changed in which the lower Tg component is shifted to a higher temperature and the high Tg component is shifted to a lower temperature.

IPNs prepared with a flexible and a rigid component often show a synergistic effect in some material properties[1-3] In IPN terminology, a full IPN is a system in which both polymer components are crosslinked. This produces a simultaneous IPN if both networks are cured together and sequential IPN if one component is polymerized followed by swelling of it in the second monomer, which is then polymerized. A semi IPN is a material which contains only one crosslinked component, whereby the initially formed polymer may either be the crosslinked (semi - I - IPN) or the linear (semi - II - IPN). Each of these variations can affect the IPN morphology and thus the thermal and mechanical properties. In case of IPNs complete miscibility is not necessary to achieve complete phase mixing because the permanent entanglements can effectively minimize phase separation. The interpenetrated and entangled networks can increase the phase stability and therefore enhance the properties of the resulting material.

Numerous IPNs based on a variety of materials have been developed in the past and have important applications as damping materials. The damping characteristics of a polymer is related to its structure and is dominated by its glass transition. True IPNs show a single glass transition similar to what would be expected of miscible blend. However, IPNs often, do show some small-scale phase separation, which can account for the very broad transitions. It is this very broad transition region that makes IPNs desirable as damping material. A high loss over a fairly wide temperature and frequency range is usually desirable for a good damping material.

The IPNs of polyurethanes are reported to show not only desirable damping abilities but also interesting mechanical properties. A brief report based on the exhaustive literature survey related to the IPNs of polyurethanes with a variety of other polymers is given below.

2.1 Review On IPNs Of Polyurethanes

The IPNs of polyurethanes with epoxy resins, polyesters and many of the vinyl monomers have been extensively reported in the literature[4,5]. Among them, the IPNs with polyacrylates are observed to exhibit interesting properties. Polyacrylates find applications in many different areas because of their excellent transparency but suffer from drawbacks like brittle nature and poor impact resistance. These problems can be overcome by blending them with an elastomeric material like polyurethane.

- ***IPNs of PU with polyacrylates***

Number of groups have carried out extensive research on the IPNs of PU and a variety of polyacrylates. The work carried out by Sperling et al[6-10] in the field of IPNs is very well-known. They have constructed a metastable phase diagram for simultaneous interpenetrating networks (SIN) and related composition, using PU / PMMA IPN system as the model material[11].

Hourston and co - workers have carried out a detailed investigation on the synthesis and properties of various PU / polyacrylate IPNs. They used polyurethanes derived from NCO terminated commercial prepolymer Adiprene L - 100 and varying acrylates such as poly(ethyl methacrylate)[12], poly(methyl acrylate - co - ethyl acrylate)[13] and poly(methyl acrylate)[14]. Substantial phase separation was observed in TEM but DMA results indicated a certain degree of phase mixing in these IPNs. High damping characteristics were exhibited by some compositions of these IPNs .

Kim, Klempner and Frisch[15-18] have carried out in depth study of the PU / PMMA semi and full IPNs and their linear blends (neither network crosslinked). The engineering properties, morphology, glass transition behavior, volume resistivity behavior and viscoelastic properties of the IPNs were investigated in detail. As a combined result of increased modulus and tensile strength, the tear strength of the polyurethane - rich IPNs, pseudo - IPNs, and linear blends was observed to be higher than that of the pure polyurethane. In the studies on IPNs of poly (carbonate - urethane) and PMMA, Frisch et al[19] observed that all the full IPNs exhibited a single glass transition temperature as determined by DSC and DMA, which together with TEM observations suggested single-phase morphology even though the linear chain blends were completely immiscible. The effect of pressure on the morphology and glass transition behavior of PU / PMMA simultaneous IPNs was investigated by Kim et al[20]. The PU phase decreased gradually in domain size with increasing synthesis pressure. Morphology revealed that, at 50/50 weight ratio, for low-pressure polymerisation the PU phase was more continuous and for high-pressure polymerisation the PMMA phase was more continuous.

Suthar et al[21-27] have developed numerous IPNs from the PUs derived from castor oil and PMMA, using MDI[21], 2,4 - TDI[22], HMDI[23] or IPDI[24] and crosslinker EGDMA through free radical polymerisation. The IPNs with other acrylates like poly(n - butyl methacrylate)[21], poly(methyl acrylate)[25], poly(2 - hydroxyethyl methacrylate)[26] and PMMA[27] were also developed by them. They were characterized by their resistance to chemical reagents, thermal behavior, and mechanical properties. Phase separation was observed through SEM and dielectric properties at different temperatures. Number of other authors[28-32] have reported studies on castor oil PU / PMMA IPNs. Zhang et al[30-32] studied the synthesis, properties, and morphology of castor oil PU / PMMA IPNs and developed adhesives suitable for metals. The adhesive had the optimal properties when the NCO / OH ratio was 1.5 and the content of MMA was 60 %.

Various aspects of the PU / polyacrylate IPNs have been investigated by number of authors in order to establish structure properties relationship in these IPNs. Wang et al[33,34], established a correlation between the morphology and mechanical properties of IPNs, comprised of HTPB based polyurethane and PMMA. Morphology and mechanical properties of IPNs with varying amounts of TDI and N,N - di (2 - hydroxyisopropyl)aniline were investigated through SEM, DSC, and dynamic mechanical thermal analysis (DMTA). Hardness, tensile strength, and elastic modulus of the different IPNs were measured as a function of PMMA content.

In the study of mechanical and morphological properties of PU / poly(n - butyl acrylate) based IPNs, Fox et al[35] have reported very high phase separation indicating incompatibility. Zhang et al[36-38] studied the glass transition behavior and morphology of IPNs based on polymethacrylates and PUs based on hydroxyl - terminated acrylonitrile - butadiene copolymer (HTBN). The results indicated that there were two continuous phases separated from each other and two glass transition temperatures corresponding to the components in the polymer networks. They observed that the peaks in mechanical damping vs. temperature plots of IPNs containing poly (butyl methacrylate) and poly (iso - butyl methacrylate) were broader than those of IPNs containing PMMA.

- ***PU / PMMA IPNs***

PMMA is a widely used acrylate with high modulus and excellent transparency. Many workers have tried to improve its brittle nature by toughening it with PU.

The IPNs of PMMA with unsaturated polyurethane (USPU), were synthesized and characterized by Chen et al[39,40]. DMA and swelling measurements were carried out and the results showed that the copolymers have crosslinked network structure and two - phase morphology. The Tg of the copolymers increased with increasing PMMA content and the crosslink density of the copolymers reached a maximum when PMMA content in the copolymer was 40 weight %. The USPU tends to toughen PMMA and improve the impact properties of PMMA.

The deformation and fracture mechanism in rubber toughened PMMA modified by PU / PMMA IPNs was studied using TEM by Beguelin et al[41,42]. Jung et al[43] have carried out the toughening of PMMA with PU / PMMA composite particles. The composite particles enhance the toughness of PMMA resin when they are blended with PMMA. Semi - IPNs type PU / PMMA composite particles in which PMMA is not crosslinked are found to be more effective as toughening agent than full - IPN type particles in which PMMA is crosslinked. However, the semi - IPN type particles lead to the reduction in the transparency of the PMMA matrix more significantly than the full - IPN type particles. A detailed investigation of the fatigue behavior of IPNs based on PU and PMMA by Hur et al,[44,45] showed that the fracture toughness and resistance to fatigue crack propagation was significantly improved with increasing PU content. Fracture surface morphology was observed to show stress whitening.

The effect of molecular weight of polyols and NCO:OH ratio of urethane prepolymers on properties and morphology of IPNs of PU and methacrylate polymer was investigated by Xiao et al[46]. Jehl et al[47] prepared various combinations of PU and PMMA IPNs and semi IPNs and measured the optical transmittance of these materials as a function of crosslink degree of both phases. They concluded that increase in the degree of phase dispersion favors the transparency of the IPNs. Crosslinking of the second component was reported to influence the properties of polyurethane - PMMA IPNs to a great extent[48]. The authors have also evaluated the network defects arising in PU / PMMA interpenetrating networks, where the PU networks were synthesized at various dilutions of the reaction medium and at different values of the NCO:OH ratio.

Lee et al[49,50] developed PU / PMMA IPN based polymer membrane and evaluated the pervaporation characteristics for benzene / cyclohexane mixtures. The membranes exhibited a high benzene selectivity and the swelling of the membranes was depressed with increasing NCO:OH ratio and increasing EGDMA content. The DM analysis of IPNs of HTPB based PU and PMMA crosslinked with EGDMA, prepared by Jia et al[51] demonstrated that the interpenetration of networks exists mainly between PMMA and the hard segments of PU. With increasing amounts of PMMA, the IPNs transform from reinforced rubbers to toughened plastics. They found that the mechanical properties of the full - IPNs are far superior to those of the corresponding semi - IPNs and linear blends. On the other hand, Wang et al[52] observed that the linear polymer has the highest elongation at break, and full IPNs have the highest tensile strength. With increasing MMA content and hard segment in PU, the tensile strength increases, and the elongation decreases. Akay et al[53] also observed that the hardness, elastic modulus and tensile strength increased with increasing PMMA.

The study of kinetics of formation of the networks is important in governing the final properties of the IPNs. Wang et al[54] have investigated the reaction extent and kinetic constants in the early stage of the formation of the PU / PMMA IPNs on the basis of FTIR spectra. They observed that an increase of the PMMA content accelerated the polymerisation rate of PU prepolymer formation due to the solvent effect of PMMA while an increase of the polyurethane content decreased the polymerisation rate of MMA due to the cage effect of the polyurethane. Anzlovar et al[55] and Jin et al[56,57] also studied the kinetics of formation of PU - PMMA IPNs. Anzlovar et al[55] observed that the PMMA component acts as a diluent in the mixture of PU and PMMA reducing the reaction rate and increasing the activation energy of the crosslinking reaction. Curing and mechanical behavior of full and semi - IPNs based on PU and polyacrylate was investigated by Lin and Chium[58]. They proposed the effect of interlock during IPN formation, which retarded curing rates of both networks. The same authors[58] have studied the kinetics at 70, 75, 80 and 85 °C.

Sequential PU / PMMA IPNs for the use as ureteral biomaterials have been developed by Jones et al[59]. The mechanical properties and resistance to urinary incrustation were examined using an in vitro model. Chen et al[60] developed glass fiber - reinforced PMMA / PU IPN composites which show excellent processability for pultrusion. The mechanical and dynamic mechanical properties were also examined. The flexural strength, flexural modulus and hardness of IPN composites were observed to increase with PMMA content. PU / PMMA IPNs based adhesives having good storage stability were developed by Li et al[61]. The adhesion strength was reported to increase with increasing PMMA content upto 20 – 30 % of PMMA.

Many authors have investigated the damping abilities of IPN systems. Yu et al[62,63] observed that the tan δ peaks of the IPNs were not high for the polymers not having sufficiently good damping; while relatively wider and higher tan δ peaks of the IPNs were obtained for the polymers possessing good damping[61]. The same authors have compared the damping behaviour of IPNs of castor oil based polyurethane (PU) with a series of acrylates[64]. They observed that the length of the pendant groups has an influence on the height of tan δ in the interpenetrating structure.

In general most of the polymers are incompatible owing to difference in their thermodynamic and visco - elastic properties leading to an unfavorable interaction between molecular segments and poor dispersion of the components during mixing. Similarly, IPNs also have a tendency to show phase separation due to the low entropy of mixing. IPNs synthesized so far exhibit varying degrees of phase separation depending mainly on the miscibility of the polymers. In order to optimize interpenetration it is desirable that the phases be as small as possible. Sometimes it is possible to increase compatibility between the component phases by blending polymers under conditions, which encourage synergistic interaction through co - crosslinks. The use of chain grafting agents for this purpose has been reported in the literature. The effect of composition and the amount of 2 - hydroxypropyl methacrylate (2 - HPMA), chain grafting agent on the morphology and properties of polyether - polyurethane / PMMA IPNs was studied by Wang et al[65]. 2 - HPMA could enable the grafting of the disperse phase onto the continuous phase to form a complex network and improved the chemical compatibility. The two glass transition temperatures observed in the dynamic mechanical spectrum were merged into a single with increasing amount of 2 - HPMA. When PU / PMMA weight ratio was 80 / 20, only one glass transition temperature was observed at - 47° in the dynamic mechanical analysis. The elongation at break was observed to be 987 %.

Wilson et al[66] carried out the synthesis and characterization of PU / PMMA graft copolymers. The unsaturated PUs were radically grafted using MMA and initiator, AIBN, in DMF at 80 °C. Scarito and Sperling[67] examined the effect of glycidyl methacrylate (GMA) in the epoxy / acrylate system. They have reported that incorporation of only 3 % GMA, in both the components during simultaneous network formation, could bring sufficient mixing yielding materials with only one glass transition temperature. The

IPNs of polyurethane (PU) and 2 - hydroxyethyl methacrylate (2-HEMA) terminated polyurethane (HPU) developed by Liu et al[68] showed good compatibility between their constituents. As the HPU content increased, the tensile strength of the IPNs first increased and then decreased. For the highest tensile strength, the optimum HPU content was reported to be about 25 weight %.

We have undertaken the comparative study of PU / PMMA semi and full IPNs based on the four different PU systems discussed in chapter 1. The composition of PU with NCO:OH ratio 1.3 and diol : triol ratio 1 : 1.5 (B1) was selected for development of IPNs. In order to develop compatibilised IPNs we have made use of 2 - HEMA and glycidyl methacrylate. Glycidyl methacrylate has a polar epoxy group while 2 - hydroxyethyl methacrylate (2 - HEMA) has a free OH group, which can interact with the free NCO groups of the polyurethane. Hence they are expected to enhance the compatibility and molecular mixing in the PU / PMMA IPNs.

The IPNs were developed with different proportions of PMMA and also with different crosslink density of the PMMA network. To select a blend ratio and a crosslinking system suitable for a particular application, a clear understanding of the change in properties with blend composition and crosslinking systems is essential. Therefore the IPNs were thoroughly characterized for thermo-mechanical and morphological properties.

2.2 Experimental

2.2.1 Materials

Sources of the chemicals used for the synthesis of the PU network of the IPNs are given in section 1.3.1, while those for the synthesis of the PMMA network are given in Table – 2.1. The monomers were distilled before use. AIBN was purified by dissolving in chloroform and reprecipitating in methanol.

Table 2.1 : Chemicals used for the synthesis of IPNs

Materials	Source
1. 2,2'-Azobisisobutyronitrile (AIBN)	Spectrochem, Bombay, India
2. Methylmethacrylate (MMA)	Sisco chemicals, Bombay, India
3. Glycidylmethacrylate (GMA)	Fluka AG, Switzerland
4. Divinylbenzene (DVB)	Fluka AG, Switzerland
5. 2-Hydroxyethyl methacrylate (2-HEMA)	Sisco chemicals, Bombay, India

2.2.2 Synthesis of IPNs

The IPNs were prepared from B1 composition of all the four polyurethane systems described in chapter 1. Methyl methacrylate (MMA) was used as the monomer for the second network and divinyl benzene (DVB) was used as acrylate crosslinker. The concentration of GMA and 2 - HEMA was kept constant at 2 % (w/w) of the total acrylate concentration.

In a five - neck reaction kettle fitted with a mechanical stirrer and nitrogen inlet, 1.0 mole of HTPB or PPG, dried in vacuum for about an hour was taken. A calculated quantity of TDI or MDI (3.25 moles) was then added dropwise, under nitrogen atmosphere at room temperature. The prepolymerization was continued for an hour. To this, TMP (1.5 moles), MMA, DVB (4 % w / w) and 2 - HEMA or GMA (2 % w / w) were added successively. 2, 2' - azobisisobutyronitrile (AIBN) was added as its solution in the monomer. Stirring was continued for 30 minutes, followed by the addition of the catalyst dibutyl tin dilaurate (DBTDL) and triethylamine. The temperature was increased to 60 °C to initiate the polymerisation of the PMMA network and stirring was continued for 15 minutes. Degassing was carried out in order to remove the entrapped air. The mixture was poured onto a bordered glass plate and placed in a closed chamber in order to prevent loss of monomer due to evaporation. Curing was carried out at room temperature for about 15 hours and then in an electrical oven at 80 ± 1 °C for 3 hours.

For the semi IPNs one of the networks was crosslinked while other was linear. In case of semi IPN type I PU was crosslinked while in type II PMMA was crosslinked.

2.2.3 Characterization

To understand the resistance of the material towards failure or crack growth, knowledge of mechanical properties is essential. The nature of the failure or cracking of a material can be investigated using SEM and can further be related to the strength of the material.

The synthesized IPNs were tested for various properties as per the procedure described in Section 1.3.3.

2.3 Results And Discussion

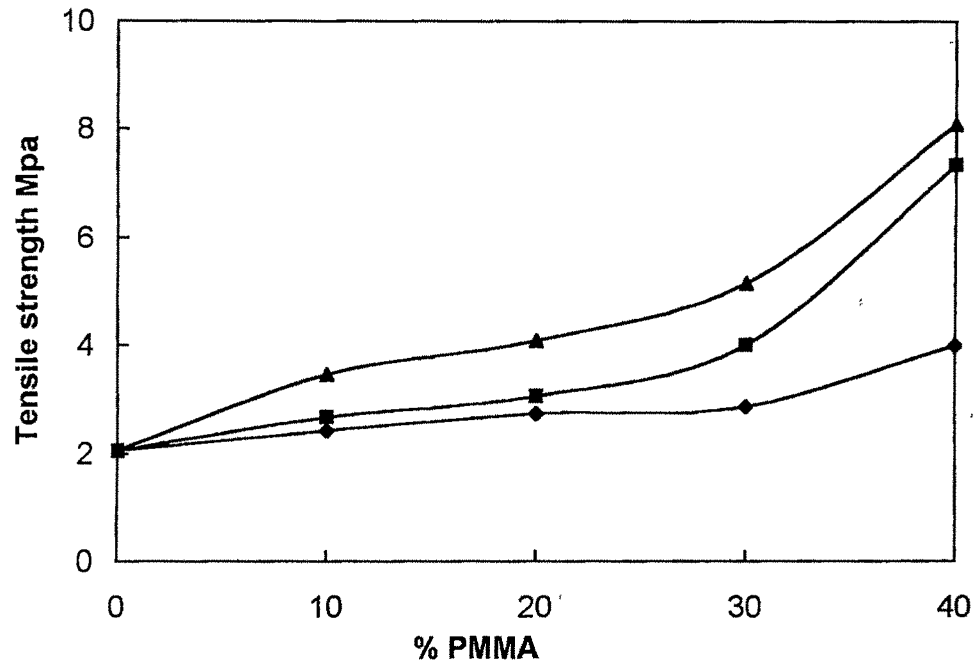
2.3.1 HTPB - MDI (H/M) based PU / PMMA IPNs

The effect of GMA and 2 - HEMA on the properties of PU / PMMA, IPNs was examined by preparing three sets of IPNs from HTPB - MDI - TMP based PUs (H / M PU). The first set contained various ratios of PU / PMMA (90 / 10, 80 / 20, 70 / 30 and 60 / 40 respectively) and was designated as U / M. The second set contained, in addition to the above compositions, 2 % GMA and was designated as U / M / G. In the third set designated as U / M / H, GMA was replaced by 2 - HEMA.

Some authors[69,70] have reported glycol based PU / PMMA interpenetrating networks to be non - transparent due to the incompatibility of PMMA and glycols. The U / M films in the present system were comparatively less transparent than U / M / G and U / M / H films. This can be an indication of better phase mixing in the systems containing 2 - HEMA and GMA.

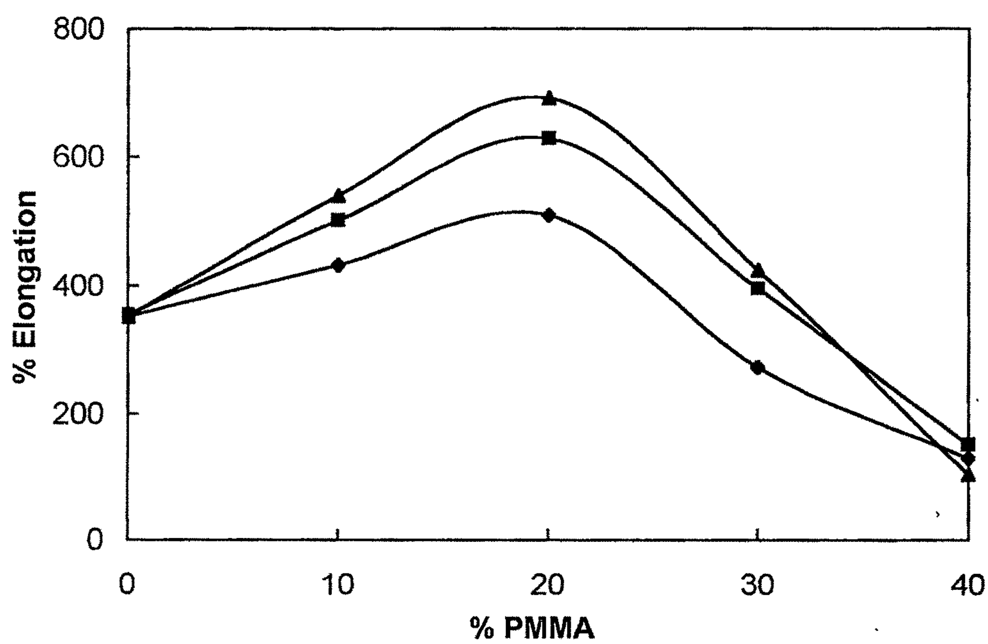
Mechanical Properties

The effect of weight percentage of PMMA on the tensile strength and elongation at break of the IPNs is illustrated in Fig. 2.1 and 2.2. It is observed that all the IPNs show higher tensile strength than the pure PU. Among the IPNs, the set containing 2 - HEMA i.e. U / M / H showed highest tensile strength at all IPN compositions. The U / M interpenetrating network on the other hand showed the least tensile strength. Thus in the presence of 2 - HEMA there exists satisfactory rubber - matrix adhesion in the IPNs under study. This may be due to the physical entanglements of the two phases, which prevents interfacial,



◆ : U / M, ■ : U / M / G, ▲ : U / M / H

Fig. 2.1 : Effect of weight percentage of PMMA on tensile strength of the H / M PU-PMMA IPNs.



◆ : U / M, ■ : U / M / G, ▲ : U / M / H

Fig.2. 2 : Effect of weight percentage of PMMA on % elongation of the H / M PU-PMMA IPNs.

de - cohesion as seen from the SEM (Fig. 2.3c) and discussed later. The U / M / G interpenetrating networks exhibit higher tensile strength than U / M but lower than U / M / H indicating improved phase mixing compared to U / M interpenetrating networks. Thus although both, 2 - HEMA and GMA lead to an increase in the tensile strength, 2 - HEMA appears to bring better miscibility.

Furthermore, it was observed that the tensile strength increases with increasing PMMA weight percentage in all IPNs. However, with an increase in the PMMA content from 30 % to 40 % a sudden increase in the tensile strength was observed in all the three sets. This can be attributed to an increase in crosslink density arising from enhanced physical crosslinks caused by interpenetration as well as improved homogeneity of the 60 / 40 IPNs as observed in SEM.

Percentage elongation was observed to increase with weight percentage of PMMA (Fig. 2.2) upto 20 %. Further increase in PMMA showed considerable decrease in elongation. Surprisingly the elongation of all the 90 / 10 and 80 / 20 IPNs was even higher than that of the parent PU. Similar observation was made by Varghese and Krishnamurthy[71] in the case of castor oil based PU / PMMA and PU / poly (butyl acrylate) IPNs. The observed increase in elongation was attributed to the topological interpenetration[72], which leads to interwoven or interlocked structure without chemical bonding.

The high tensile strength and lowest elongation of the 60 / 40, PU / PMMA IPNs could be due to the onset of phase inversion in which PU acts as the plasticizer and PMMA as the continuous phase.

Scanning Electron Microscopy

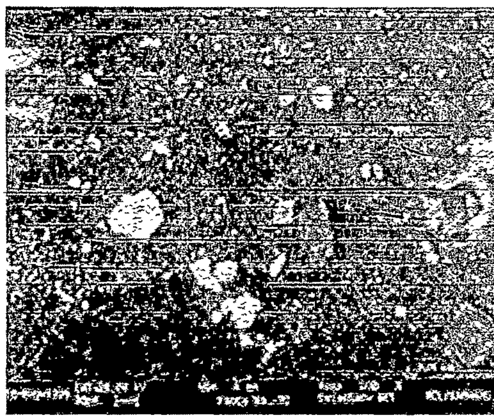
The SEMs of tensile fractured specimens of 60 / 40, PU/ PMMA IPNs are shown in Fig. 2.3(A - C). The SEM of U / M IPN (Fig. 2.3A) exhibits a large extent of phase separation. With addition of GMA and 2 - HEMA, an increased phase mixing is observed (Fig. 2.3B and C). The entanglements of bridged vinyl monomer in the PU network is more pronounced in the case of U / M / H (Fig. 2.3C) compared to U / M / G system (Fig. 2.3B). This is probably due to better compatibility of the two phases in this system. The U / M / G, 60 / 40 composition also shows the presence of cavities created during the fracture process. No such cavities were observed in the electron micrograph of U / M / H IPN of same composition. However, a single phase as reported by Scarito and Sperling[67] for epoxy / n - butyl acrylate and GMA based IPNs, was not observed. This may be because of much higher concentration of GMA used by them.

The significant rise in tensile strength with an increase in PMMA content from 30 % to 40 % can be explained from Fig. 2.3C and 2.3D. As the percentage of PMMA increases the bicontinuous morphology probably leads to the beginning of phase inversion. Further the small holes and randomly distributed particles observed in Fig. 2.3D are absent in Fig. 2.3C, indicating improved morphology of the IPN containing 40 % PMMA.

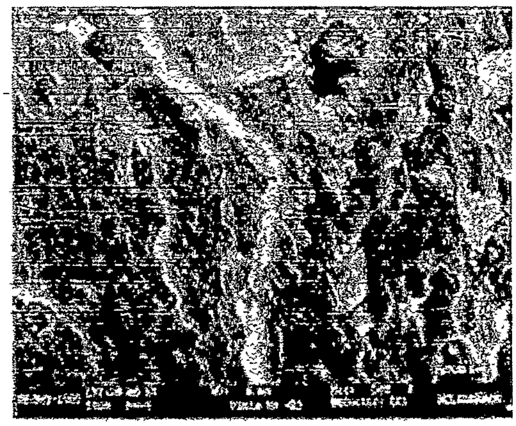
- ***Thermal Analysis***

- ***Differential Scanning Calorimetry (DSC)***

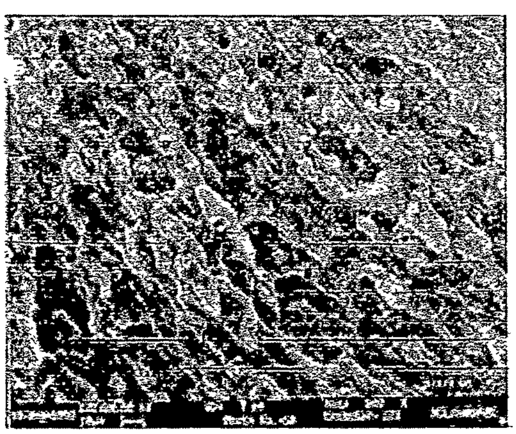
The DSC thermograms of PU and 60 / 40, PU / PMMA, IPNs are shown in Fig. 2.4. The thermogram of PU exhibits only one Tg corresponding to the soft segment. IPNs show the glass transition of PU around - 60 $^{\circ}$C and an additional Tg around 10 - 15 $^{\circ}$C.



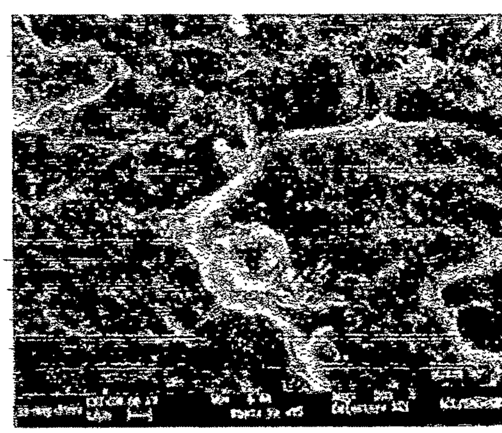
(A) (500 X)



(B) (500 X)



(C) (500 X)



(D) (500 X)

Fig. 2.3 : SE Micrographs of H / M PU / PMMA IPNs

(A) 60 : 40 U / M, (B) 60 : 40 U / M / G (C) 60 : 40 U / M / H
and (D) 70 : 30 U / M / H

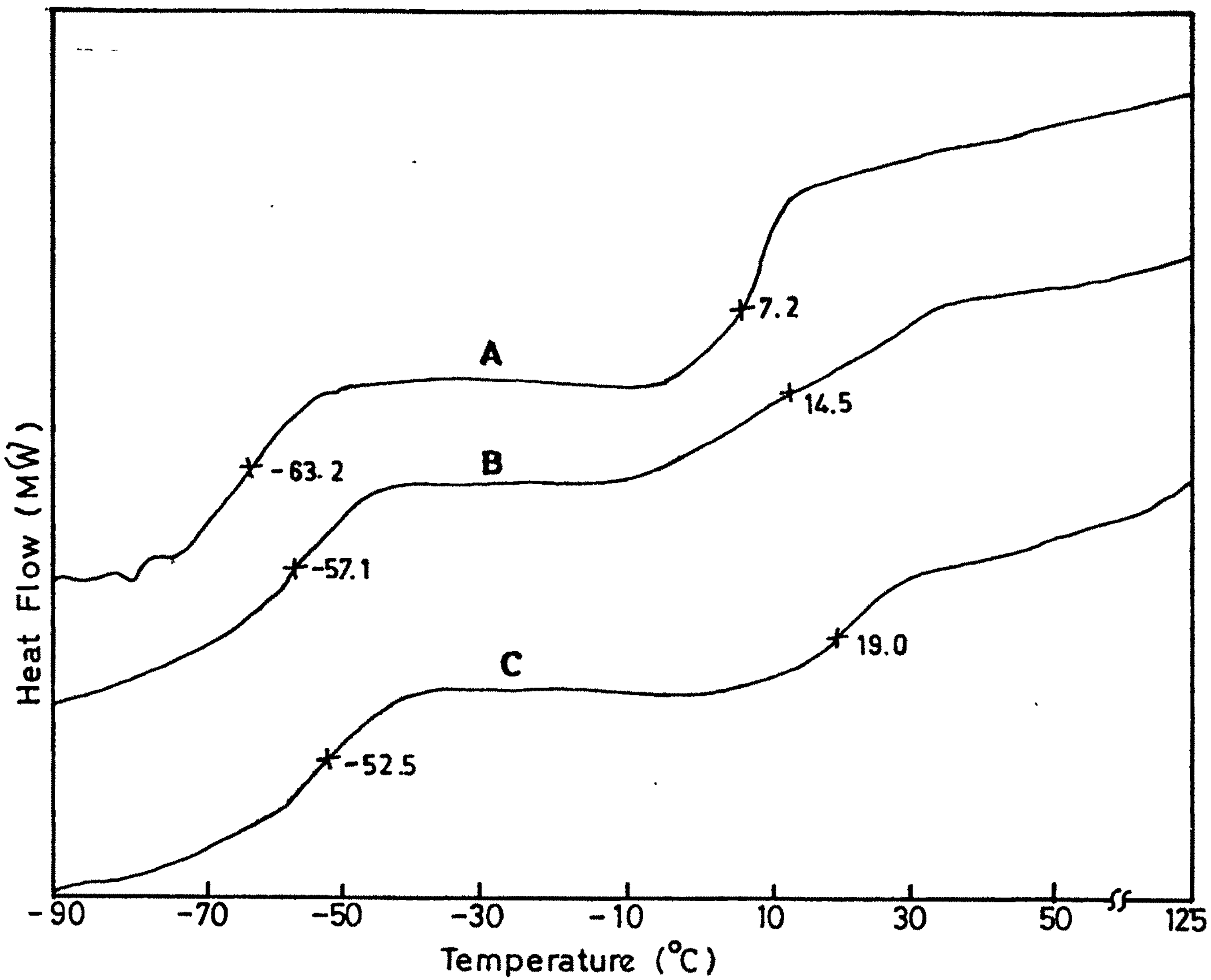


Fig. 2.4 **DSC** thermograms of 60:40 H/M PU IPNS **(A)** U/M **(B)** U/M/G **(C)** U/M/H

Further the Tg of PU in IPNs was observed to be shifted to the slightly higher side compared to the PU network. A shift in the Tg of PU network was also observed by Hourston and Zia[11] in the study of unsaturated PU / polymethyl acrylate grafted IPNs. Grafting as well as some spontaneous mixing was suggested to be responsible for the shift in the glass transition temperature of PU. The PU used in the present investigation is also derived from unsaturated HTPB. Hence it is likely that possible grafting of MMA on PU is playing some role in the observed shift in Tg. Probably the PMMA segments close to the active sites interact with PU segments and give rise to the additional Tg at about 10 °C. The remaining PMMA segments constitute a pure phase. However, this Tg may also arise from β relaxation of methyl group of PMMA[69].

In case of U / M / H or U / M / G IPNs shift in the Tg of PU network was observed to be much higher than in U / M (Fig. 2.4), indicating increased molecular interactions.

- ***Thermo-gravimetric analysis***

The thermal stabilities of IPNs were evaluated by TGA. The representative thermograms are presented in Fig. 2.5. The degradation onset of the PU network was at 315 °C. All the IPNs were stable upto 325 °C followed by a rapid weight loss around 500 °C. Almost complete decomposition was observed beyond 650 °C. It is observed from Fig. 2.5 B that the U / M / H IPN showed higher thermal stability than U / M / G IPN. The relative thermal stability of IPNs was evaluated by comparing decomposition temperatures at various percentage weight losses (Table 2.2). The percentage decomposition temperatures increased with decreasing urethane content in the IPNs. The higher thermal stabilities of these IPNs can be explained on the basis that the MMA liberated during degradation may act as a radical scavenger for PU degradation products.

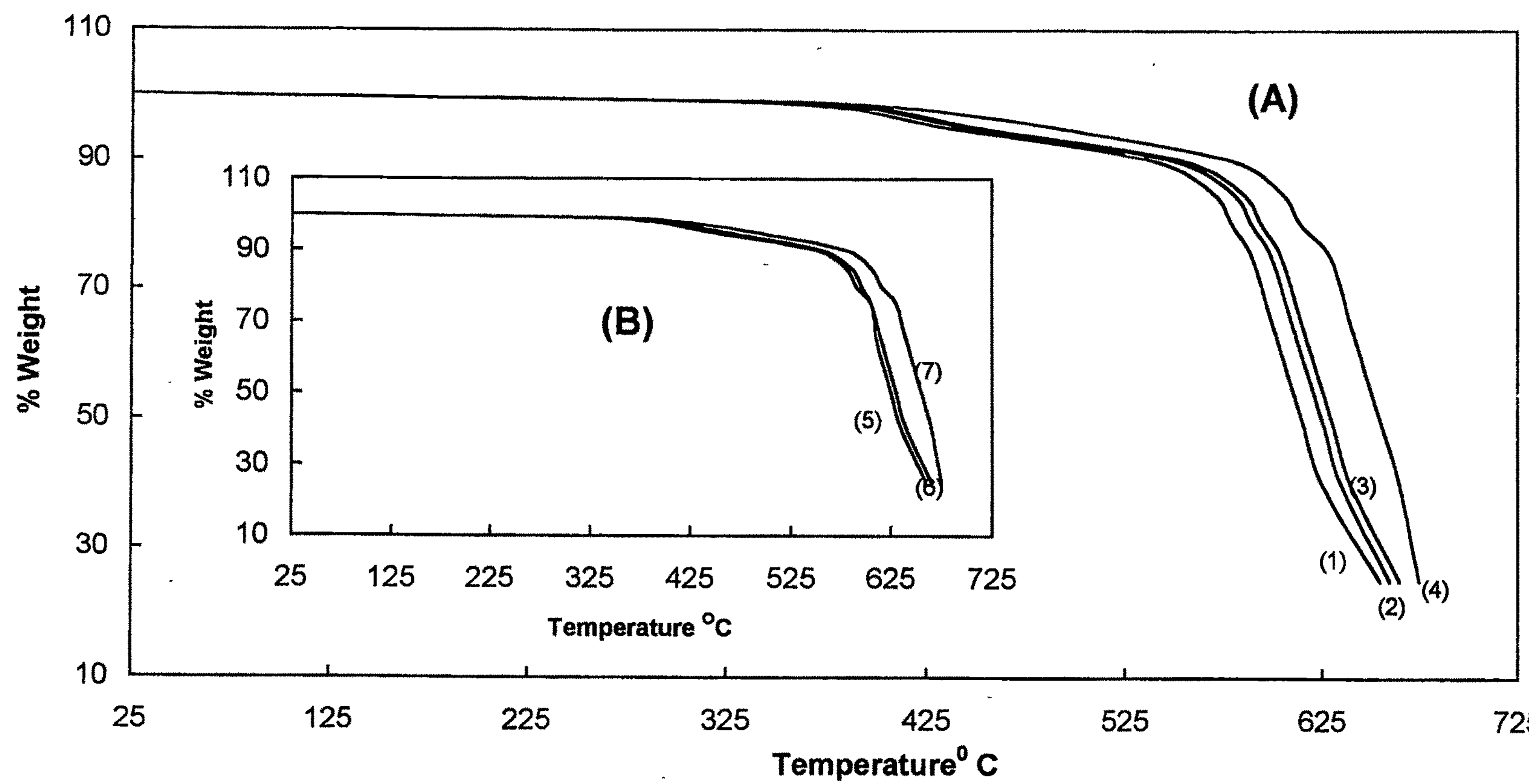


Fig. 2.5 : Thermogravimetric plots for (A) U / M / H IPNs (1) 90:10 (2) 80:20 (3) 70:30 (4) 60:40 and (B) 60 :40 IPNs (5) U /M (6) U/M /G (7) U / M/ H

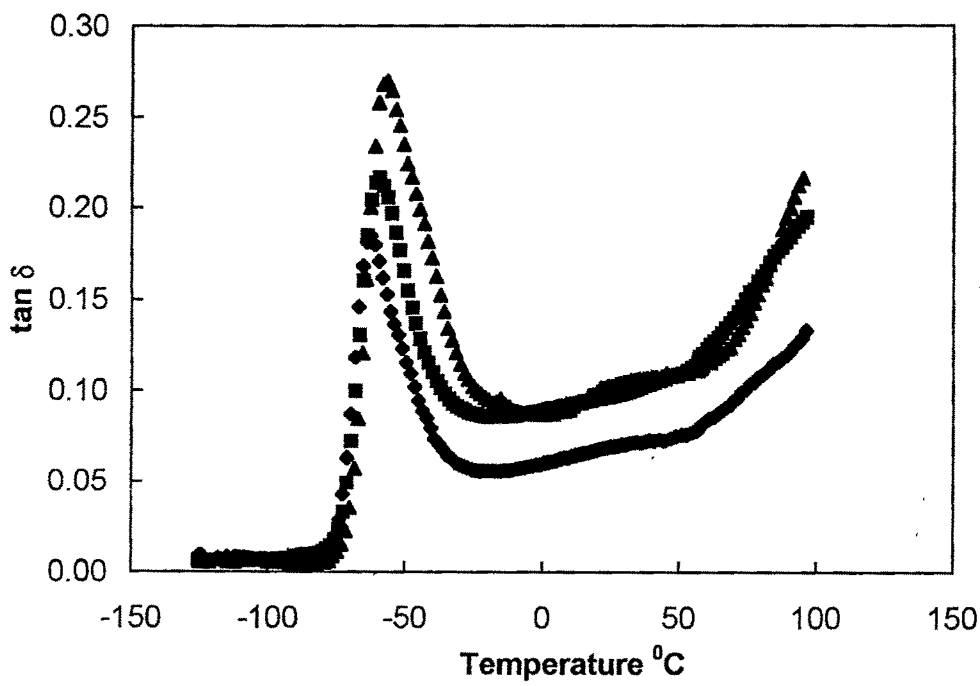
The initial slow weight loss around 325–355 °C is attributed to the base PU in the sample. The considerable weight loss in the range 450 to 550 °C can be assigned to the degradation or decrosslinking of the IPNs under investigation. The final weight loss at 550 – 650 °C, indicates the complete decomposition of the IPNs.

Table 2.2 : Decomposition temperatures of H / M PU IPNs

% Degradation	Temperature °C						
	U/M 60:40	U/M/G 60:40	U/M/H 60:40	U/M/H 70:30	U/M/H 80:20	U/M/H 90:10	PU
1	325	335	355	330	325	320	315
5	445	460	490	450	445	435	430
25	605	605	630	605	600	590	585
50	625	630	655	630	625	615	610
75	660	665	675	665	660	655	670

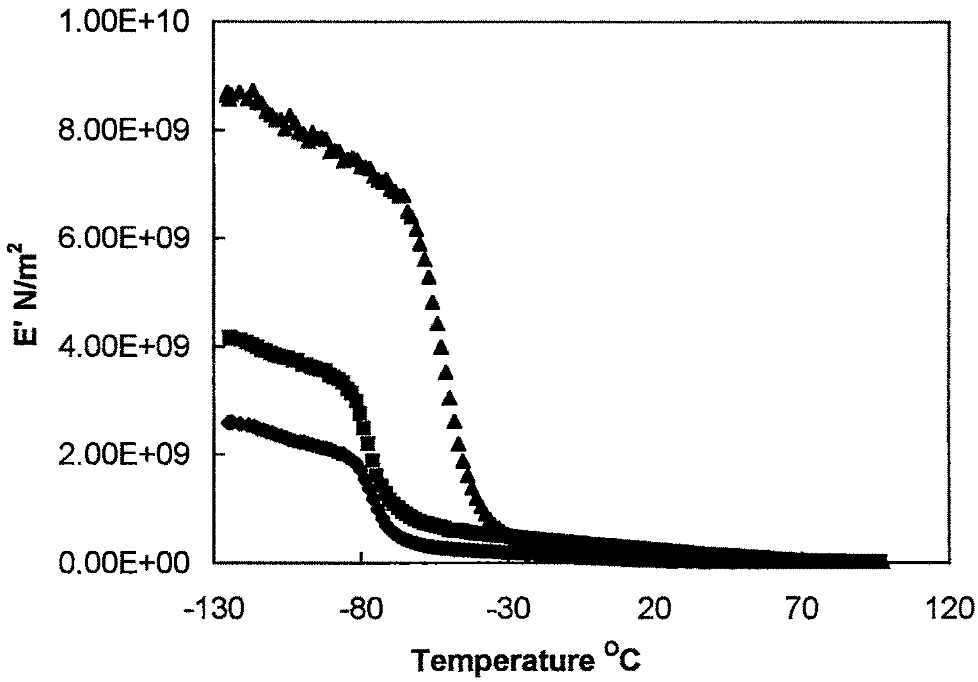
Dynamic Mechanical Analysis

The common feature of the tan δ (Fig. 2.6), linear loss modulus E' (Fig. 2.7) or storage modulus E" (Fig. 2.8) vs. temperature plots for all the three types of IPNs is the existence of glass transition region between - 65 to - 75 °C, suggesting rubbery nature of IPNs above room temperature. Interpenetrating networks of PU / PMMA are probably micro - separated two - phase systems of non - polar PU component (due to nonpolar polyol, HTPB) in the polar matrix of PMMA or vice versa. The Tg of PMMA was observed as a continuous increase in E" and tan δ rather than clear sharp peaks as in the case of pure polymers. Thus, the polybutadiene based PU seems to show appreciable phase separation with PMMA. Earlier reports on caprolactone based PU/ PMMA IPNs[73,74] showed the presence of two distinct Tgs with



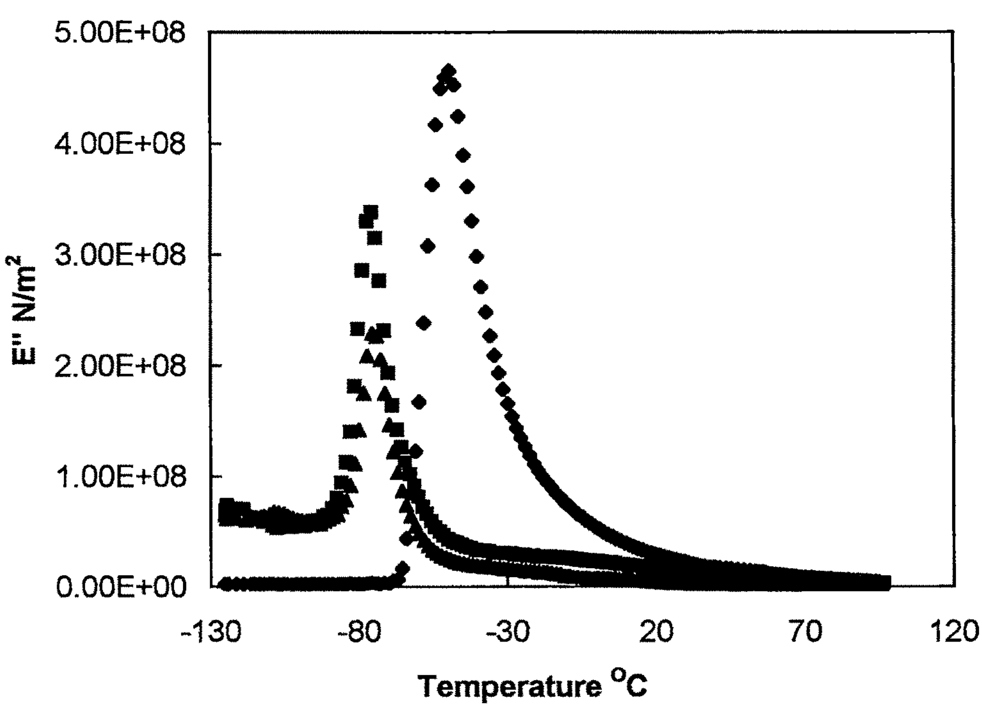
◆ : U / M, ■ : U / M / G, ▲ : U / M / H

Fig. 2.6 : Variation of tan δ with temperature



◆ : U / M, ■ : U / M / G, ▲: U / M / H

Fig. 2. 7 : Variation of storage modulus of 60 :40 H / M IPNs at 1 Hz



◆ : U / M, ■ : U / M / G, ▲: U / M / H

Fig. 2. 8 : Variation of loss modulus of 60 :40 H / M IPNs at 1 Hz

large domains clearly visible under electron microscope. The use of 2 - HEMA and GMA in IPNs not only leads to broadening of the peaks but also towards inward shift of the loss peaks when compared to those of individual network. This is also a sign of improved miscibility although a single Tg could not be observed.

Fig. 2.6 shows the representative plot of tan δ vs. temperature for the 60 / 40, PU / PMMA IPNs at 1 Hz. A small but distinct shoulder occurs on the high temperature side of the main transition. This shoulder may correspond to the third Tg (10 °C) observed in DSC thermograms.

The loss factor peak heights are commonly used to obtain information about the continuous phase. The material exhibiting higher loss factor peak usually represents the continuous phase. The loss factor half-peak width has been used as an indication of the miscibility of IPNs by Fox et al[75]. The mixing of two components broadens the tan δ peak and leads to an increase in the half peak width (HPW). The (HPW) of the U / M / H IPN is found to be highest (Table 2.3). This is due to the broadening of the tan δ peak because of large difference in the Tg of the two networks. The energy of activation for the glass transition calculated from the relation between frequency and temperature of tan δ_{max}[76] (section 1.4.6) are found to be almost similar for the three IPNs within experimental error. Due to the frequency dependence of the transition phenomenon, Tgs obtained from DMA (Table 2.3) differ only to a small extent from those obtained by DSC[77].

- ***Swelling behaviour***

The swelling behaviour of selected IPNs in organic solvents was studied and the molecular weight between crosslinks $\mathbf{M_C}$ was

Table 2.3 : DMA data for 60 : 40, H / M PU IPNs at 1 Hz

Code	T_g °C	tan δ_{max}	Half peak width °C	E''_{max} N/m^2	E_{act} k cal/mol
U/M 60:40	-62.7	0.19	23.9	4.1×10^8	41.9
U/M/G 60:40	-59.4	0.22	27.5	4.3×10^8	44.3
U/M/H 60:40	-56.8	0.27	30.5	4.4×10^8	44.7

determined from the Flory - Rehner equation[78] (section 1.2.5). Using values of M_C, the crosslink density υ_e and degree of crosslinking υ were calculated from the equations (1) and (2) respectively.

$$\upsilon_e = \rho / M_C \tag{1}$$

$$\upsilon = 1/2M_C \tag{2}$$

The swelling data for the IPNs are given in Table 2.4 A and Table 2.4 B respectively. It is observed that with increasing PMMA content, M_C decreases and crosslink density increases. It is also seen that the degree of crosslinking is in the order, U/M/H > U/M/G > U/M. These observations are quite in agreement with the results obtained from the mechanical thermal and morphological studies.

Table 2.4A: Swelling data in toluene for 60 : 40 H / M PU IPNs

Code	Mc	$\nu \times 10^4$	$\nu_e \times 10^4$
PU	6731	0.74	1.48
U/M 60:40	2900	1.72	3.79
U/M/G 60:40	1944	2.57	5.92
U/M/H 60:40	1296	3.90	8.33

Table 2.4B : Swelling data for U / M / H IPNs in toluene

Code	Mc	ν X 10^4	ν_e X 10^4
U/M/H 60:40	1296	3.90	8.33
U/M/H 70:30	3026	1.65	4.02
U/M/H 80:20	4093	1.22	3.91
U/M/H 90:10	5416	0.92	2.53

Conclusion

The studies on HTPB - MDI based PU / PMMA IPNs showed that incorporation of only 2 % GMA or 2 - HEMA leads to an improvement in the thermo-mechanical properties and morphology. On comparison of IPNs containing 2 - HEMA and GMA it was observed that 2 - HEMA more effectively improves the molecular mixing of two phases, leading to enhanced thermo-mechanical properties. The bicontinuous morphology observed in SEM and the broadening of the tan δ peaks in DM analysis supported this observation. Hence the IPNs based on other PU systems were developed using 2 - HEMA.

2.3.2 HTPB - TDI (H /T) based PU / PMMA IPNs

The HTPB / TDI based PU / PMMA IPNs with 90 / 10, 80 / 20, 70 / 30, 60 / 40, 50 / 50 and 40 / 60 compositions were prepared described earlier. In order to investigate the effect of 2 - HEMA concentration on IPN properties, 70 / 30 IPN composition was prepared using 0, 2, 4 and 6 % of 2 - HEMA. All the IPNs containing 2 - HEMA were observed to be transparent.

- ***Mechanical Properties***

With increasing PMMA content in IPNs tensile strength was observed to increase (Fig. 2.9) gradually in the beginning but dramatically beyond 30 % PMMA. The elongation at break increases initially upto 20 % and then decreases. However, it remains higher than that of the parent PU upto 30 % PMMA. The improvement in elongation is found to be more in comparison to loss in tensile strength. The slow change in the tensile properties at low PMMA content is because of its inability to establish its identity as a separate phase and hence shows complete molecular mixing. The drastic increase in tensile strength and decrease in elongation after incorporation of 40 % PMMA may be due to the onset of phase inversion as observed in case of H / M PU / PMMA IPNs. Thus in the PU rich region the IPNs behave as reinforced elastomers.

Fig. 2.10 shows the effect of 2 - HEMA concentration on the tensile strength and elongation of IPNs containing 30 % PMMA. The IPN not containing 2 - HEMA showed the lowest tensile strength and elongation. With increasing concentration of 2- HEMA both the properties increase upto 4 % followed by a decrease at 6 % concentration. The enhanced mechanical strength at 4 % HEMA concentration could be due to the optimum reaction of NCO end groups of PU with the OH groups of 2 - HEMA. It could also be the result of perfect interpenetration, which leads to enhanced coexistence of two networks. As the 2 - HEMA concentration increases further the tensile strength gradually decreases while elongation shows rapid decrease. This may be because of the formation of a third phase of polyhydrixyethyl methacrylate (PHEMA). Beyond 6 % concentration of 2 - HEMA, the IPNs exhibited visual phase separation, which could be judged from the stickiness of the PHEMA phase. Thus optimum

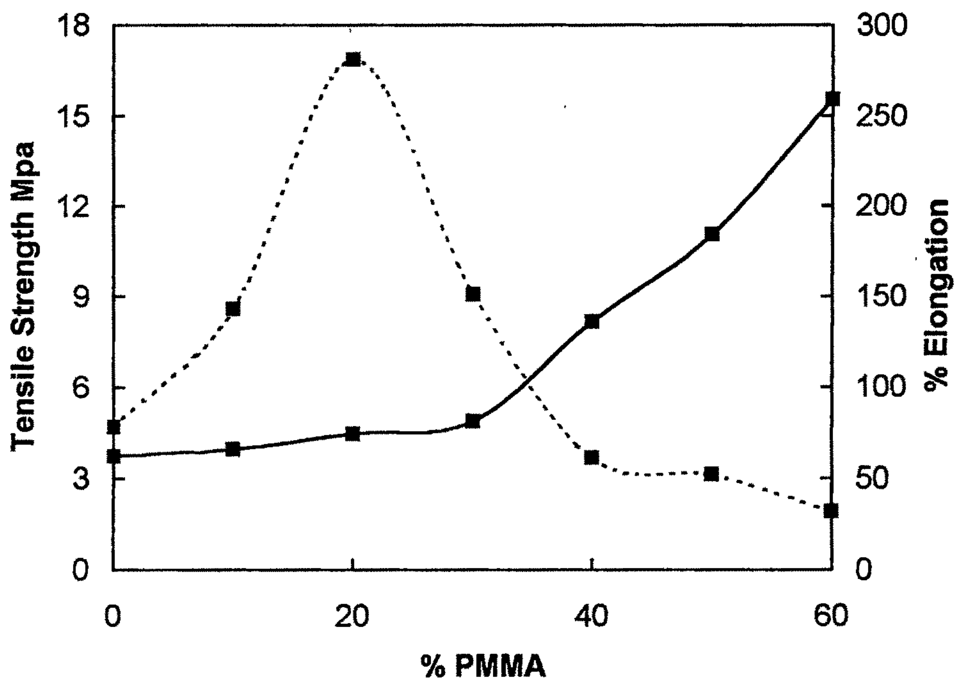


Fig. 2.9 : Effect of weight percentage of PMMA on tensile strength(_____) and % elongation (-----) of the 70:30 PU-PMMA IPNs.

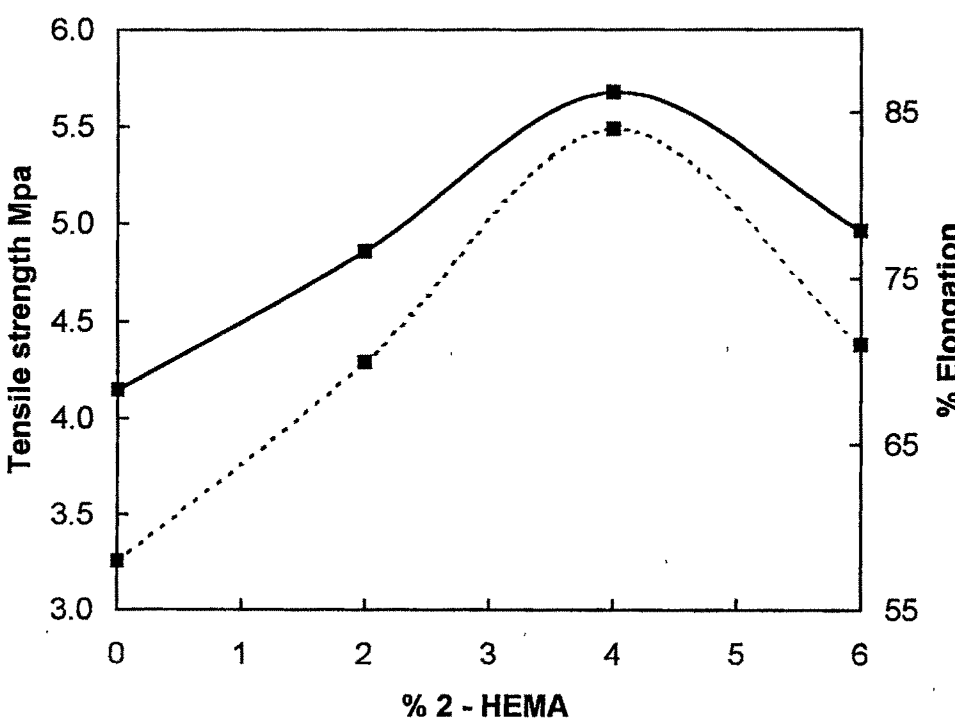


Fig. 2.10 : Effect of weight percentage of 2- HEMA on tensile strength (_____) and % elongation (------) of the 70:30 PU-PMMA IPNs.

mechanical properties were observed at 4 % concentration of 2 - HEMA.

• *Thermal Analysis*

Differential Scanning Calorimetry (DSC)

The DSC curves of selected IPNs are shown in Fig. 2.11. As observed in the case of H / M PU based IPNs the thermograms showed presence of two Tgs. The low temperature one corresponding to the PU soft segment and the high temperature one resulting from the possible grafting of MMA on PU or due to the β relaxation of methyl groups of PMMA. With increasing concentration of HEMA, both the Tgs were observed to shift to the higher side. This may be because of increased interaction and interpenetration of PMMA and PU segments. At 4 % HEMA concentration, the high temperature Tg becomes more dominant and the transition corresponding to the PU component become relatively unclear. No significant change was observed in the transition behaviour with increase in the HEMA concentration from 4 % to 6 %. The inward shift of the transitions and dominance of the high temperature Tg indicates increased molecular mixing of the two phases.

• ***Thermo-gravimetric analysis***

The H / T PU exhibited an IDT of about 385 °C. The TG plots in Fig.2.12A show that the thermal stability of PU increases with increasing concentration of PMMA in the IPNs, and Fig. 2.12B shows enhancement in thermal stability on incorporation of 2 - HEMA into the IPNs. This may be because of the close juxtaposition of the IPNs, which allows PMMA and its degradation products to act as free radical scavengers for the PU, thereby retarding its further degradation. The IPNs containing 2 - HEMA exhibited single step degradation indicating mixing of the two

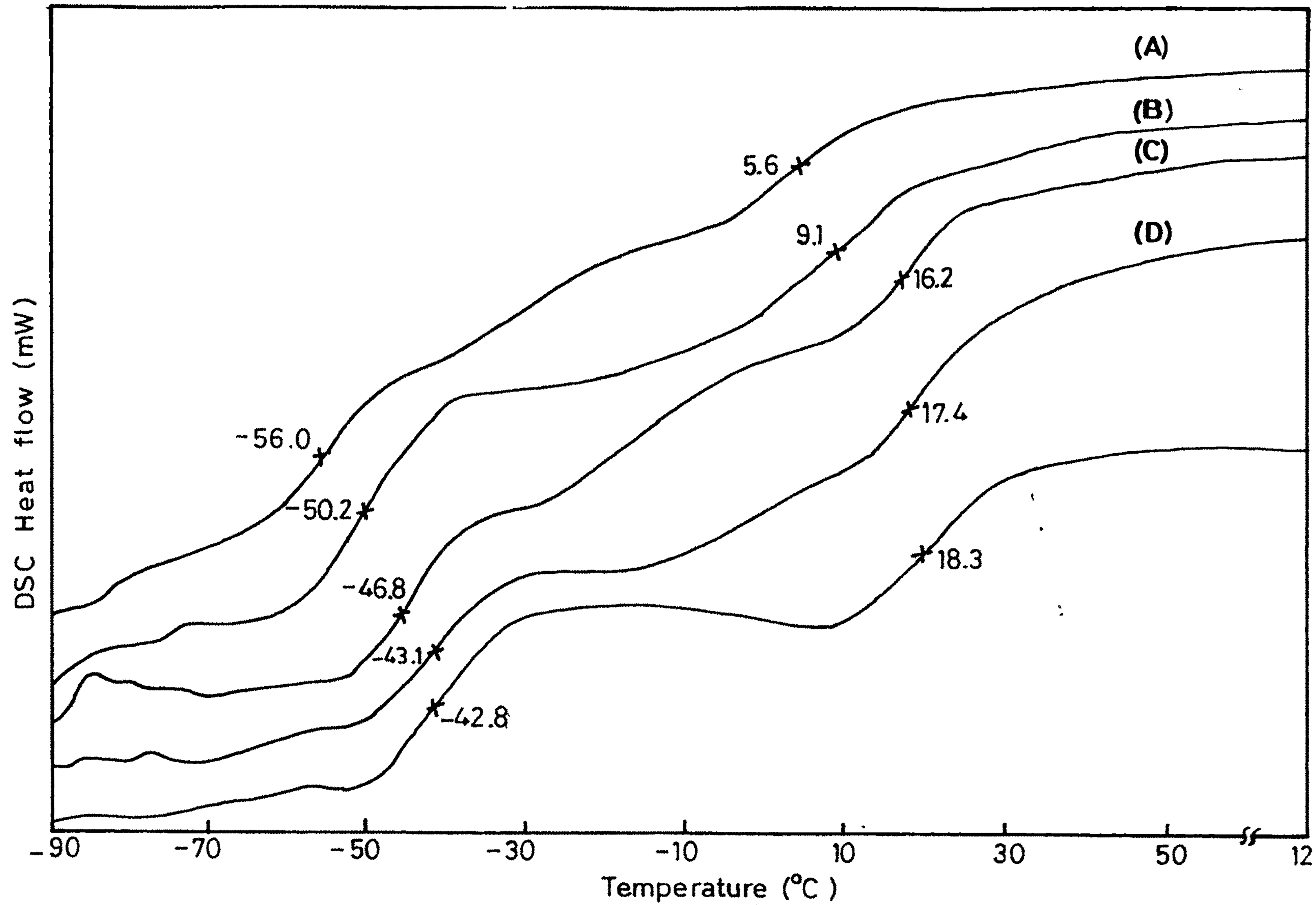


Fig. 2.11 **DSC** thermographs of H/T based PU/PMMA IPNS. 70 :30 composition with **(A)** 0 **(B)** 2 **(D)** 4 and. **(E)** 6 % AND 60 40 composition with **(C)** 2 % 2-HEMA concentration.

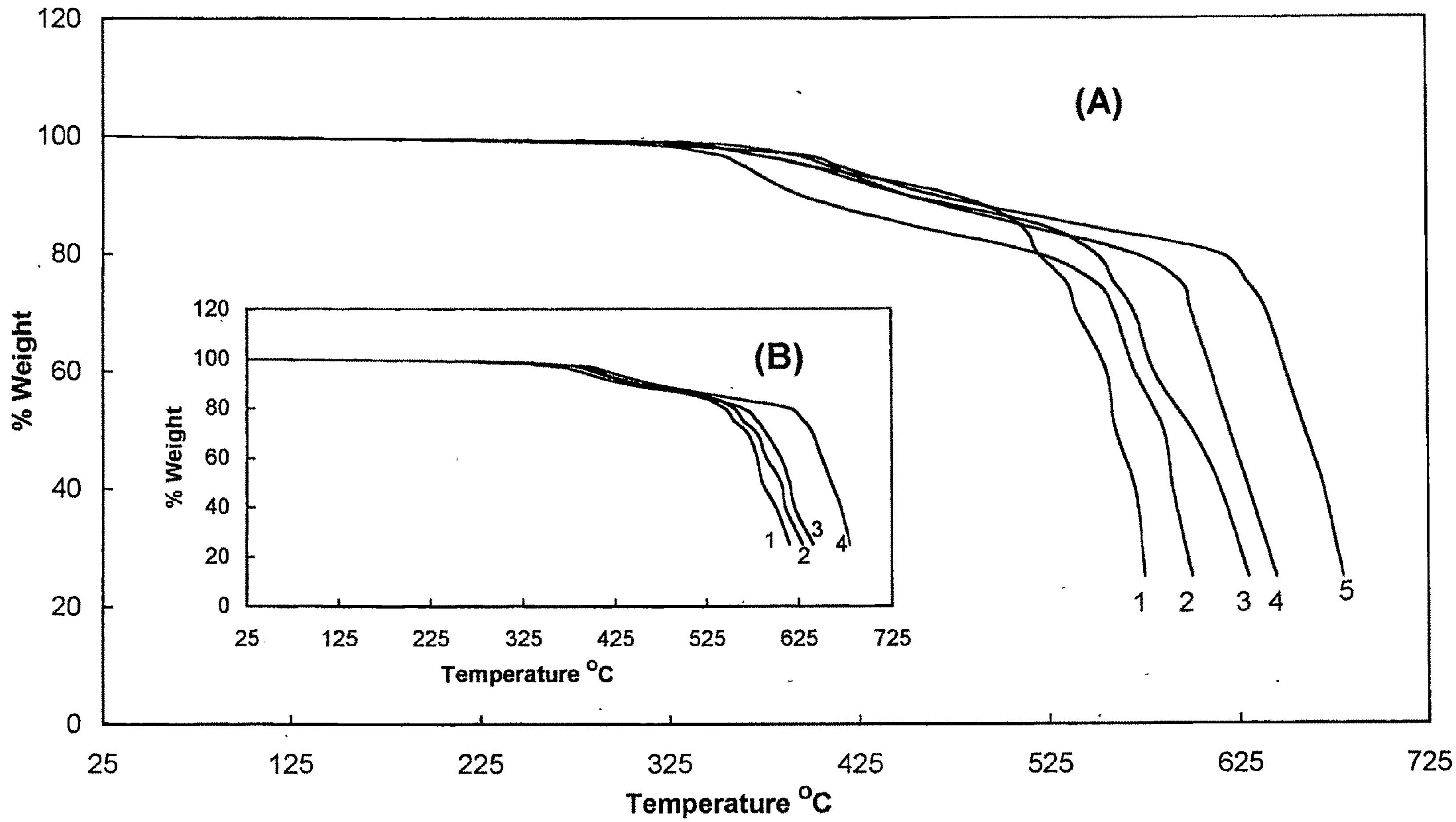


Fig. 2.12 : Thermogravimetric plots for (A) H/T PU / PMMA IPNs (1) 80:20, (2) 70:30, (3) 60:40, (4) 50:50, (5) 40:60 and (B) 70:30 IPN with (1) 0 , (2) 2 , (3) 4 , (4) 6 % of 2- HEMA

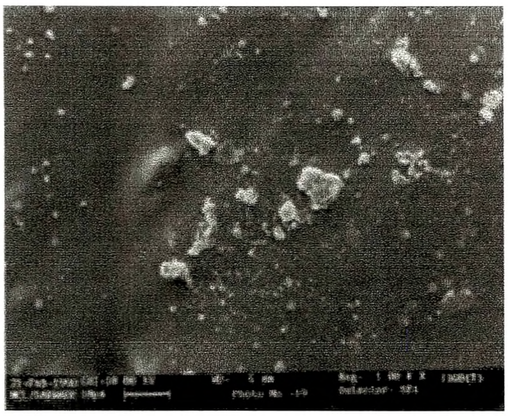
phases. Not much difference was observed in the thermal stability from 4 to 6 % of HEMA concentration in IPNs. The decomposition temperatures were observed to shift towards the higher (Table - 2.5) side with increasing 2 - HEMA concentration and PMMA content in the IPNs. All the IPNs were found to be thermally stable up to 325 °C and decompose completely around 650 °C.

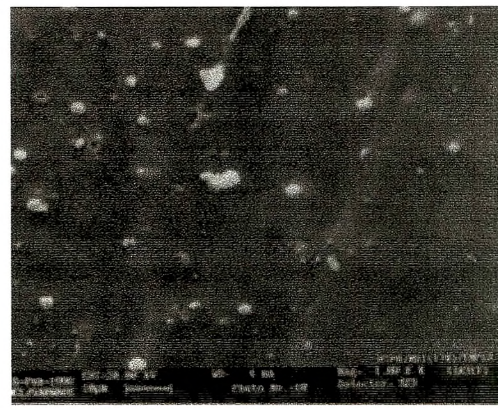
Table 2.5: Decomposition temperatures of 70: 30 H/T PU IPNs

% Degradation	Temperature °C				
	PU	% 2 - HEMA			
		0	2	4	6
1	295	315	325	360	330
5	385	430	435	495	485
25	575	590	610	635	625
50	590	615	635	650	650
75	605	645	655	675	670

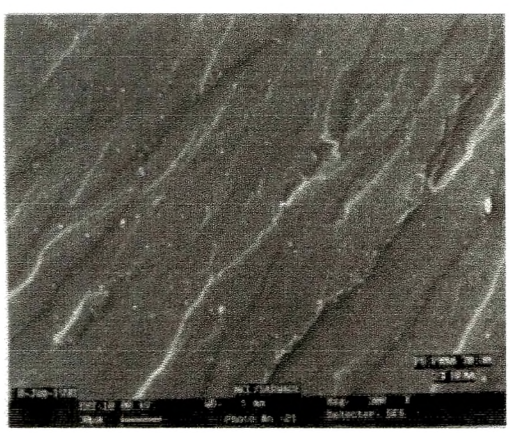
Scanning Electron Microscopy

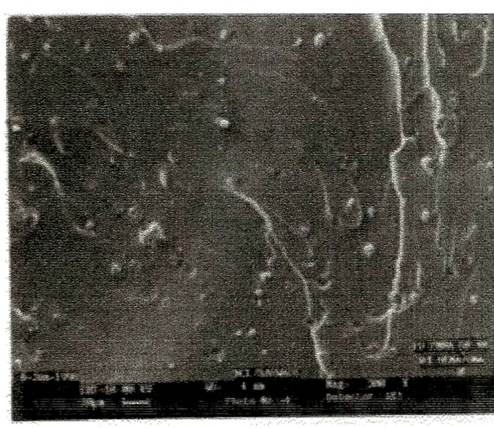
The morphology of H / T based PU / PMMA IPNs is represented in Fig. 2.13 and 2.14. The 70 / 30 IPN prepared without 2 - HEMA (Fig. 2.13 A) clearly shows phase separation as observed in the case of H / M based IPNs. With incorporation of HEMA the distribution of dispersed phase becomes more uniform and the domain size also decreases (Fig. 2.13 B). With increase in HEMA concentration from 2 % (Fig. 2.13 B) to 4 % (Fig. 2.13 C), the IPN revealed morphology where both the phases assume total continuity with no resolved domain of either component. This behaviour is also reflected in the results of mechanical and dynamic mechanical properties of IPNs. However further increase





(A) (1 KX) (B) (1 KX)





(C) (500 X) (D) (500 X)

Fig. 2.13 : SE Micrographs of 70 : 30 H / T PU / PMMA IPNs containing (A) 0, (B) 2, (C) 4 and (D) 6 % HEMA

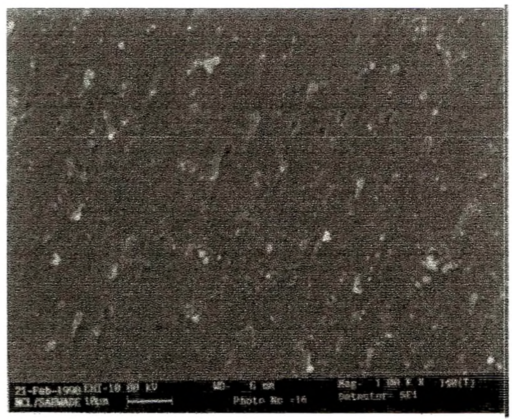
in the 2 - HEMA concentration does not further improve the morphology but deteriorates it to some extent due to the formation of PHEMA (Fig. 2.13 D).

The morphology of 70 / 30, 60 / 40, 50 / 50 and 40 / 60 IPNs containing 2 % of HEMA is exhibited in Fig.2.13B and Fig.2.14 A- C. As the concentration of PMMA increases from 30 to 50 % the morphology becomes increasingly homogenous. The morphology of blend rich in PU is smooth which is the characteristic of rubbers. At 50 / 50 composition it is difficult to identify the continuous and disperse phase and hence can be viewed as co - continuous morphology similar to the 60 / 40 IPN of H / M based PU. Further increases in PMMA content lead to phase transformation. The rough fractured surface (Fig. 2.14C) is indicative of a ductile fracture in case of 40 / 60 IPN.

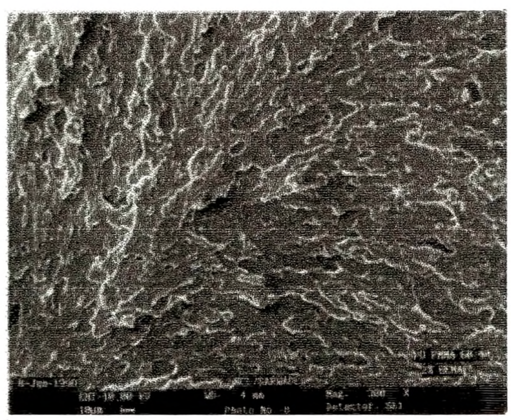
- ***Dynamic Mechanical Analysis***

Fig. 2. 15 shows the tan δ vs. temperature plots for H / T based PU / PMMA IPNs. It is observed that as the acrylate concentration increases from 30 – 40 % the broadening and inward shift of tan δ peaks is observed. However, further increase in PMMA content to 60 % decreases the broadening and inward shift of tan δ peak (not shown in Fig.). Thus the blends rich in PU exhibited good damping characteristics.

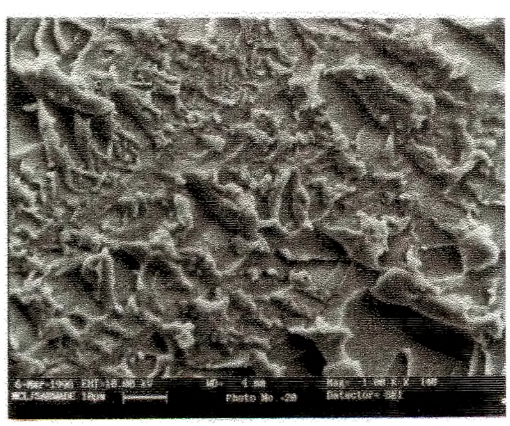
The 70 / 30 blends showed similar shift in tan δ peaks on incorporation of 2 - HEMA. At 4 % of HEMA concentration, a very broad tan δ peak over a wide range of temperature was observed. Beyond 4 % the tan δ peak shifted to the lower temperature. Thus at 4 %, optimum segmental mixing of the components was observed. The height of the loss tangent peaks also increases with



(A) (1KX)



(B) (1 KX)



(C) (500 X)

Fig. 2.14 : SE Micrographs of H / T PU / PMMA IPNs
(A) 60 : 40, (B) 50 : 50, (C) 40 : 60.

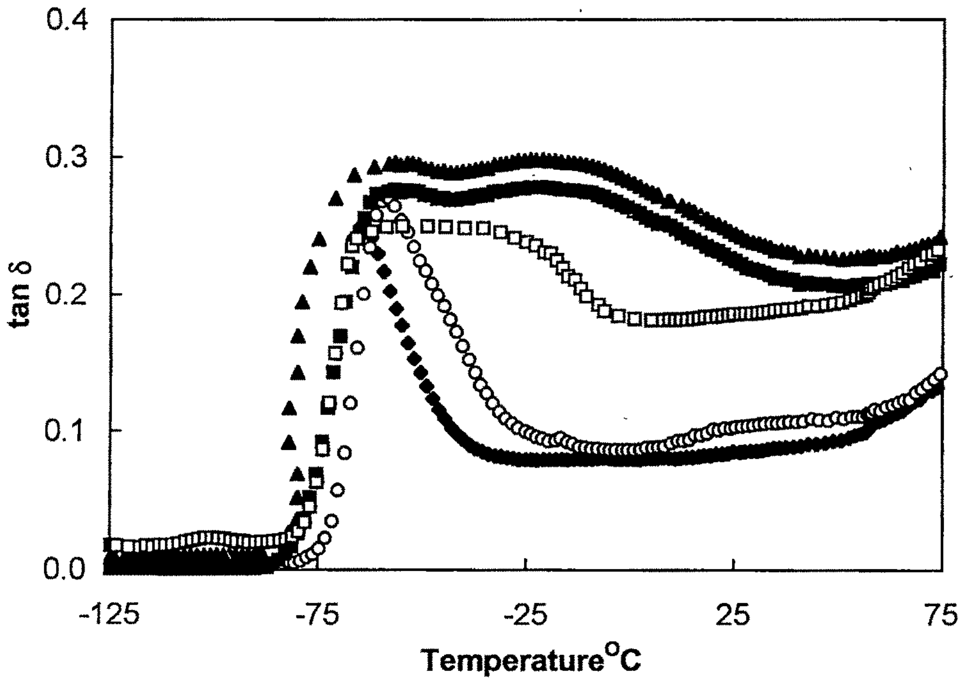


Fig. 2.15: Variation of tan δ at 1 Hz for 70 :30 H / T PU/PMMA IPNs with
◆ : 0 , ○ : 2 , ▲ : 4 , ■ : 6 %, 2 - HEMA and
□ : 60:40 IPN with 2 % HEMA

increasing HEMA concentration up to 4 % and decreases with further increase in HEMA concentration. Evidence of phase mixing is also seen from the data of half peak width (HPW) given in Table 2.6 for the IPNs. The HPW goes on increasing with increasing weight % of PMMA upto 50 %. Similarly HPW also increases with increasing 2 - HEMA concentration upto 4 %.

The plot of loss modulus vs. temperature (Fig.2.16) shows three distinct regions: a glassy region, a transition region and a rubbery region, for all the IPNs. In the glassy region all compositions exhibit comparable modulus values. The modulus increases with increasing PMMA content, because of increased crystallinity. As PU content decreases the crystallinity, the lower modulus of PU rich blends is observed. The plot of storage modulus vs. temperature (Fig.2.17) also shows the three distinct regions. The modulus increases with increasing PMMA and HEMA content. Thus study of H/T PU/PMMA IPNs showed that at 4 % HEMA concentration, better compatibility of phases is observed which may be assigned to perfect entanglements of both networks leading to decreased phase separation which may be the result of the optimum reaction between OH of HEMA and NCO groups of PU.

Table 2.6 : DMA data for H / T PU IPNs at 1 Hz

Composition	% 2-HEMA	Tg °C	Tan δ_{max}	Half peak Width °C	E"$_{max}$ N/m^2	E$_{act}$ k cal/mol
60:40	2	-49.9	0.25	56	5.2 x 10^8	41.2
70:30	0	-65.2	0.28	21	2.3 x 10^8	38.2
70:30	2	-58.7	0.28	29	4.6 x 10^8	35.4
70:30	4	-46.9	0.30	85	9.9 x 10^8	40.1
70:30	6	-47.7	0.28	73	9.9 x 10^8	39.2

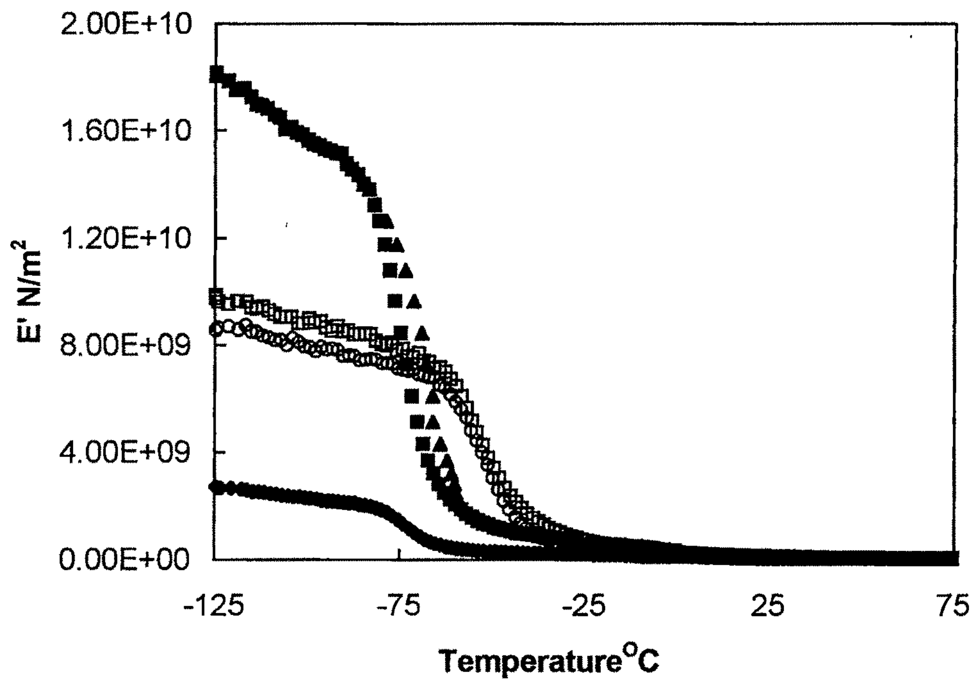


Fig. 2.16: Variation of loss modulus (E') at 1 Hz for 70 :30 H / T PU/PMMA IPNs with ◆ : 0 ,○ : 2 , ▲ : 4 ,■ : 6 % HEMA and □ : 60 : 40 IPN with 2 % HEMA

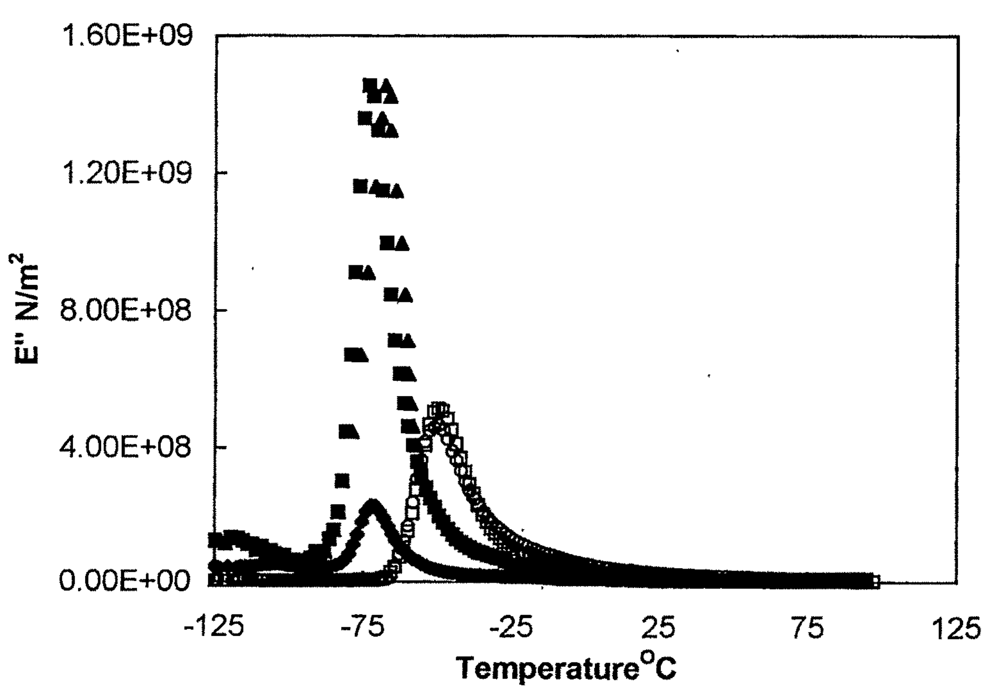


Fig. 2.17 : Variation of loss modulus (E") at 1 Hz for 70 :30 H / T PU/PMMA IPNs with ◆ : 0 , ○ :2 , ▲ : 4 , ■ : 6 % HEMA and □ : 60 : 40 IPN 2 % HEMA

- ***Swelling behaviour***

The data from swelling studies in toluene is represented in the form of molecular weight between crosslinking (Mc), degree of crosslinking (V) and crosslink density (Ve) in Table 2. 7. As observed in the case of H/M PU/PMMA IPN, the Mc decreases and the degree of crosslinking and crosslink density increases with increasing PMMA content and 2 - HEMA concentration. This may be attributed to the increased interpenetration. The increase in 2 - HEMA concentration from 4 to 6 % did not show much effect on swelling behaviour.

- **Conclusion**

Thus it is concluded from the above studies that upto 4 % incorporation of 2 - HEMA in the PMMA network, improves the thermo mechanical and morphological properties of IPNs. At 4 % HEMA concentration optimum properties were observed indicating optimum interpenetration. SEM showed a single uniform phase, while DMA showed a single broad tan δ peak. At 6 % of 2 - HEMA concentration, PHEMA started phase separating.

Table 2.7A : Swelling data for H / T PU IPNs in toluene

PU / PMMA	Mc	ν X10^4	ν_e X10^4
40:60	900	5.72	9.79
50:50	944	5.57	8.92
60:40	960	5.29	8.33
70:30	1026	4.65	8.02
80:20	1593	4.02	6.91
90:10	1816	3.22	5.53
PU	2420	1.74	3.48

Table 2.7B : Effect of 2 - HEMA concentration on Swelling of 70 : 30 H / T PU IPNs in toluene

% 2-HEMA	Mc	$\nu \times 10^4$	$\nu_e \times 10^4$
0	1231	4.31	7.19
2	1026	4.65	8.02
4	871	6.04	9.65
6	865	6.06	9.70

2.3.3 PPG - TDI (P / T) based PU / PMMA IPNs

The IPNs were derived form PPG / TDI based PUs and PMMA were prepared using 4 % of 2 - HEMA. In order to study the effect of crosslink density of PMMA network the 70/30 IPN was prepared using 2 to 8 % DVB. The IPNs of this PU system were colorless and absolutely transparent which is a primary indication of segmental mixing.

Mechanical Properties

The tensile strength and elongation of these IPNs was observed to increase with increasing PMMA content (Fig.2.18). The improved tensile properties indicate better and homogeneous coexistence of the two networks leading to synergistic effect. Fig.2. 19 illustrates the effect of increasing crosslink density of the PMMA network. It was observed that with increasing DVB concentration the tensile strength increases while elongation decreases. This is because the increasing crosslink density makes the sample stiffer and more rigid.

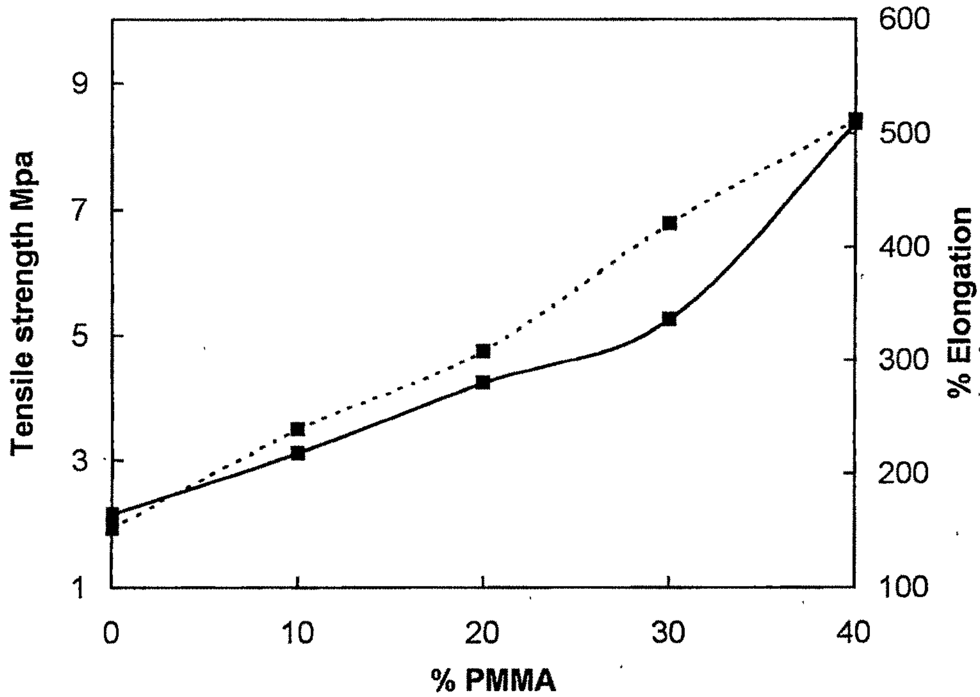


Fig. 2.18 : Effect of weight percentage of PMMA on tensile strength (——) and % elongation (------) of the 70:30 PU-PMMA IPNs.

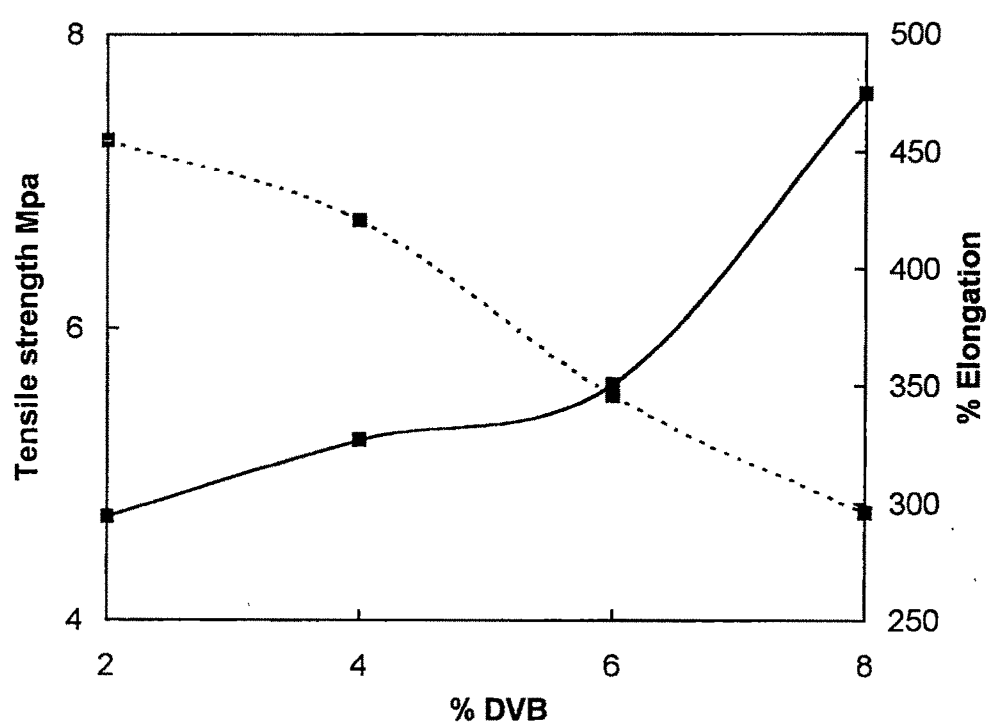


Fig.2.19 : Effect of crosslinking extent on tensile strength (——) and % elongation (------) of the 70:30 PU-PMMA IPNs.

Thermal Analysis

Differential Scanning Calorimetry (DSC)

The thermograms of P / T PU IPNs (Fig.2.20) show considerable shift in the Tg to higher side with increasing DVB concentration. Increase in crosslink density of PMMA network brings enhanced interpenetration leading to the formation of more rigid network. This in turn shifts the Tg to the higher side. The observed increase in tensile strength and elongation with increasing PMMA content also supports this observation.

Thermo-gravimetric analysis

These IPNs also exhibited an increase in thermal stability with increasing PMMA content as well as DVB concentration (Fig. 2. 21 A & B). As the concentration of DVB increases from 2 to 8 % the network becomes more rigid and the decomposition temperatures shift to higher side (Table 2.8).

Table 2.8 : Decomposition temperatures of 70 : 30 P/T PU IPNs

% Degradation	Temperature °C				
	PU	% DVB			
		0	2	4	6
1	200	315	330	340	350
5	350	425	435	450	500
25	425	595	605	610	640
50	470	625	630	645	650
75	515	655	665	670	675

Scanning Electron Microscopy

The morphology of P / T based PU / PMMA interpenetrating networks with different concentration of the crosslinker, DVB, is

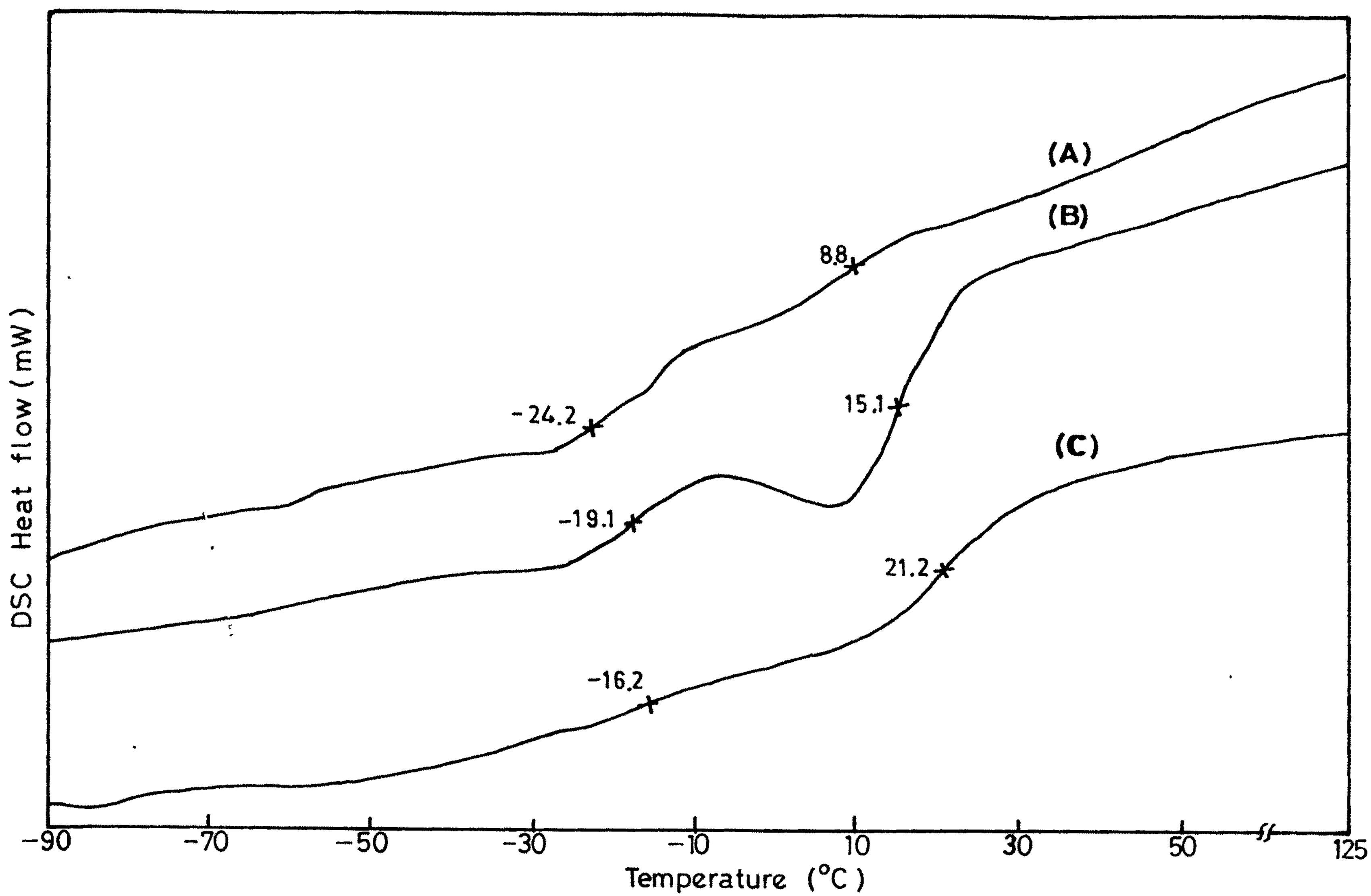


Fig. 2.20 **DSC** thermograms **of** P/T PU IPNs containing **(A)** 2 **(B)** 4 and **(C)** 8% DVB

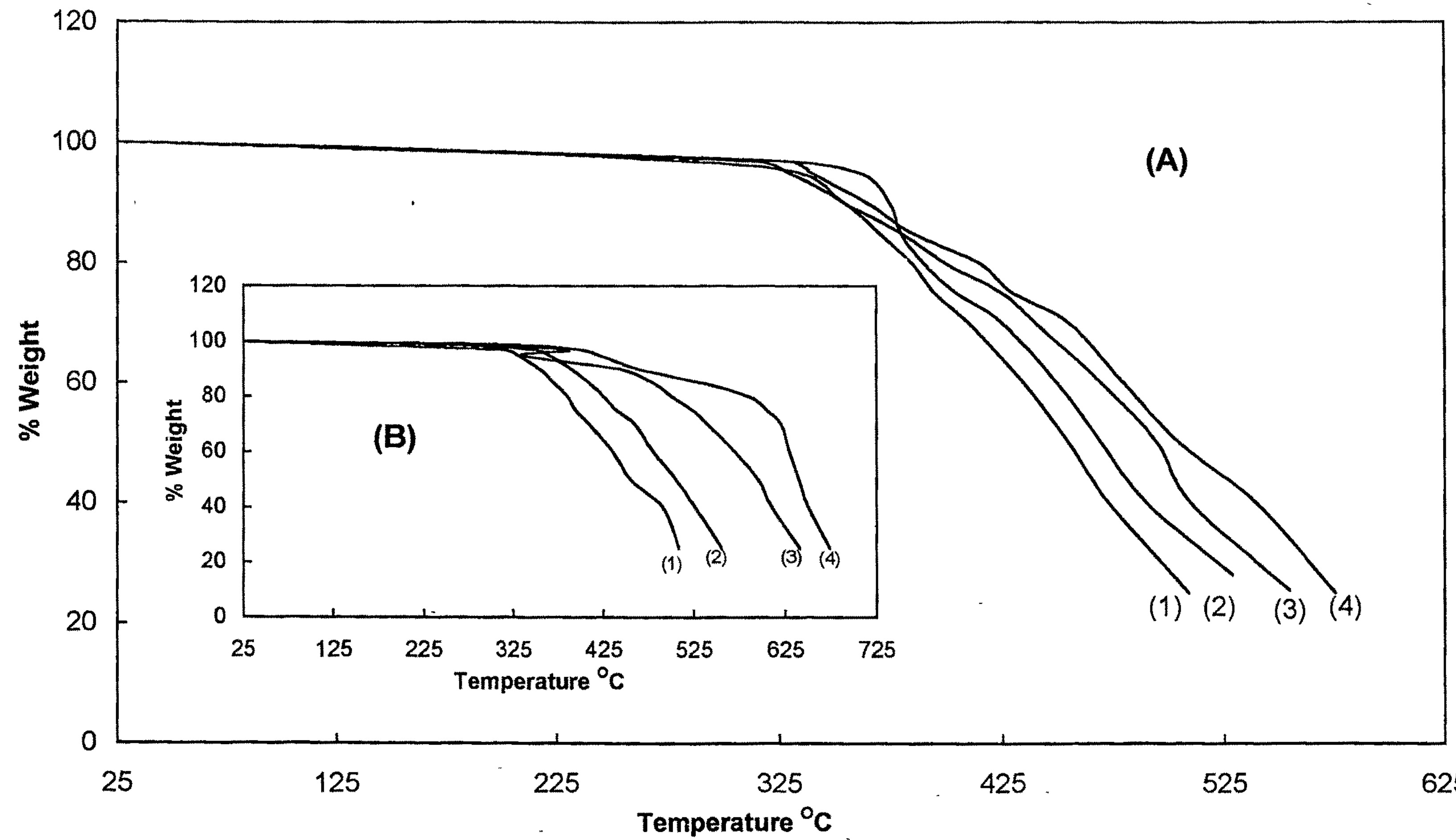
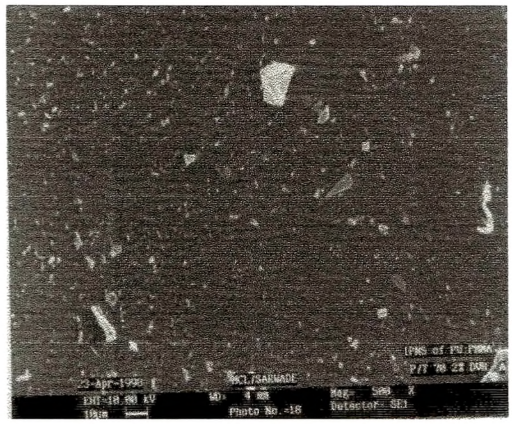
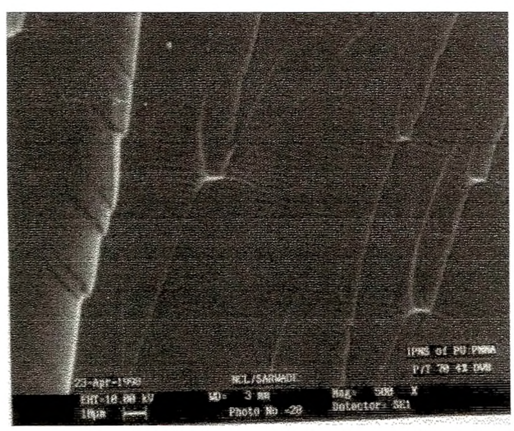


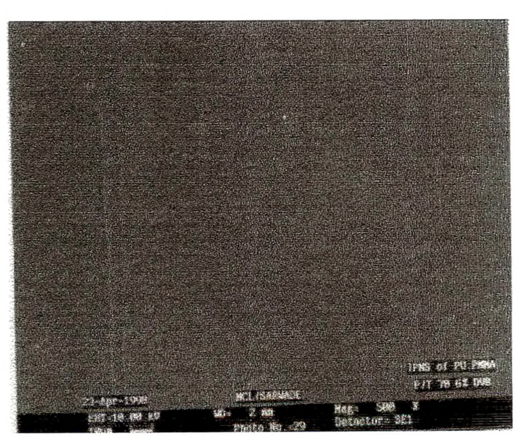
Fig. 2.21: Thermogravimetric curves for (A) P/T PU / PMMA IPNs (1) : 90:10, (2) . 80:20, (3) : 70:30, (4) : 60:40 and 70:30 IPN with (B) (1) : 2 , (2) : 4 , (3) : 6 , (4) : 8 % of DVB



(A) (500 X)



(B) (500 X)



(C) (500 X)

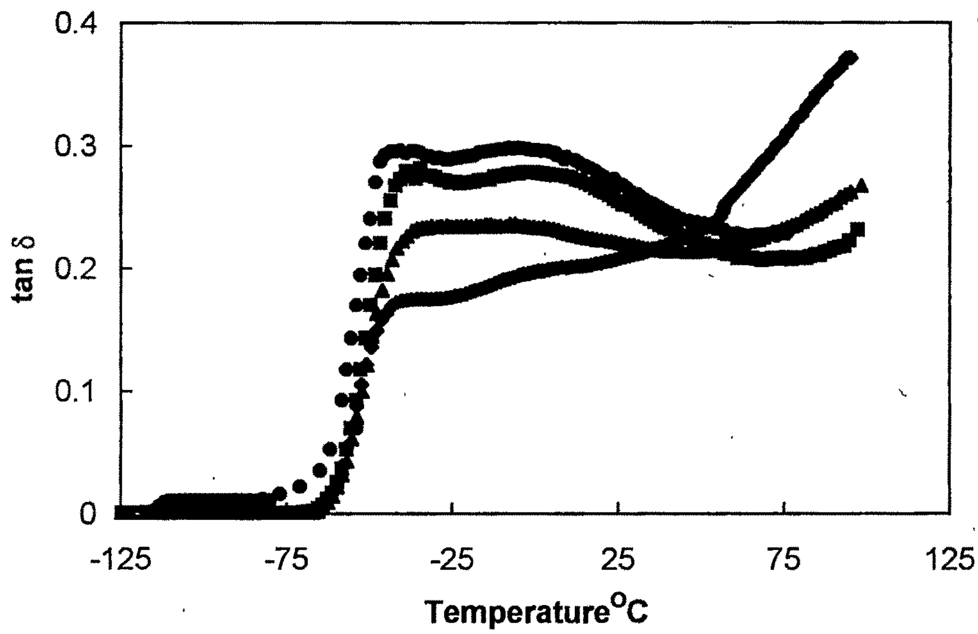
Fig. 2.22 : SE Micrographs of 70 : 30 P / T PU / PMMA IPNs containing (A) 2, (B) 4 and (C) 8 % DVB

exhibited in Fig.2.22 (A-C). Improved miscibility of phases is observed at all levels of crosslinking of the PMMA network. The increase in DVB concentration from 2 to 8 % increases the continuity of the disperse phase and leads to greater interpenetration and resulting into a single phase. The resulting reinforced elastomers show high tensile strength and elongation as discussed earlier.

Thus of all the IPN systems the morphology of P / T PUs based IPNs showed good miscibility of the two phases. This behaviour is also reflected in the mechanical and dynamic mechanical properties.

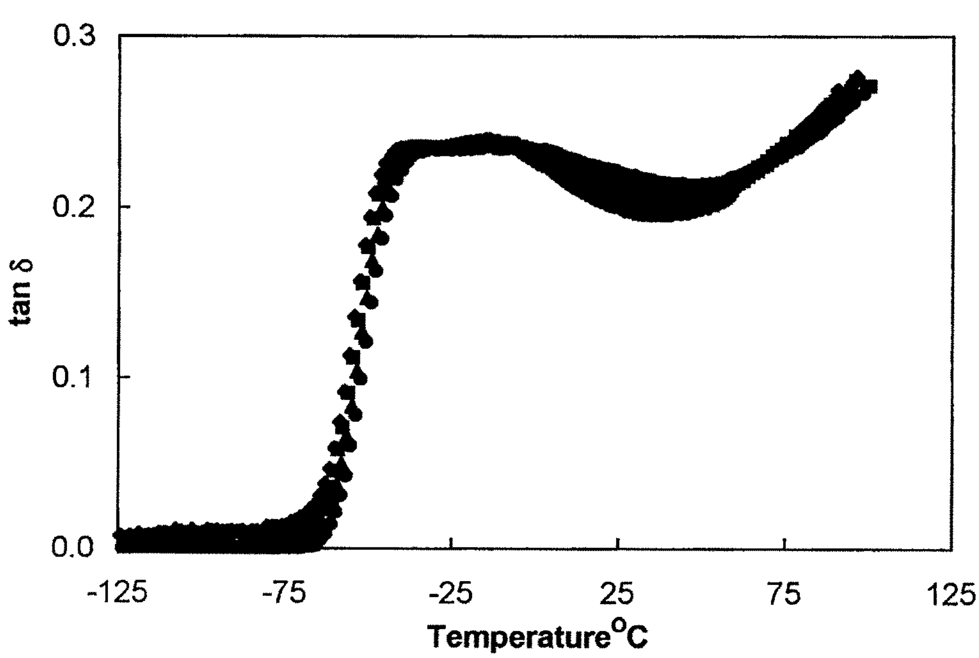
- ***Dynamic Mechanical Analysis***

This particular set of IPNs showed excellent damping abilities marked by a broad tan δ peak ranging over a very wide range of temperature (Fig.2.23 & 2.24). All the IPNs exhibited a single and very broad peak beginning from about - 50 °C. The variation of tan δ with temperature shows that as the concentration of DVB increases from 2 to 8 % the Tg shifts towards the higher temperature (Fig.2.23). This is because with increasing concentration of DVB the crosslink density increases leading to the formation of more rigid network. Further, increase in DVB concentration leads to enhanced interpenetration, which causes an inward shift of the Tg. The half peak width data in Table 2.9 also supports increased phase mixing arising due to increased crosslink density of the PMMA network as well as increasing PMMA content.



◆ : 2 %, ▲ : 4 %, ■ : 6 %, ● : 8 % DVB

Fig. 2.23 : Variation of tan δ of 70 :30 P / T PU IPNs with crosslink density of PMMA network at 1 Hz



◆ : 1 Hz, ■ : 2 Hz, ▲ : 5 Hz , ● : 10 Hz

Fig. 2. 24 : Variation of tan δ with frequency in 70 : 30 P / T PU IPN containing 4 % DVB

Table: 2.9 Effect of crosslinking on dynamic mechanical properties of 70:30 P /T PU / PMMA IPNs at 1 Hz

% DVB	T_g °C	tan δ_{max}	HPW °C	E''_{max} N/m^2	E_{act} k cal/mol
2	-27.1	0.20	n.d.	5.2×10^8	51.5
4	-20.1	0.23	75	4.7×10^8	60.2
6	-18.2	0.27	81	4.9×10^8	59.2
8	-17.4	0.29	87	5.3×10^8	62.3

n.d. – not determined

The plots of storage modulus and loss modulus (Fig. 2.25 & 2.26) show the three distinct regions as observed in the case of the HTPB based IPNs. The storage modulus was observed to increase with increasing crosslink density of the PMMA network.

- ***Swelling behaviour***

The data from swelling studies in toluene is represented in Table 2.10 in terms of molecular weight between crosslinks (Mc), degree of crosslinking (V) and crosslink density (Ve). As observed in the case of H / M PU IPN, the Mc decreases and the degree of crosslinking and crosslink density increases with increasing PMMA content and DVB concentration. This may be attributed to the increased interpenetration. The increase in DVB concentration from 4 to 6 % does not have much effect.

- ***Conclusion***

The IPNs based on P/T PU system showed excellent vibration and sound damping abilities. The DM analysis showed a broad tan δ peak extending over a wide range of temperature even with 4 % HEMA concentration. With increasing crosslink density of the PMMA network, a shift to higher temperature was observed.

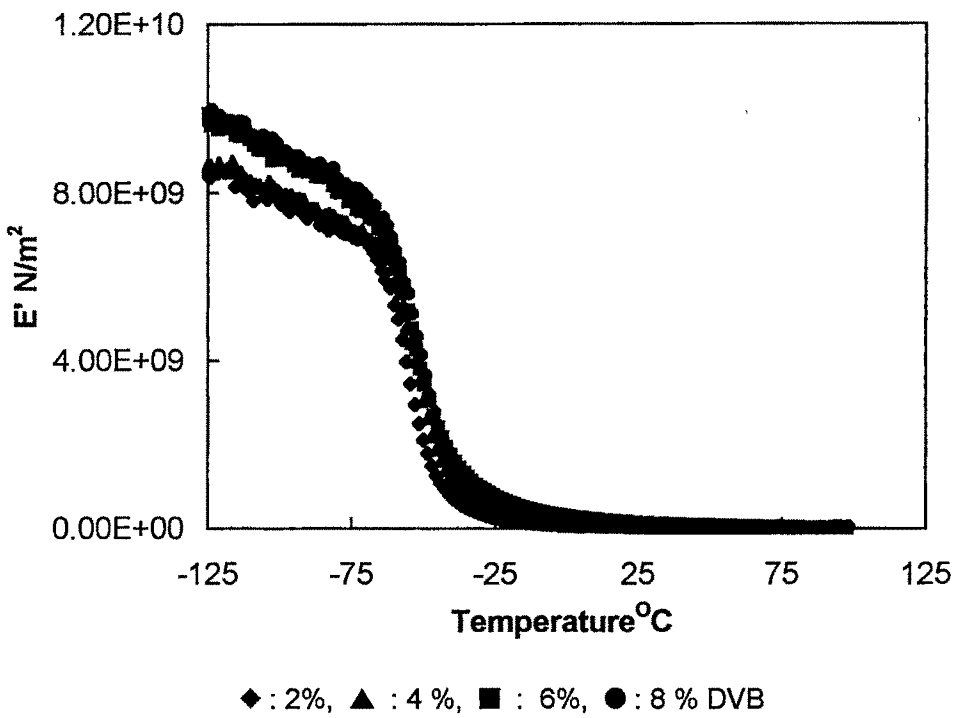


Fig. 2. 25 : Variation of storage modulus (E') of the 70 :30 P / T PU IPNs with crosslink density of PMMA network at 1 Hz

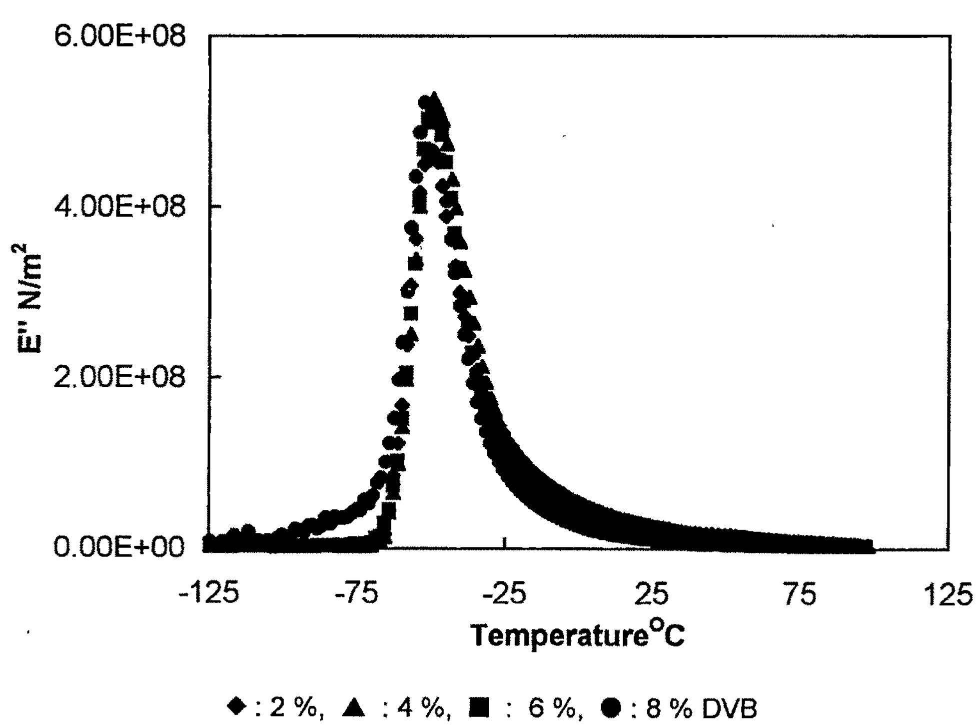


Fig. 2. 26 : Variation of loss modulus (E") of the 70 :30 P / T PU IPNs with crosslink density of PMMA network at 1 Hz

Table 2.10A : Swelling data for P/T PU IPNs in toluene

Code	Mc	$\nu \times 10^4$	$\nu_e \times 10^4$
PU	3350	1.83	3.62
90:10	2149	2.42	5.53
80:20	1593	4.02	6.91
70:30	998	5.65	8.02
60:40	860	6.10	8.33

Table 2.10B : Effect of crosslinking on swelling of 70 : 30 P / T PU IPNs in toluene

% DVB	Mc	$\nu \times 10^4$	$\nu_e \times 10^4$
2	1034	4.61	7.69
4	998	5.65	8.02
6	951	5.55	8.89
8	903	5.70	9.76

Single phase morphology was observed irrespective of crosslinker concentration. Tensile tests showed a constant increase in the tensile strength as well as elongation with increasing PMMA content. However, increasing crosslink density of PMMA network led to a decrease in elongation though showed improved tensile strength.

2.3.4 PPG - MDI (P / M) based PU / PMMA IPNs

The PU/PMMA IPNs derived from PPG - MDI were difficult to synthesize. Phase separation was observed even on incorporation of only 30 % of PMMA. In addition, the samples appeared to be mechanically weak and absolutely translucent. Probably this highly flexible PU system is unable to behave compatibly with the PMMA network and shows antagonism effect. Hence the system was not further investigated.

2.3.5 PU / PMMA semi IPNs

The semi-I-IPNs (PU network crosslinked) based on H / M, H / T, P / T and P / M PUs with NCO : OH ratio 1.3 and diol : triol ratio 1 : 1.5 (B1 composition) and PMMA were developed. The HTPB based IPNs were yellowish while PPG based IPNs were colorless. It was observed that H / T system requires least time for curing and was capable of incorporating highest percentage of acrylate (40 %) without any phase separation. In the case of P / T and H / M systems, the IPN with 40 % PMMA showed slight phase separation. In P / M system the time required for curing was higher and phase separation was observed even at 30 % acrylate concentration. Hence the IPN with 40 % acrylate could not be synthesized in this case. The semi – II – IPNs (PMMA network crosslinked) could be developed only for HTPB based PUs.

- ***Mechanical Properties***

Effect of acrylate concentration on tensile strength of semi IPNs is illustrated in Fig. 2.27. As observed in the case of full IPNs, the tensile strength increases with increasing PMMA content in all the semi IPNs. The P / T PU based IPNs showed higher values of tensile strength while elongation was found to be higher in the case of H / M PU based IPNs (Fig. 2.28). It was further observed that in P / T IPNs elongation continuously increases with increase in PMMA content while in HTPB based PU IPNs elongation increased upto 20 % of acrylate content and then

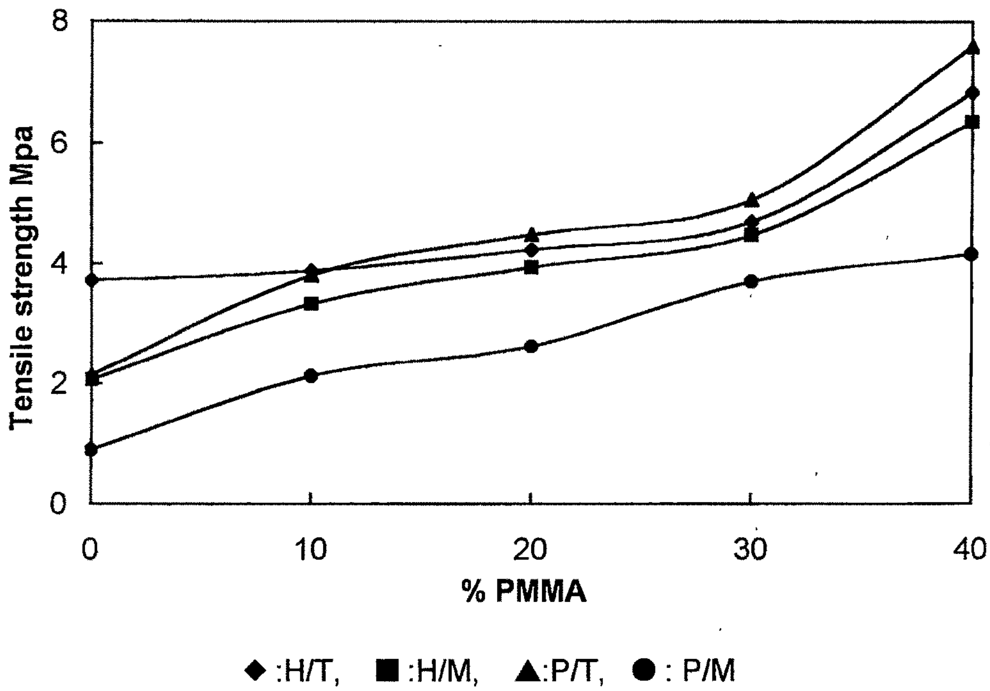


Fig. 2.27 : Effect of weight percentage of PMMA on tensile strength of semi -I - IPNs of B1 PU systems

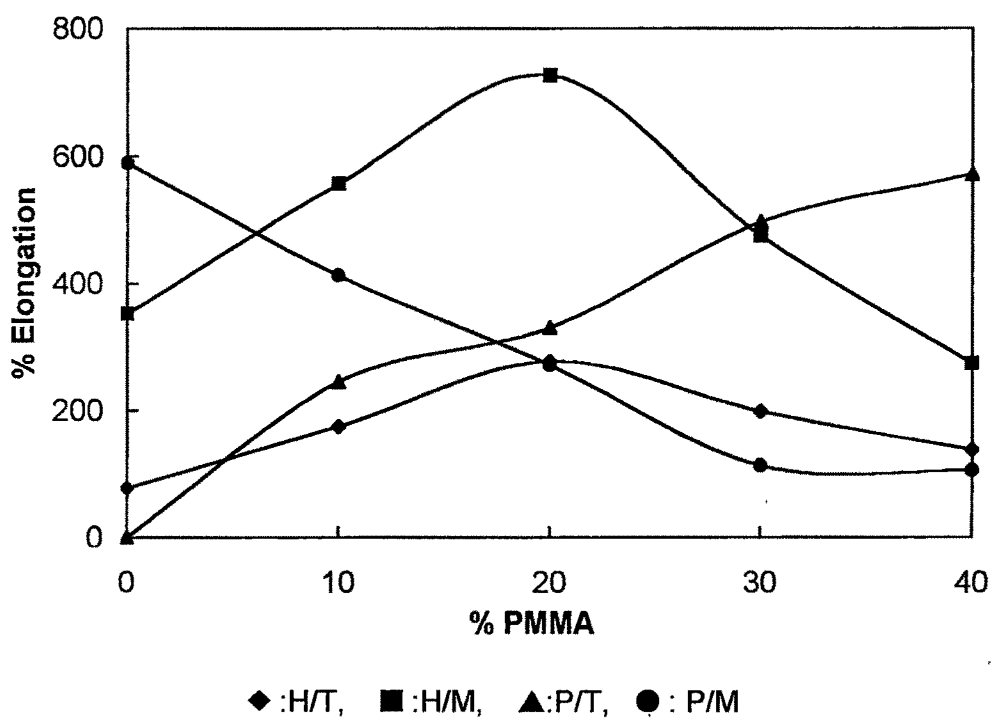


Fig. 2.28 : Effect of weight percentage of PMMA on % elongation of semi - I - IPNs based on B1 PU systems

decreased as observed in the corresponding full IPNs. However, elongation was observed to be higher than the parent PU except for the P/M IPNs. The poor mechanical properties of the later can be attributed to the poor interpenetration of the networks due to the difference in the crosslinking rates of the two networks. This can also be supported from the slow curing rate and phase separation observed in these systems. Secondly, the possible swelling of the already formed PU network weakens the coexistence and decreases the reinforcing effect.

• *Thermal Analysis*

Differential Scanning Calorimetry (DSC)

The DSC thermograms of semi IPNs are shown in Fig. 2.29. As observed in the case of full IPNs, the semi also IPNs showed the existence of the additional Tg around 10 ^{o}C. In all the semi IPNs except P / M based IPNs, the PU transition was observed to have shifted considerably in comparison to the pure PU network and the shift was observed to be highest in the P / T based semi IPNs.

Thermo-gravimetric analysis

As observed in the case of full IPNs, the thermogravimetric curves of the semi IPNs (Fig. 2.30 A & B) based on various PUs showed the trend P / T > H / T > H / M > P / M (Fig. 2.30A and Table 2.11). However, this trend is different from the trend of thermal stability observed for the PUs (Table 2.11). This is because, the thermal behaviour of the IPNs depends on the interpenetration of the two phases. P / T PU IPN showed the greatest mixing of the two phases. The observed lowest thermal degradation can be explained from the perfect interpenetration observed in SEM and DM analysis.

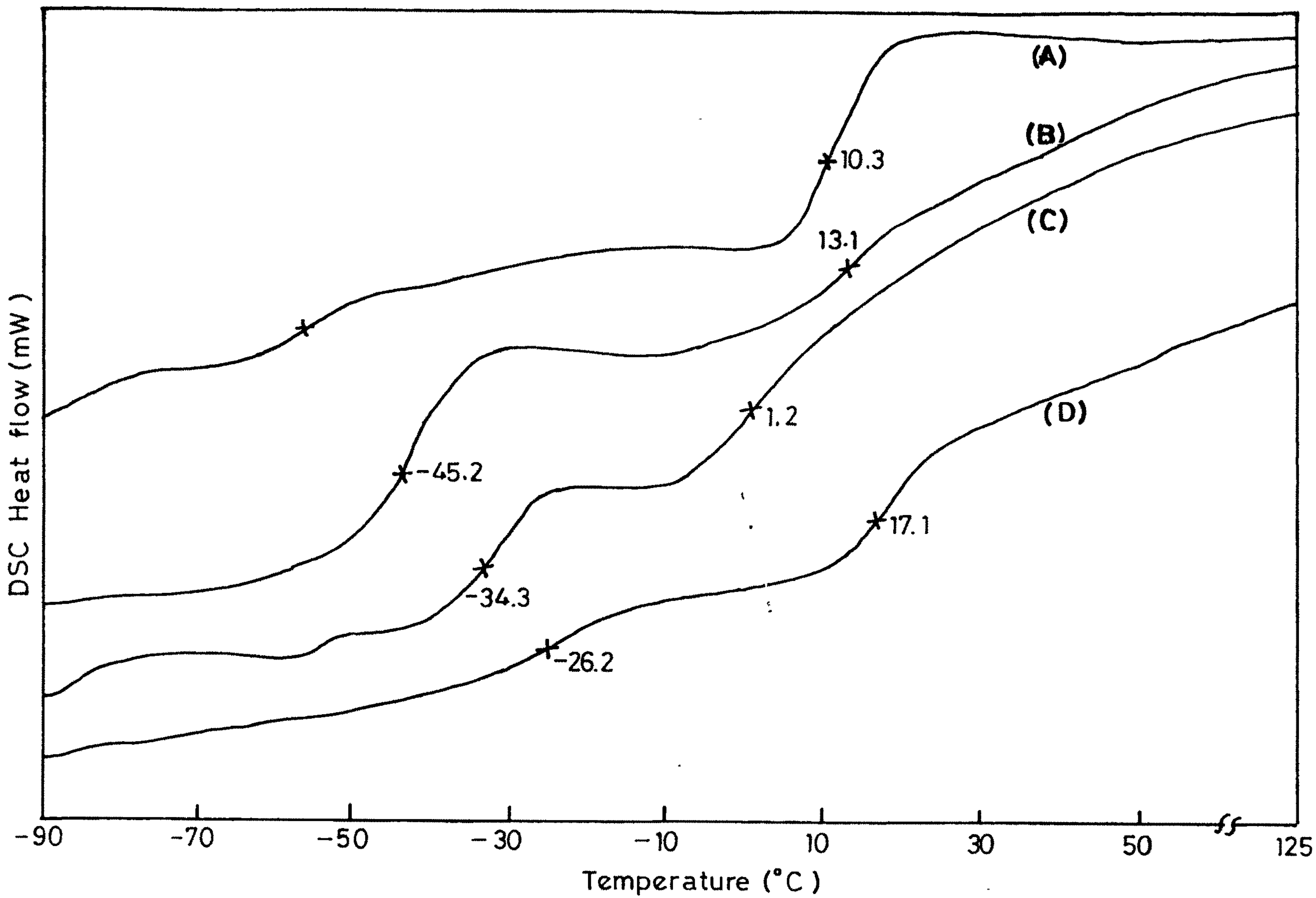


Fig. 2.29 **DSC** thermograms of semi -I-IPNs OF B_1 PUs **(A)** H/M **(B)** H/T **(C)** P/M **(D)** P/T.

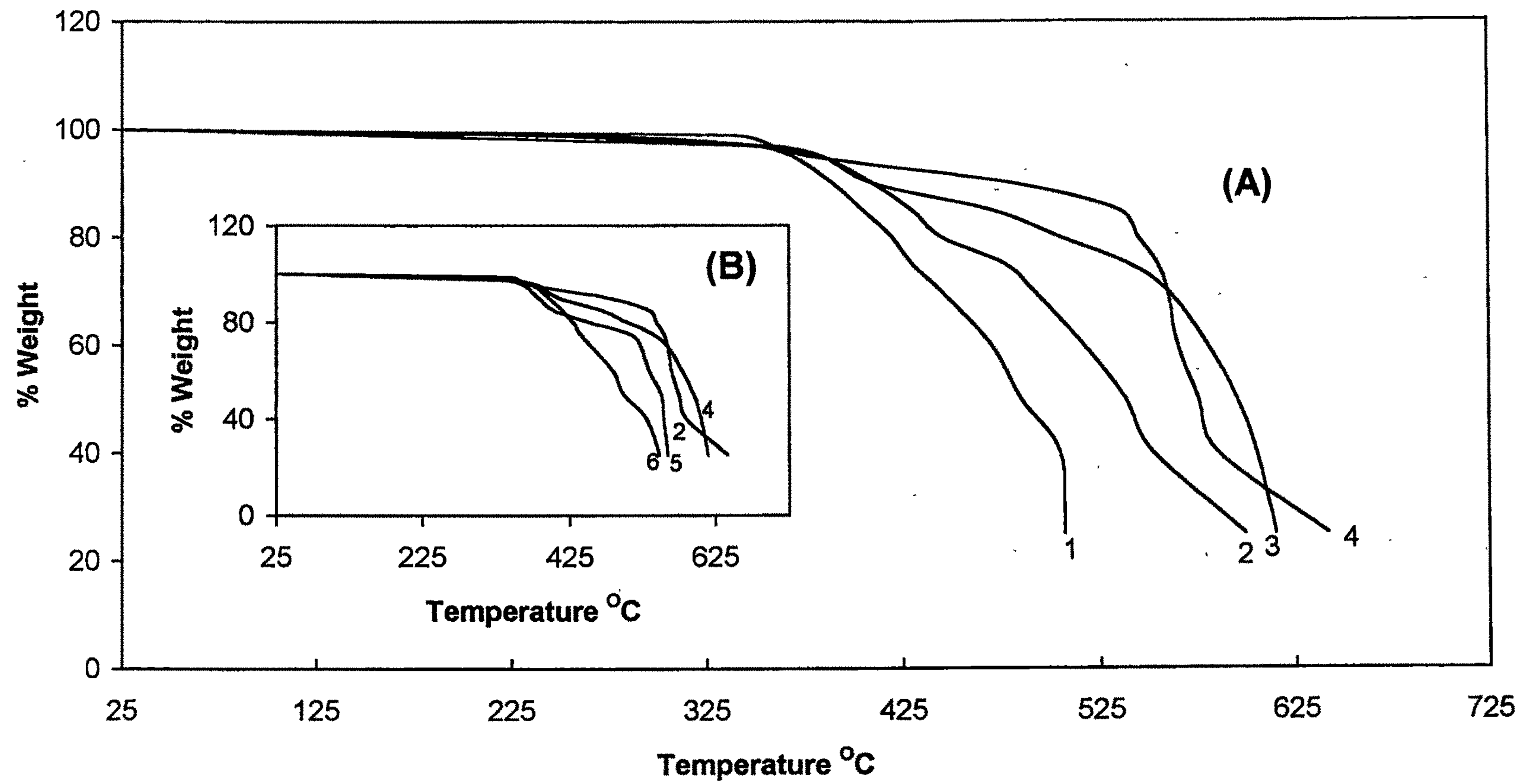


Fig. 2. 30 : Thermo-gravimetric plots for 70 : 30 (A) semi - I - IPNs : (1) : P/M, (2) : H/M, (3) : P/T, (4) : H/T ; and (B) semi - II - IPNs : (5) : H/T semi II, (6) : H/M semi II

The thermal stability of semi I type IPNs was observed to be higher then semi II types of IPNs (Fig. 2.30 B).

Table 2.11: Decomposition temperatures of 70 : 30 semi IPNs

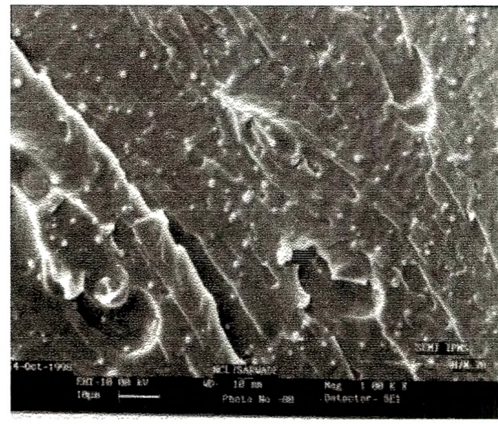
% Degradation	Temperature °C					
	Semi I				Semi II	
	P / M	H / T	P / T	H / M	H / T	H / M
1	310	360	330	330	340	310
5	405	495	435	450	485	435
25	595	635	630	605	620	590
50	605	650	640	630	640	620
75	615	670	660	650	650	640

Scanning Electron Microscopy

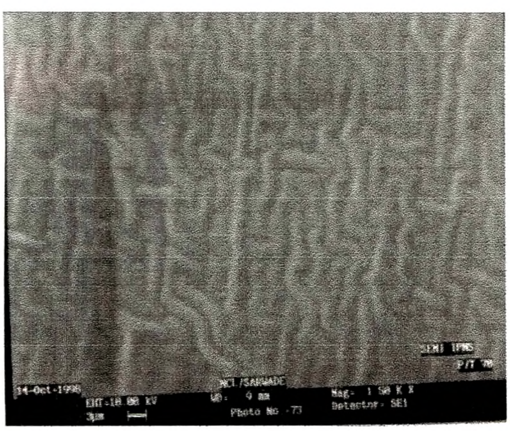
As in full IPNs, semi I IPNs (Fig. 2.31 A – D) also, show improved miscibility in the case of P / T based semi IPN. Uniform surface of this IPN is clearly seen in Fig. 2.31 C. The SEM of H / T based semi IPN (Fig. 2.31 A) exhibits relatively course morphology but the features seem to be of a ductile fracture. In H / M based IPN (Fig. 2.31 B) a uniformly distributed disperse phase is observed while in P / M based IPNs (Fig. 2.31 D) complete phase segregation is seen.

The comparison of the morphology of the semi IPNs of type I and type II (Fig. 2.31 A,B & E,F) derived from HTPB based PU shows that the latter exhibited rough fractured surface a typical character of brittle fracture while the former exhibited relatively smooth surface indicating ductile fracture.

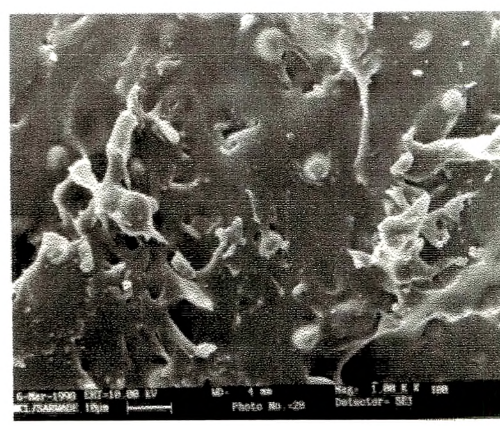
(A) (500 X)



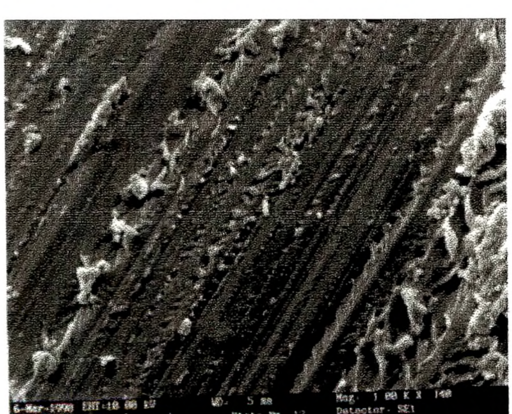
(B) (1KX)



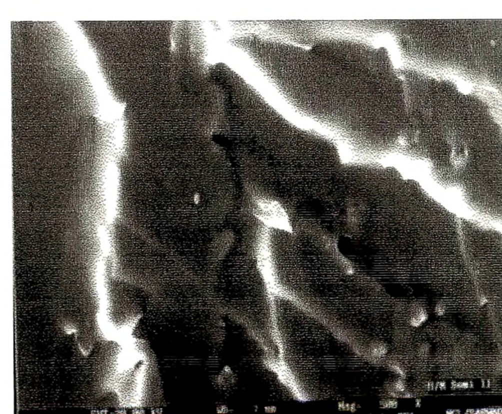
(C) (1KX)



(D) (1KX)



(E) (1 KX)



(F) (500 X)

Fig. 2.31:SE Micrographs of 70 : 30 PU / PMMA semi IPNs
type I (A) H / T, (B) H / M (C) P / T and (D) P / M and
type II (E) H / T (F) H / M

- ## Dynamic Mechanical Analysis

The damping behaviour of the semi IPNs based on different PU systems resembled to that of the corresponding full IPNs but differed from each other (Fig. 2.32- 2.34). The P / T system which showed very good phase mixing exhibited a very broad tan δ peak as observed in the case of corresponding full IPNs. The semi IPNs of HTPB PUs also showed somewhat broadening of the tan δ peaks. While P / M semi IPN showed a distinct Tg for PU and a continuous increase in the tan δ corresponding to the PMMA transition, and hence, phase separation. The HPW and inward shift of Tg showed an increase from P / M to H / M to H / T to P / T (Table – 2.12).

Table 2.12 : DMA data for 70 : 30, semi IPNs type I, at 1 Hz

Code	T_g °C	tan δ_{max}	HPW °C	E''_{max} N/m²	E_{act} k cal/mol
P / M	-63.2	0.18	22.1	2.2×10^8	53.2
H / M	-42.1	0.19	29.2	3.4×10^8	42.3
H / T	-59.2	0.25	28.0	5.5×10^8	32.5
P / T	-28.0	0.24	69.0	2.3×10^8	49.6

- ## *Swelling behaviour*

The results observed in the above properties are supported by the results of the transport properties of the semi IPNs in toluene (Table 2.13). Molecular weight between crosslinks, Mc increase while ν and ν_e decreases from P / T to H / T to H / M to P / M. The increasing crosslink density of P / T IPN indicates enhanced interpenetration responsible for good thermo-mechanical and morphological properties.

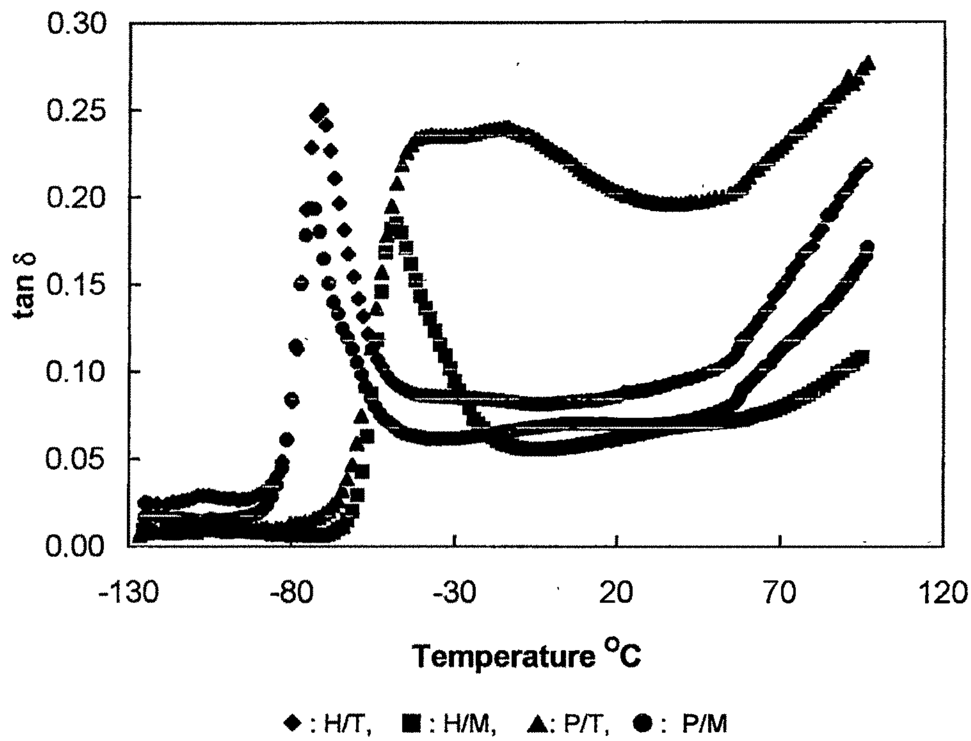


Fig. 2. 32 : Variation of tan δ of 70 :30 semi - I- IPNs at 1 Hz

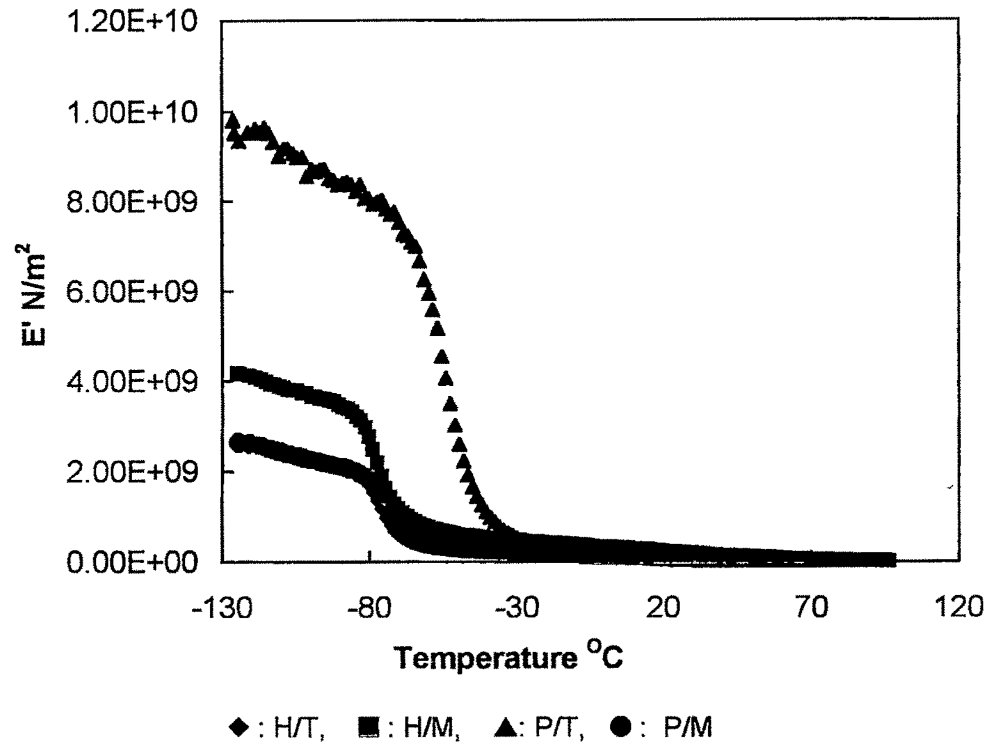


Fig. 2. 33 : Variation of storage modulus of 70 :30 semi - I - IPNs at 1 Hz

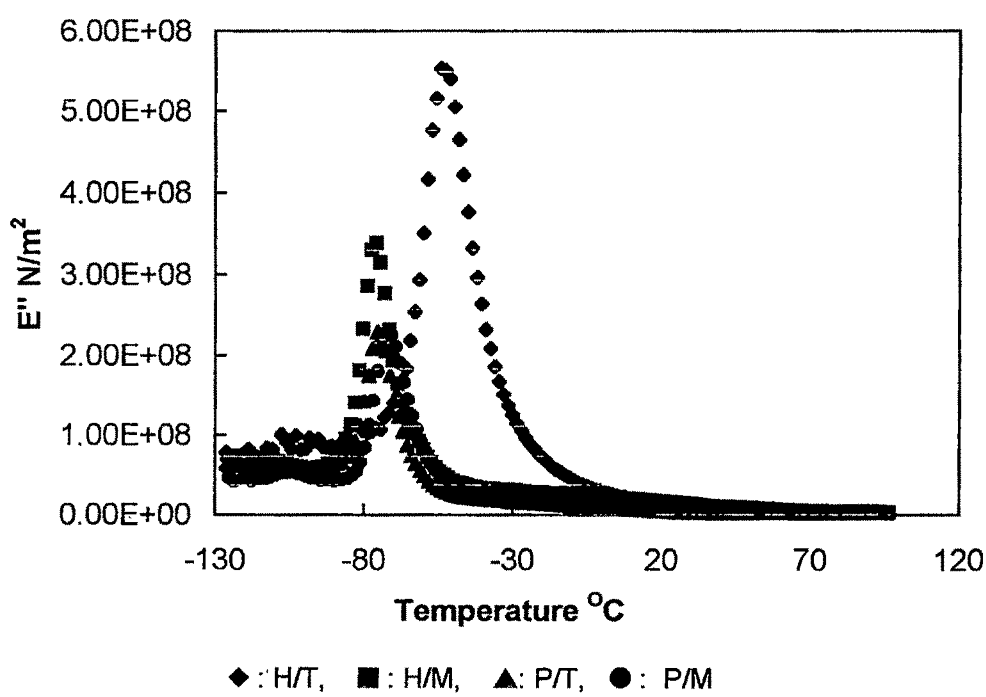


Fig. 2. 34 : Variation of loss modulus of 70 :30 semi- I - IPNs at 1 Hz

Table: 2.13 : Swelling data for 70 : 30, semi IPNs in toluene

Code	Semi IPN type	Mc	ν X10^4	ν_e X10^4
H / M	2	3900	1.28	2.89
H / T	2	2944	1.69	3.32
H / M	1	4093	1.22	3.91
H / T	1	3026	1.65	4.02
P / T	1	1296	3.90	8.33
P / M	1	5416	0.92	2.53

- ***Conclusion***

As observed in the case of the full IPNs, the P / T PU based semi IPNs showed a single phase morphology and a single broad tan δ peak indicating a homogeneous phase mixing. These semi IPNs also exhibited enhanced mechanical and thermal properties. The P / M PU based semi IPNs were mechanically weak and exhibited a narrow tan δ peak revealing poor morphology. Thus the overall trend observed in full and semi IPNs was similar. Nevertheless, full IPNs exhibit superior mechanical properties compared to the semi IPNs.

The present study on IPNs revealed that the compatibilised blends of PU and thermoplastic material like PMMA behave like reinforced elastomers. The properties of IPNs depend not only on the PU composition but also on the miscibility of the components. The IPNs showed improved properties with incorporation of 2 - HEMA irrespective of the PU composition. The blends of PUs with an elastomer have been discussed in the next chapter.

References

1. Sperling L. H. *Interpenetrating polymer network and Related Material.* Plenum, New York, 1981.
2. Frish H. L., Frisch K. C. and Klempner D., *Pure Appl. Chem.*, **53**, 1557, 1981.
3. Lipatove Y. S. and Sergeeva L. M., *Interpenetrating polymeric Network,* Naukova Dumka, Kiev. 1979.
4. Hau F. J. and Hu C. P., *Eur. Polym. J.*, **36**, 27, 2000.
5. Calleja F. J., Privalko E. G., Sukjhorukov D. I., Fainleib A. M., Sergeeva L. M., Shantalii T. A., Shtompel V. I., Paradas M. M., Ferrer G. G. and Privalko V. P., *Polymer,* **41**, 4699, 2000.
6. Sperling L. H. and Friedman D. W., *J. Polym. Sci.*, **7**, 425, 1969.
7. Sperling L. H., Taylor D. W., Kirkpatrick M. L., George H. F. and Bardman D. R., *J. Appl. Polym. Sci,* **14**, 73, 1970.
8. Sperling L. H., Thomas D. A., Lorenz S. E. and Nagel E. J., *J. Appl. Polym. Sci,* **19**, 2225, 1975.
9. Sperling L. H., *Macromol. Rev.*, **12**, 141, 1977
10. Sperling L. H. and Ferguson K. B., *Macromolecules,* **9**, 743, 1975.
11. Sperling L. H., Mishra, V., *Macromol. Symp.*, **118**, 363, 1997.
12. Hourston D. J. and Schafer F. U., *J. Appl. Polym. Sci.*, **62**, 2025, 1996.
13. Hourston D. J. and Zia Y. J., *J. Appl. Polym. Sci.*, **29**, 2963, 1984.
14. Hourston D. J. and McCluskey, J. A., *J. Appl. Polym. Sci.*, **30**,1984, 2957.
15. Kim S. C., Klempner D., Frisch K. C. and Frisch H. L., *Macromolecules,* **10**, 1187 and 1191, 1977.
16. Kim S. C., Klempner D., Frisch K. C. and Frisch H. L., *J. Appl. Polym. Sci.*, **21**, 1289, 1977.

17. Kim S. C., Klempner D., Frisch K. C., Frisch H. L., Ghiradella H., *Am. Chem. Soc.*, Div. Org. Coat. Plast. Chem., Pap., **35**, 31, 1975.
18. Klempner D., Xiao X. H., Frisch K. C., Cassidy E. and Frisch H. L., *Polym. Mater. Sci. Eng.*, **51**, 503, 1984.
19. Frisch H. L., Zhou P., Frisch K. C., Xiao X. H., Huang M. W. and Ghiradella H., *J. Polym. Sci., Part A: Polym. Chem.*, **29**, 1031, 1991.
20. Lee D. S., Lim D. S. and Kim S. C., *Proc. - Pac. Chem. Eng. Congr.*, 3rd, Volume 2, 81. Edited by: Kim, Chul; Ihm, Son Ki. Korean Inst. Chem. Eng.: Seoul, S. Korea. 1983.
21. Patel P., Suthar B., J. *Polym. Sci., Part A: Polym. Chem.*, **27**, 3053, 1989.
22. Patel P. and Suthar B., *Polym. - Plast. Technol. Eng.*, **28**, 1, 1989.
23. Patel M. and Suthar B., *Angew Makromol. Chem.*, **149**, 111, 1987.
24. Patel M. and Suthar B., *J. Polym. Sci., Part A: Polym. Chem.*, **25**, 2251, 1987.
25. Suthar B., Jadav K. and Dave M., J. *Appl. Poly. Sci.*, **54**, 1127,1994.
26. Suthar B., Klempner D., Frisch K.C., Petrovic Z., Jelcic Z., J. *Appl. Poly. Sci.*, **53**, 1083,1994.
27. Patel M., Suthar B., *Eur. Polym. J.*, **23**, 399, 1987.
28. Du Y., Han X. and Liu W., *Huaxue Tongbao*, **11**, 33,1989.
29. Athawale V. and Kolekar S., *Eur. Polym. J.*, **34**, 1447, 1998.
30. Ding H., Zhang L. and Zhang N., *Hebei Gongye Daxue Xuebao*, **25**, 37, 1996.
31. Zhang L., Ding H. and Tai, H., *Hebei Gongye Daxue Xuebao*, **25**, 23, 1996.
32. Zhang L. and Ding H., *J. Appl. Polym. Sci.*, **64**, 1393, 1997.
33. Wang S.H., Zawadzki S., Akcelrud L., *Polym. Mater. Sci. Eng.*, **77**, 555, 1997.

34. Wang S. H., Zawadski S. and Akcelrud L., *Mater. Sci. Forum*, **28**, 282, 1998.
35. Fox R. B., Armistead J. P., Roland C.M., Moonay D. J., *J. Appl. Polym. Sci.*, **41**, 1281,1990.
36. Li B., Zhang D., Peng X. and Qian B., *Gaofenzi Tongxun*, **3**, 208, 1983.
37. Zhang D. and Yang D., *Yingyong Huaxue*, **2**, 24, 1985.
38. Li B., Zhang D., Peng X. and Qian B., *Gaofenzi Tongxun*, **3**, 202,1983.
39. Chen D., Li Y., Wang X., Zhang L. and Zhou H., *Hecheng Shuzhi Ji Suliao*, **13**, 16,1996.
40. Chen D., Li Y., Wang X., Zhang L. and Zhou H., *Hecheng Shuzhi Ji Suliao*, **13**, 39, 1996.
41. Benguelin P. and Kausch H. H., *Deform. Yield Fract. Polym. Int. Conf.* 10th, 286, 1997.
42. Beguelin P. and Kausch H. H., J. Phys. IV, 7(C3, *International Conference on Mechanical and Physical Behaviour of Materials under Dynamic Loading*, 5th, 1997), C3/ 933 - C3 / 938, 1997.
43. Jung D. W., Noh S. T. and Young W. *J. Ind. Eng. Chem.* **4**, 135, 1998.
44. Hur T., Manson J. A., Hertzberg R. W. and Sperling L. H., *ACS Symp. Ser.*, 395 and 309, 1989.
45. Hur T., Manson J. A. and Hertzberg R. W., *Polym. Mater. Sci. Eng.*, **58**, 894, 1988.
46. Xiao H. X., Frisch K. C. and Frisch H. L., *J. Appl. Polym. Sci.*, **67**, 473, 1998.
47. Jehl D., Widmair M. and Meyer G. C., *Eur. Polym. J.*, **19**, 597, 1983.
48. Hermant I. and Meyer G. C., *Eur. Polym. J.*, **20**, 85, 1984.
49. Lee M. J., Kim H. S. and Kim W. Y., *Polymer*, **23**, 479, 1999.
50. Lee M. J., Kim H. S. and Kim W. Y., *Polymer*, **22**, 926, 1998.
51. Jia D. M., You, C. J., Wu B. and Wang M. Z., *Int. Polymerisation Process.*, **3**, 205, 1988.

52. Wang Z. Q., Shi L. Y. and Zhang Z. P., *J. Appl. Polym. Sci.*, **68**, 1363, 1998.
53. Akay M., Rollins S. N. and Riordan E., *Polymer*, **29**, 37, 1988.
54. Wang J., Mao K., Li Y. and Tang X., *Gaodeng Xuexiao Huaxue Xuebao*, **12**, 120, 1991.
55. Anzlovar A., Anzur I., Malavasic T., *Polym. Bull. (Berlin)*, **39**, 339, 1997.
56. Jin S. R., Widmaier J. M. and Meyer G. C., *Polym. Commun.*, **29**, 26, 346, 1988.
57. Jin S. R. and Meyer G. C., *Polymer*, **27**, 592, 1986.
58. Lin M. S. and Chium G. A., *J. Polym. Res.*, **3**, 165 and 173,1996.
59. Jones D. S., Bonner M. C., Gorman S. P., Akay M. and Keane P. F., *J. Mater. Sci. Mat. Med.*, **8**, 713, 1997.
60. Chen C. H. and Ma C. C. M., *Composites*, **28**, 65, 1997.
61. Li X. and Ding H., *Hebei Gongye Daxue Xuebao*, **25**, 9, 1996. Makromol. Chem., Macromol. Symp., **10 - 11**, 593, 1987.
62. Yu X., Chen Q., Geng K., Yan J. and Wang Y., *Acta Polymerisation. Sin.*, **1**, 98, 1989.
63. Chen Q., Yu X., Wang Q, and Ding J., *Matter, Sci. Prog.*, **4**, 71, 1990.
64. Chen Q., Hanhua G., Chen D., He X. and Yu X., *J. Appl. Polym. Sci.* **54**, 1191, 1994.
65. Wang J., Li Y., Zhang Y. and Tang X., Hecheng Xiangjiao Gongye, **14**, 116, 1991.
66. Wilson D. and George M. H., *Polym. Commun.*, **31**, 90, 355, 1990.
67. Scarito P. R. and Sperling L. H., *Polym. Eng. Sci.*, **19**, 297, 1979.
68. Liu C. J., Hsieh K. H., Ho K. S. and Hsieh, T. T., J. *Biomed. Mater. Res.*, **34**, 261,1997.
69. Chaudhary V. and Gupta R., *J. Appl. Polym. Sci.*, **50**, 1075, 1993.

70. Djomo H., Morin A., Aamiyinidu M. and Meyer G., *Polymer*, **24**, 65, 1983.
71. Varghese T. L. and Krishnamurthy V. N., *J. Polym. Mater.*, **13**, 245,1996.
72. Kurtius A. J., Kovitoh M.J. and Thomas D.A., Sperling L. H., *Polym. Eng. Sci..*, **12**, 101,1972.
73. Kim S.C., Klempner D., Frisch K.C., Frisch H.L.and Radegon W., *Macromolecules* **9**, 258,1976.
74. Kim S.C., Klempner D., Frisch, K.C., Frisch H.L. and Ghiradella H., *Polym. Eng. Sci.*, **15**, 339,1975.
75. Fox R. B., Bittner J. L., Hinkley J. A. and Carter W., *Polym. Eng. Sci..*, **25**, 157,1995.
76. Desai S., Thakore I. M., Sarawade B. D. and Devi S., *Polym Eng Sci*, ***40**, 1200, 2000.*
77. Desai S., Thakore I. M., Sarawade, B. D. and Devi S. *Eur. Polym. J.*, **36**, 711, 2000.
78. Desai S., Thakore I. M. and Devi S., *Polym. Int.*, **47**,172, 1998.