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Preparation of epoxy/urethane graft interpenetrating polymer networks and study of mechanical, thermal and morphological properties

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***Abstract*:** This paper describes the preparation of Epoxy/Urethane (EP/PU) graft interpenetrating polymer networks (g-IPNs) and investigates the effect of EP/PU weight ratio and urethane's prepolymer molecular weight on the mechanical, morphological and thermal properties of the IPN system. Here, g-IPN was prepared by thorough mixing of an isocyanate-terminated urethane prepolymer with an epoxy resin followed by simultaneous curing of the resins. Polytetra hydrofuranate (PTHF), molecular weights (M_w) 1000, 2000 and 3000 g/gmol, was used to prepare urethane prepolymers. EP/PU weight ratios were 75/25, 50/50, 30/70 and 15/85. Disappearance of epoxide and isocyanate functional groups was followed by Fourier Transform Infrared spectroscopy (FT–IR), showing curing of the resins. Differential Scanning Calorimetry (DSC) was used to investigate the glass transition temperature (T_g) of the IPNs. Thermal Gravimetric Analysis (TGA), Dynamic Mechanical Thermal Analysis (DMTA), tensile measurements and Scanning Electron Microscopy (SEM) were used to study thermal, mechanical and morphological properties of the prepared systems. The best mechanical properties were obtained at EP/PU weight ratio 75/25 which also shows a fine and uniformly dispersed morphology. Moreover, at this ratio, with increasing PTHF M_w in the urethane prepolymer, the mechanical properties were improved whereas a decrease was observed in T_g and thermal degradation temperature of g-IPNs.

Keywords: Interpenetrating polymer networks, Epoxy resin, Urethane prepolymer.

Introduction

The interpenetrating polymer networks (IPNs) are a unique type of polyblend which is defined as a mixture of two or more crosslinked polymer networks that have partial or total physical interlocking between them [1–3]. In fact, formation of IPNs is the only way of intimately combining crosslinked polymers [4]. If a high degree of intermixing is intended, the Simultaneous IPN (SIN), in situ mixing and polymerization of monomers or prepolymers, is preferred. This is due to the compatibility of the monomeric mixture, which is much higher than that of a polymeric mixture [5]. The resulting mixture exhibiting (at worst) only limited phase separation while normal blending or mixing of polymers results in a multiphase morphology due to the well-known thermodynamic incompatibility of polymers. However, if mixing is accomplished simultaneously with crosslinking, phase separation may be kinetically controlled by permanent interlocking of entangled chains [4]. The morphology of IPNs are particularly complicated and has been the subject of many studies [6, 7].

The entanglements in IPNs must be of a permanent nature and are made so by homocrosslinking of the two or more polymers [4]. These entanglements of multiple

crosslinked polymers lead to forced miscibility compared to simple blends and the resulting IPN materials exhibit excellent size stability and a possibly synergistic combination of the properties of their components [8-10]. These make IPNs interesting in several applications [11, 12].

In fact, g-IPNs possess high tensile modulus and strength and low elongation at break (ε_b) due to the existence of covalent chemical bonding between the networks [13]. The properties of IPN materials are determined by the kinetics of formation of the growing networks and by the thermodynamics of mixing of the constituent polymers [14].

Epoxy resins are widely used as the matrices of high-performance composite materials because of their stiffness, chemical resistance, and high temperature stability. However, they suffer from a low fracture strength and inherent brittleness [15]. To meet the required end-use performance, they need to be modified with either thermoplastics or elastomers. The IPNs using a rubbery polyurethane phase have been considered for such applications [16]. Polyurethanes are a versatile group of polymers that can be used in a wide spectrum of polymeric products, including foams, elastomers, coating resins, adhesives, and fibers. However, their relative low thermal resistance and strength [6], high water absorption and poor heat resistance limit their applications [17]. Therefore, some researchers have proposed the change of its phase structure by blending with one or two other polymers to improve its properties [15]. Some studies have been done to enhance the mechanical properties by synthesizing a series of g-IPNs of polyurethane and epoxy resins. Actually, many valuable systems have been made by taking advantage of the IPN structure [18–22].

The object of this research is to prepare EP/PU graft interpenetrating polymer networks and to investigate the effect of Epoxy/Urethane weight ratio and urethane's prepolymer molecular weight on the mechanical, morphological and thermal properties of the IPN systems. The experimental design is in such a way to optimize the epoxy/urethane weight ratio in which the synergistic effect in properties is observed and then at this ratio the effect of PTHF molecular weight in urethane prepolymer is investigated. The properties of the prepared systems will be studied by FT-IR, tensile test, DMTA, DSC, TGA, SEM and Wide-Angle X-ray Diffraction (WAXD).

Results and Discussion

In Fig. 1. FTIR spectra for the mixture of epoxy resin with urethane prepolymer prior to curing (Fig. 1a) and after formation of the g-IPN (Fig. 1b) are shown.

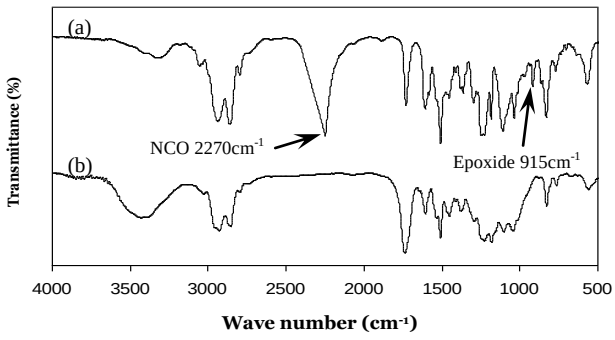

Fig. 1. FTIR spectra of (a) mixture of epoxy resin and NCO terminated urethane prepolymer, (PTHF M_w 1000g/gmol), 50/50 wt%, prior to curing, (b) cured system.

As it can be seen, in the mixture of two resin systems, the absorption bands for –NCO and epoxide group are appeared at 2270 cm^{-1} and 915 cm^{-1}, respectively. However, these bands are disappeared as the mixture is heated up to cure temperature of the individual systems; an indication of formation of the corresponding networks and completion of the curing reactions.

Mechanical Properties

-Effect of Epoxy Weight Ratio

The results of mechanical properties for IPN systems at various EP/PU weight ratios (PTHF M_w=1000 g/gmol) are shown in Figs. 2 and 3 and summarized in Table 1. As it is shown, there is an ascending order for the tensile modulus and strength with increasing EP/PU weight ratio (Fig. 2) but the trend for the tensile strength is reversed at epoxy weight ratio above 75 (wt%).

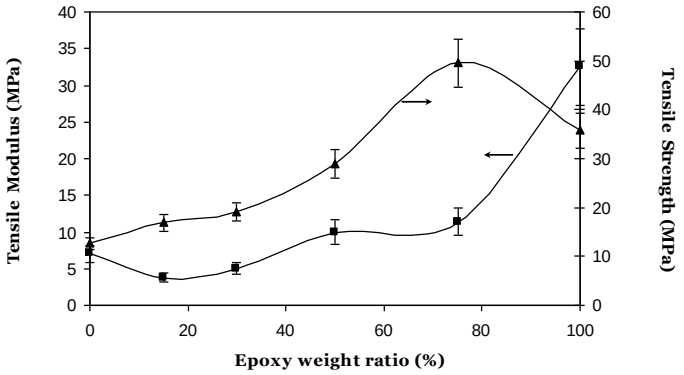

Fig. 2. Tensile modulus and strength vs. epoxy weight ratio for g-IPNs, (■ Tensile modulus, ▲ Tensile strength).

For ε_b and toughness (calculated from the area under stress-strain curve) a decrease is observed up to 50 (wt%) of epoxy but beyond that an increase is seen with a maximum at 75 (wt%) of epoxy. The initial increase in tensile modulus and strength and the reduction in toughness and ε_b are attributed to the increase in epoxy percentage which has a higher tensile modulus and strength and a lower toughness and ε_b than the PU component.

The distinct increase in tensile strength and modulus at EP/PU weight ratio 75/25 can be due to the a good interpenetration of epoxy and urethane chains which improves their compatibility, fills the defects existing in the single polymers, and increases the effective crosslinking density. Also, the increase in interpenetrating surface area leads to a more energy absorption by PU phase. Moreover, PU particles embedded in epoxy phase acts as stress concentration points which can initiate crazes and stop its development, thus toughness and ε_b amount increases [23]. Based on these results, a synergistic increase in tensile properties for EP/PU g-IPN 75/25 is observed. At this ratio, EP/PU g-IPN has a ε_b 8.85% and a tensile strength of 49.56 MPa (compared with 1.88% and 35.74MPa for pure epoxy). Considering these facts, this ratio seems to be the optimized one, and therefore, in the course of the research the effect of PTHF molecular weight was only studied at this ratio.

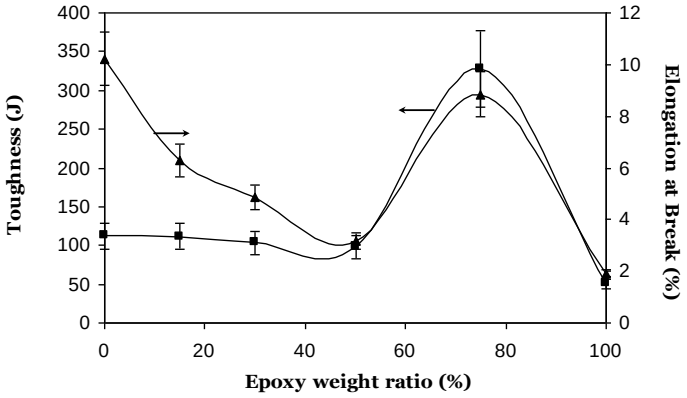

Fig. 3. Toughness and elongation at break vs. epoxy weight ratio for g-IPNs, (■ Toughness, ▲ Elongation at break).

Tab. 1. Mechanical properties of pure components and EP/PU g-IPNs with various EP/PU weight ratios.

Epoxy Weight Ratio (%)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Toughness (J)
0	7	12.6653	10.22	112.001
15	3.8	16.9202	6.27	111.350
30	5	19.0444	4.84	103.255
50	10	28.9956	3.16	98.048
75	11.4	49.5689	8.85	327.998
100	32.5	35. 7419	1.88	51.673

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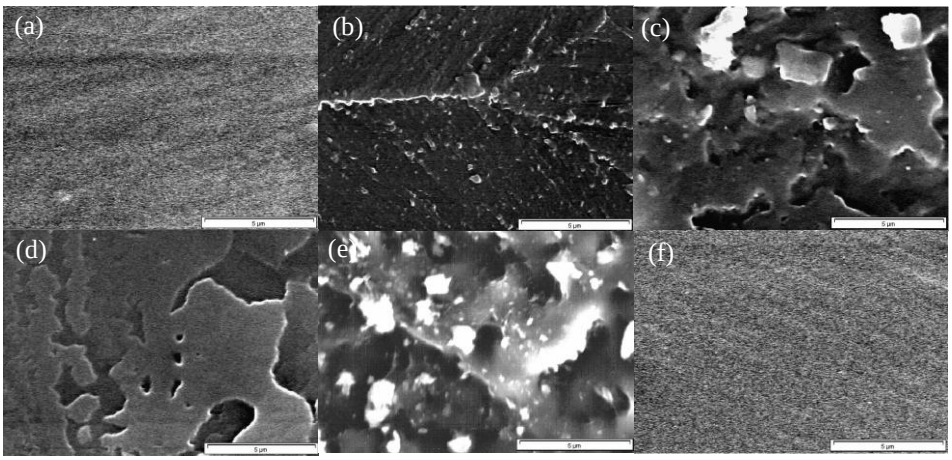


Fig. 4. SEM micrographs for g-IPNs with various EP/PU weight ratios: (a) pure epoxy, (b) g-IPN 75/25, (c) g-IPN 50/50, (d) g-IPN 30/70, (e) g-IPN 15/85, (f) pure PU1000.

The microstructure of the polymer blend is also important in determining its physical and mechanical properties [7]. In fact, the morphological changes and also the size

of the dispersed phase can be responsible for the enhancement of the mechanical properties [24].

In Fig. 4 SEM micrographs of g-IPNs at various EP/PU weight ratios (PTHF M_w=1000 g/gmol) are compared to the micrographs of pure individual systems, i.e. epoxy and PU (Figs. 4a and 4f). The IPN system with EP/PU 75/25 (wt%) showed a homogeneous and finely dispersed PU phase in epoxy matrix (Fig. 4b). At EP/PU weight ratio 15/85, again dispersed phase morphology is observed but the size of the dispersed phase is much bigger than that of with EP/PU weight ratio 75/25. Therefore, it is reasonable to have an improvement in properties at EP/PU g-IPN 75/25 (wt%) [24]. For EP/PU g-IPN 50/50 (wt%), a co-continuous morphology with a dispersed phase is seen. Comparing this with EP/PU g-IPN 30/70 (wt%), which shows an almost co-continuous morphology, the tensile modulus and strength are increased but the changes in toughness and ε_b are not that significant.

-Effect of PTHF M_w

Molecular weight of the IPN ingredients affects the morphology and in turns the physical and mechanical properties of the IPN. In this part of research, the effect of PTHF M_w in PU prepolymer on the mechanical properties of the g-IPN is investigated.

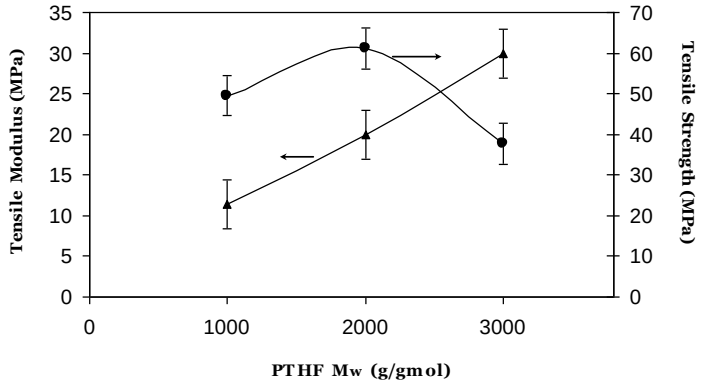


Fig. 5. Variations of tensile modulus and strength of EP/PU g-IPN 75/25 with PTHF M_w, (▲ Tensile Modulus, ● Tensile strength).

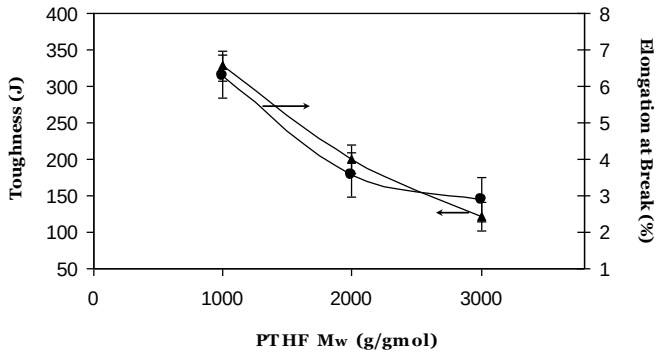


Fig. 6. Variations of toughness and elongation at break of EP/PU g-IPN 75/25 with PTHF M_w, (▲Toughness, ● Elongation at break).

In Fig. 5 the variations of tensile modulus and strength with PTHF M_w are shown. As it can be seen, there is a continuous increase in tensile modulus with M_w while this for tensile strength is up to M_w=2000 and a decrease is observed at higher M_w.

Tab. 2. Mechanical properties and T_g values for the cross linked PU at various PTHF M_w.

PTHF M_w (g/gmol)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Toughness (J)	T_g measured by DSC(ºC)
1000	11.4	49.5689	6.27	327.998	-35.1
2000	20	61.1272	3.56	200.441	-71.6
3000	30	37.7735	2.88	120.900	-74.7

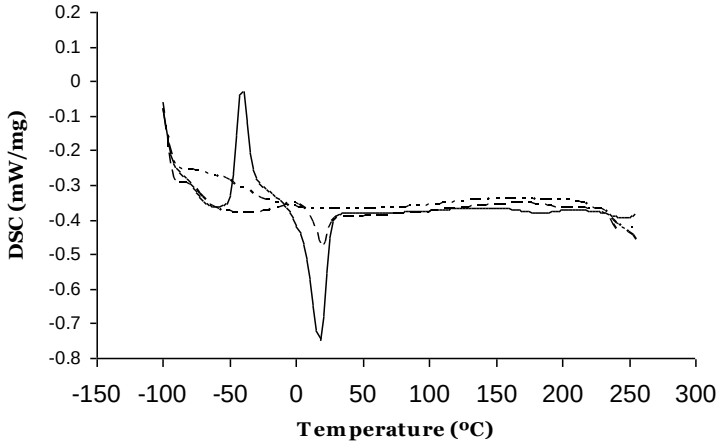


Fig. 7. DSC curves of cross linked PU at various PTHF M_w, (_ _ _ M_w 1000, — · — M_w 2000, —— M_w 3000).

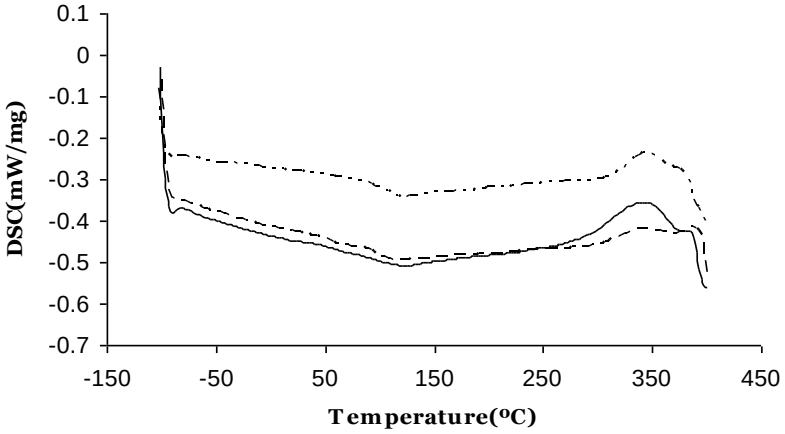


Fig. 8. DSC curves of EP/PU g-IPN 75/25 with various PTHF M_w (_ _ _ M_w 1000, — · — M_w 2000, —— M_w 3000).

In Fig. 6 the variations of ε_b and toughness for EP/PU g-IPN 75/25 with increment of PTHF molecular weight, are shown. With increasing PTHF M_w, both parameters are decreased. The results for the effect of PTHF M_w on the mechanical properties are summarized in Table 2.

The crystallinity of PTHF and the interfacial strength between the phases can be accounted for the observed variations in the mechanical properties. According to DSC results for the cross-linked PU there is a melting and a crystallization peak related to the presence of PTHF which with increasing the M_w of PTHF become more evident (Fig. 7). XRD results for the IPN systems (Fig. 9) reveal the presence of the crystallite although this was not detectable in their DSC thermograms (Fig. 8) perhaps due to low percentage of PU phase and/or restrictions caused by epoxy chains. On the other hand, the increase in M_w of PTHF will result in a decrease in the density of –NH groups in PU prepolymer and in doing so the hydrogen bonding and the interfacial interactions are reduced.

At lower M_w the properties are mainly determined by the extent of crystallinity, however, as the M_w is increased the interfacial interactions become the dominant factor. The continuous increase in modulus and the decrease in toughness and ε_b with increasing M_w are reasonable since the crystallinity is increased. This is also true for tensile strength but beyond M_w= 2000 the trend is reversed which is because of weakening of the interfacial strength as the result of the decrease in hydrogen bonding.

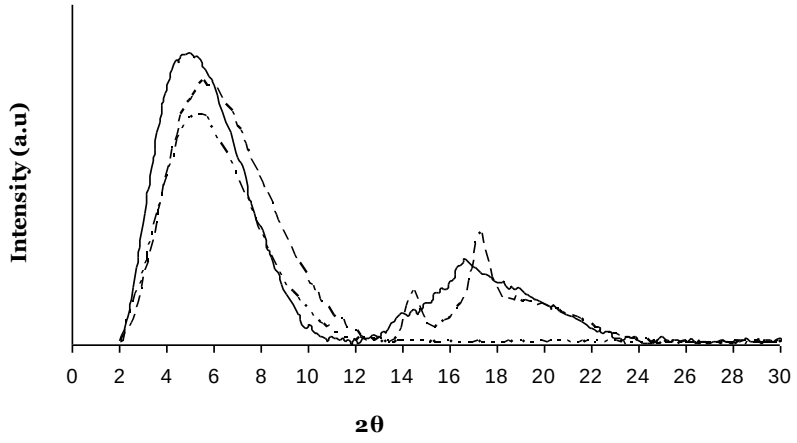


Fig. 9. XRD micrographs of EP/PU g-IPN 75/25 with various PTHF M_w, (_ _ _ M_w 1000, _ · · _ M_w 2000, ____ M_w 3000).

Thermal Properties

-Differential Scanning Calorimetery Analysis (DSC)

DSC has been widely used to characterize IPN systems. This is perhaps due to the fact that the glass transition temperature (T_g), obtained from DSC thermograms, is one of the most fundamental features and is directly related to the properties of the polymer [22]. DSC curves for g-IPNs (PTHF M_w=1000g/gmol) with different epoxy weight ratio are shown in Fig. 10. The primary relaxation observed is regarded as the α-relaxation and has been designated to be T_g of the EP/PU g-IPN. The fact that there is only a single T_g within the temperature range of -35.1 °C to +118.9 °C

expresses that there is a good compatibility between PU and EP phases thus a distinct phase separation did not happen between them.

This can be due to their appropriate physical interpenetration which also leads to observation of almost homogeneous phase morphology [25, 26]. This is of course somehow different from the results obtained in SEM micrographs where a two-phase morphology is observed. It is believed that the degree of phase separation and the sensitivity of the DSC used, may not be high enough to detect this. It could be observed that in all specimens, T_g of the EP/PU g-IPNs lie between the T_gs of pure PU and EP. Moreover, with the decrease of PU prepolymer content, the total fractional free volume decreased, corresponding to the increase in T_g of the IPN system. This increase in T_g of EP/PU g-IPNs is related to the interlocking of PU and EP chains, which restrict the mobility of PU chains, and hence an upward shift in T_g of IPN is observed. The T_g values, measured by DSC, for IPN systems as well as the pure components are listed in Table 3.

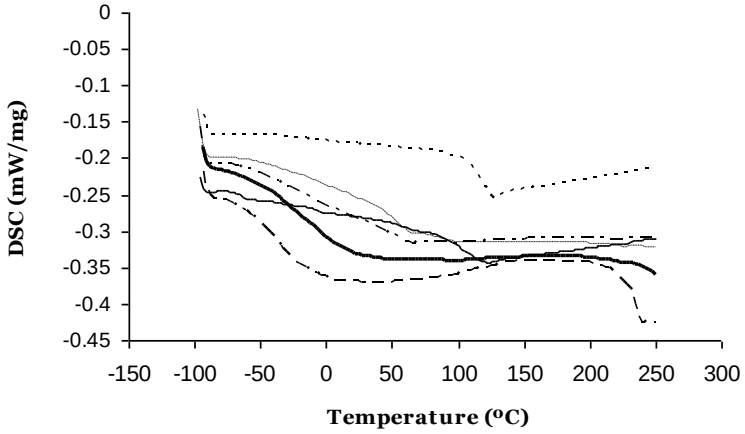


Fig. 10. DSC curves of g-IPN with various EP/PU weight ratios, (..... pure epoxy, ——g-IPN 75/25, — . . — g-IPN 50/50, — — - g-IPN 30/70, ▬▬ g-IPN 15/85, - - . . - - pure PU).

Tab. 3. T_g values of pure components and g-IPNs with various EP/PU weight ratios.

Sample	T_g measured by DSC (ºC)
Pure Epoxy	118.9
EP/PU g-IPN 75/25	102.6
EP/PU g-IPN 50/50	61.0
EP/PU g-IPN 30/70	-26.2
EP/PU g-IPN 15/85	-30.4
Pure PU-1000	-35.1

In Fig. 8. DSC curves of EP/PU g-IPN (75/25) at various PTHF molecular weights are shown. With the increase in PTHF M_w, T_g of IPN is decreased. This can be attributed to the increase in chain flexibility as the result of the increase in the number of ether linkages and also the reduction of hydrogen bonding as described previously.

-Dynamic Mechanical Thermal Analysis (DMTA)

Fig. 11 compares the DMTA results for EP/PU g-IPN (polyol M_w =1000 g/gmol) at various epoxy weight ratios with the pure components. In general, a single T_g is observed for IPNs which lies between the T_g of the pure PU and epoxy (Fig. 11a).

With increasing the epoxy weight ratio, the IPN's T_g is shifted toward higher temperatures and the behavior becomes closer to pure epoxy. This increase in Tg can be due to the presence of some covalent chemical bonding (grafting) and also interactions between the polar groups of the networks which result in an increase in crosslink density and/or inducing the rigid structure of epoxy into the PU network [26].The variations in the storage modulus (E') of the IPNs almost follow a similar trend seen for the T_g (Fig. 11b). Here, the degree of phase separation is to some extent that the peaks for T_gs of the components are quite close to each other and have some overlapping and appear in form of a shoulder. The area under each peak depends on the % of the components in the system. Here, the shoulder belongs to urethane phase which has a lower % and the main peak is for the epoxy component.

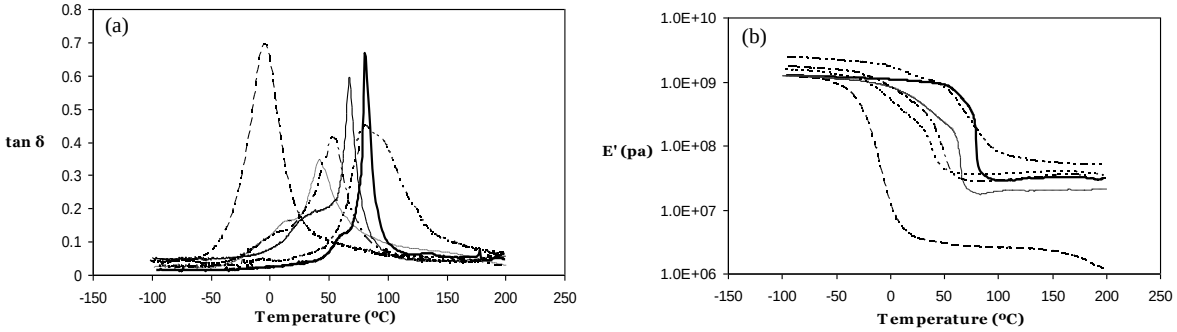


Fig. 11. DMTA curves of g-IPN with various EP/PU weight ratios. tan δ (a), storage modulus (b),(____ pure epoxy, _ . . _g-IPN 75/25, ____ g-IPN 50/50, _ . _ . . g-IPN 30/70, ... g-IPN 15/85, _ _ _ _ pure PU).

-Thermal Gravimetric Analysis (TGA)

Fig. 12 shows the thermal gravimetric results of EP/PU g-IPNs with various epoxy ratios (polyol M_w =1000 g/gmol), as compared to pure components. The onset of thermal degradation temperature (T_{onset}) is determined from the intersection of the two tangents [25] and the results are summarized in Table 4.

As it can be seen, pure PU shows a twin degradation curve in which the first one (T_{onset1}) is believed to be related to the degradation of soft segments and the second one (T_{onset2}) to the hard segments. In IPNs, this twin degradation curve is also observed (up to the epoxy weight ratio 50), however, with increasing EP/PU weight ratio, the T_{onset1} is shifted to higher temperatures while T_{onset2} to lower, depending on the ratio and the interactions between the components. Besides, at EP/PU weight ratio 50/50 and above, the degradation behavior changes and it happens in a single stage process.

No significant changes in the thermal behavior of IPN systems were observed when PTHF M_w in the systems was increased. In fact, the degradation curves were almost superimposed and T_{onset} was 382.1, 380.4 and 379.1 ^oC for M_w= 1000, 2000 and 3000 g/gmol, respectively. With increasing PTHF M_w, the number of polar groups in

urethane prepolymer is decreased and also the hydrogen bonding between the components. This suggest that the degradation temperature of the IPN systems is mainly affected by the extent of the hydrogen bonding between PU chains themselves and also with epoxy chains and to a less extent to the molecular weight of the PU soft segment.

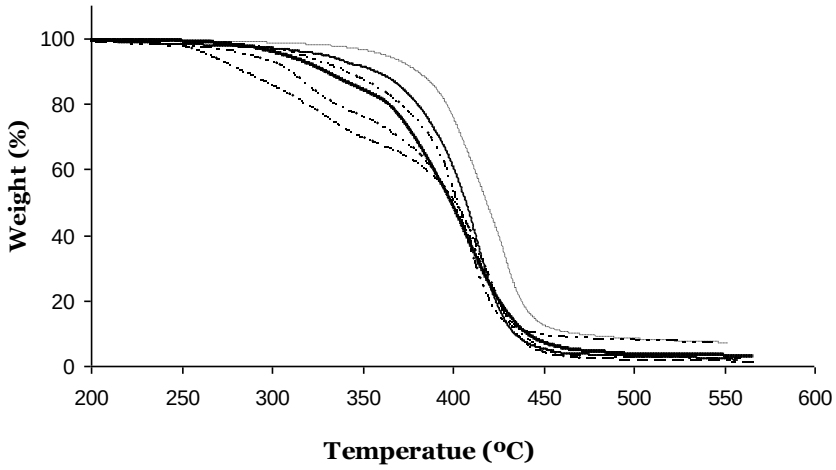


Fig. 12. TGA curves of g-IPN with various EP/PU weight ratios, (.....pure epoxy, ——— g-IPN 75/25, —·—·— g-IPN 50/50, ▬▬ g-IPN 30/70, - - - - g-IPN 15/85, - - - - pure PU).

Tab. 4. TGA results for g-IPNs with various EP/PU weight ratios.

Sample	$T_{onset\ 1}$(ºC)	$T_{onset\ 2}$(ºC)
Pure Epoxy	386.6	-
EP/PU g-IPN 75/25	382.1	-
EP/PU g-IPN 50/50	375.3	-
EP/PU g-IPN 30/70	377.9	299.1
EP/PU g-IPN 15/85	386.6	296.1
Pure PU-1000	395.7	254

Conclusions

Epoxy/Urethane graft interpenetrating polymer networks were prepared by a simultaneous polymerization method and the effect of epoxy/urethane weight ratio and urethane's prepolymer molecular weight on the mechanical, morphological and thermal properties of the IPN system were studied.

The tensile modulus and strength of the IPN systems (with polyol M_w=1000) were increased with increasing EP/PU weight ratio but the trend for the tensile strength was reversed at epoxy ratios above 75 (wt%). For the elongation at break and toughness a decrease was observed up to 50 (wt%) of epoxy but beyond that an increase was seen with a maximum at 75 (wt%) of epoxy.

SEM results for g-IPN at EP/PU 75/25 showed good dispersion of PU phase in epoxy matrix. For EP/PU 15/85, the size of the dispersed phase was much bigger than that of with EP/PU weight ratio 75/25. For EP/PU 50/50, a co-continuous morphology with a dispersed phase was seen. Comparing this with EP/PU 30/70, which showed an

almost co-continuous morphology, the tensile modulus and strength were increased but the changes in toughness and ε_b were not that significant.

At EP/PU 75/25, with increasing PTHF M_w in IPNs, a continuous increase in tensile modulus was observed, while this for tensile strength was up to M_w=2000 and then a decrease occurred. The elongation at break and toughness showed a decrease with increasing PTHF M_w.

DSC results proved that there is good compatibility between PU and EP phases.

A similar trend for the variations of T_g with EP/PU weight ratio was observed in both DSC and DMTA experiments.

A two-step thermal degradation curve was observed for the IPNs (up to the epoxy weight ratio 50). With increasing EP/PU weight ratio, the T_{onset1} was shifted to higher temperatures while T_{onset2} to lower. No significant changes in the thermal behavior of IPN systems were observed when PTHF M_w in the systems was increased.

Experimental

Materials

Epoxy resin Epon 828 DGEBA (diglycidyl ether of Bisphenol A, EMM 184-190g) was supplied by Shell Chemicals Co. (USA). Epoxy hardener, Aradur 917, was obtained from Huntsman Advanced Materials (Switzerland). TDI (Toluene Diisocyanate, an 80/20 mixture of 2,4/2,6 isomers), dibutyltin dilaurate (urethane catalyst), tributylamine (epoxy catalyst) and glycerol (urethane cross-linker) were Merck grade. PTHF (Polytetra hydrofuranate, M_w= 1000, 2000 and 3000 g/gmol) was supplied by Arak Petrochemical Co. (Iran). Glass fiber tissue AEMS 20 gr/m^2 was purchased from Tishan Co. (China).

PTHF, glycerol and epoxy resin were dried at 80 ºC in vacuum for 24 h before use. Other raw materials were used without further purification.

Instruments

Differential Scanning Calorimetery (DSC) and Thermal Gravimetric Analysis (TGA), PL (Polymer Laboratories Co. England), were used to study the thermal behavior of the IPNs. The analyses were carried out at a heating rate of 10 ºC/min and under nitrogen atmosphere. Dynamic Mechanical Thermal Analysis (DMTA) was performed using Tritec 2000 DMA (Triton Technology Co. England). FTIR spectra were recorded on an Equinox 55 FTIR spectrophotometer (Bruker Co. Germany). The WAXD studies of the samples were carried out using a SIEMENS D5000 X-ray diffractometer (Germany) and under CuKα radiation. Scanning Electron Microscopy (SEM) images were prepared from the cryogenically fractured (in liquid N_2) surface of the samples, using a S360 (Cambridge Co. England). Tensile properties of the specimens were determined with a tensile testing machine STM-150 (Santam Co. Iran).

Synthesis of polyurethane prepolymer

The isocyanate-terminated polyurethane prepolymer was prepared by reacting TDI with PTHF. For this purpose, a weighed amount of TDI was placed in a round-bottomed, three-necked flask, equipped with a mechanical stirrer and dry nitrogen inlet, and heated to 60 ºC. While stirring vigorously, a predetermined amount of

PTHF (NCO:OH ratio was 2:1), with a certain M_w, was added slowly to the flask. The isocyanate content was continuously determined according to ASTM D 2572. The end of the reaction was regarded as the point in which the isocyanate content (%NCO) reaches its theoretical value [13].

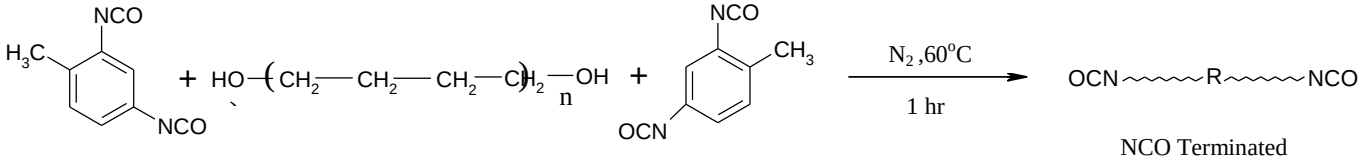
Synthesis of Epoxy/Urethane Graft IPN

For the synthesis of EP/PU g-IPN, a simultaneous synthesis method was used. Here, a predetermined amount of epoxy precursor and its hardener (100:90) was thoroughly mixed with urethane prepolymer at room temperature and under dry nitrogen atmosphere. Then the urethane cross linker (glycerol), epoxy catalyst and finally urethane catalyst were added to the mixture. The mixing was further continued for about 15 min. The mixture was then degassed under vacuum for about 30 min and cured in an oven at 120 ºC for 6 h.

To prepare the specimens for tensile testing, a composite lamina was prepared by full impregnating a glass fiber tissue with the resin mixture (96 %wt resin). The samples were then cured at 120 ºC for 6 h.

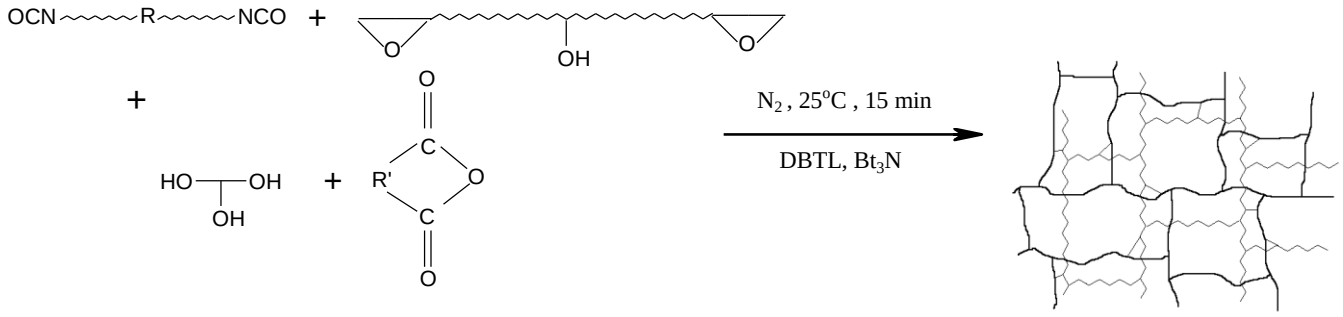
The preparation steps for EP/PU g-IPN are shown in Scheme 1.

Scheme of Urethane Prepolymer Preparation



NCO Terminated
Urethane Prepolymer

Scheme of Grafting Process between Epoxy and Urethane



Epoxy/Urethane Graft IPN

Scheme 1. Preparation steps for EP/PU g-IPN.

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