Polyurethane–Epoxy Maleate of Bisphenol A Semi-Interpenetrating Polymer Networks

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ABSTRACT: Semi-interpenetrating polymer networks were synthesized starting from polyurethane (PU) and epoxy maleate of bisphenol A (EMBA). Differential scanning calorimetry and swelling measurements showed good miscibility and the presence of the strong intermolecular interactions within the synthesized networks. The physico-mechanical properties increased against PU to a maximum value with the increasing of EMBA content up to 12 wt % and then decreased with further increasing EMBA content. Generally, with exception of the elongation at the limit of elasticity, the mechanical properties improved very much under action of the UV radiation. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 138–144, 2002

Key words: semi-interpenetrating polymer networks; polyurethane; epoxy maleate of bisphenol A; mechanical properties; swelling

INTRODUCTION

Interpenetrating polymer networks (IPNs) are combinations of two or more network polymers synthesized in juxtaposition.[1] Compositions in which one or more polymers are crosslinked and one or more polymers are linear or branched are semi-interpenetrating polymer networks (SIPNs). The study of IPNs has received considerable interest because most of them exhibit better mechanical properties than their individual networks because of a synergistic effect induced by the forced compatibility of the components.[2] IPN PU-based compositions have been the subject of many previous studies.[3–8]

Thermoplastic polyurethane (PU) was widely investigated and utilized in many technical applications for its high tensile strength, processibility, and mechanical properties.[9] Epoxy resins, which are associated with high modulus and strength, have been used as matrices in the composite aeronautic industry, as structural adhesives, high-performance structural composites, and elsewhere.[10] However, the cured resins are brittle and have poor resistance to the crack propagation. As a result, epoxy resins must be modified with other polymers to improve their physical and mechanical properties. IPNs can be considered to fulfill these requirements.

The PU-based IPNs are relatively easy to synthesize and have outstanding properties. IPNs based on PU and epoxy have been reported by many investigators.[11–15]

In the previous article,[16] blends of PU with epoxy maleate of bisphenol A (EMBA) were synthesized and their miscibility and the physicomechanical properties were reported. In the range of composition, 9–42 wt % EMBA miscibility of the blends was examined by differential scanning calorimetry (DSC). The presence of the weak hydrogen bond interactions was observed and discussed. Generally, the physicomechanical properties of the PU–EMBA blends decreased with an increase of EMBA content. The present work re-

Table I Composition of the Synthesized SIPNs

Sample	PU (%)	EMBA (%)
PU	100.00	0
S-1	95.24	4.76
S-2	88.89	11.11
S-3	83.34	16.66
S-4	80.00	20.00
S-5	72.73	27.27
EMBA	0	100

ports attempts to improve the mechanical properties of PU in mixture with EMBA. For this PU-EMBA, SIPNs have been carried out and their miscibility and the physicomechanical properties were studied.

EXPERIMENTAL

Synthesis of PU

For synthesis of PU, a mixture constituted from poly(ethyleneadipate)diol (PEA) with $M_n = 2000$ and acidity index of 1.7 mg KOH/g and poly(ethylenediethyleneadipate)diol (PEDA) with $M_n = 2000$ and acidity index of 2.2 mg KOH/g was reacted with 4,4′-diphenyl-methane diisocyanate (MDI). Ethylene glycol (EG) was used as a chain extender. The molar ratio of the used components was as follows: PEA : PEDA : MDI : EG = 0.5 : 0.5 : 3.5 : 2.5. The reaction was carried out at temperatures in the range between 55 and 60°C,

time 4 h, as was previously reported.[17] The number-average molecular weight of the synthesized PU, determined from gel permeation chromatography (GPC), was $M_n = 56.000$. Calibration was performed by using monodisperse polystyrene standard samples, with narrow polydispersity (Polymer Laboratories GmbH, Darmstadt, Germany).

Synthesis of EMBA

EMBA was synthesized by a procedure described elsewhere.[16] The starting raw materials were maleic anhydride and a commercial Dinox epoxy resin. Dinox resin with epoxy equivalent to 0.54 and number-average molecular weight of 500 was obtained in reaction of bisphenol A with epichlorohydrin. The temperature of the reaction was 80°C. The number-average molecular weight of the synthesized EMBA, determined by GPC, was $M_n = 53.000$.

Preparation of PU-EMBA SIPNs

SIPNs of PU-EMBA were prepared after a sequential procedure by mixing the PU and EMBA solutions in dimethylformamide (DMF) in the desired proportions, as is shown in Table I
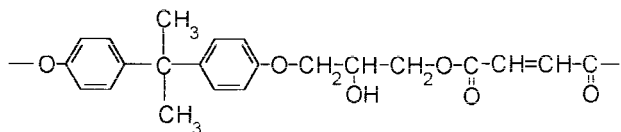
The clear solutions of PU-EMBA mixture in DMF and in the presence of benzoyl peroxide (around 0.15 wt %) were degassed in a vacuum oven at 60°C for 10 min and cast as films on glass slides by means of a doctor-blading with a slit of 0.8 mm. The transparency of the films allowed us to verify that no air bubbles remained. After the
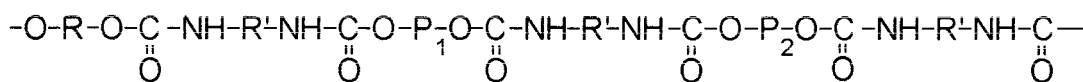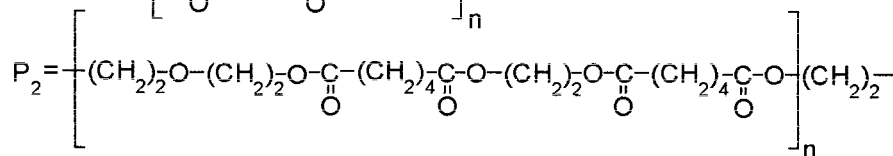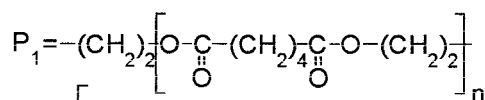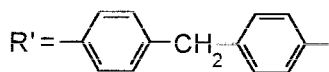
Scheme 1 Structure of PU.

Scheme 2   Structure of EMBA.

traces of solvent were completely removed, PU-EMBA mixture was thermally cured at 120°C, for 3 h. The crosslinked EMBA included in its network structure the PU linear polymer.

Characterization

The synthesized SIPNs were characterized by DSC technique by using a Mettler 12E instrument, which was heated in the range of −40 to 60°C, at a heating rate of 10°C/min., in a nitrogen atmosphere. The midpoint of the specific heat change was taken as T_g.

The physicomechanical measurements were carried out by means of TIRA-TEST 2161 apparatus, at a crosshead speed of 20 mm/min.

The effect of UV irradiation upon the synthesized SIPNs was studied by means of a device equipped with a low pressure mercury lamp, 30 W/m², and 254-nm wavelength, situated 5.5 cm away from the studied samples. The polymer films held in frames were irradiated with UV radiation at room temperature, in air.

The swelling experiments were carried out by using solvents with various solubility parameters. Strips of the samples weighing between 0.02 and 0.04 g were immersed, together with liquid under investigation, in stoppered Erlenmeyer flasks. The flasks were kept in an ultrathermostat at 25 ± 1°C and the swollen polymer was taken out after various times, dried with filter papers, and placed in a tapered flask until equilibrium swelling was obtained (8–9 days). Percentage swelling was calculated by gravimetric method.[18]

RESULTS AND DISCUSSION

The general structure of PU used in this study is shown in Scheme 1. The synthesized PU was characterized by using both IR and ^{1}H-NMR spectroscopic technique.[19] The general structure of the synthesized EMBA is shown in Scheme 2.

The cure of EMBA resin by heating at 120°C, in the presence of benzoyl peroxide and PU, was followed by IR spectroscopy. The main observation was that the band at 1640 cm⁻¹, specific to
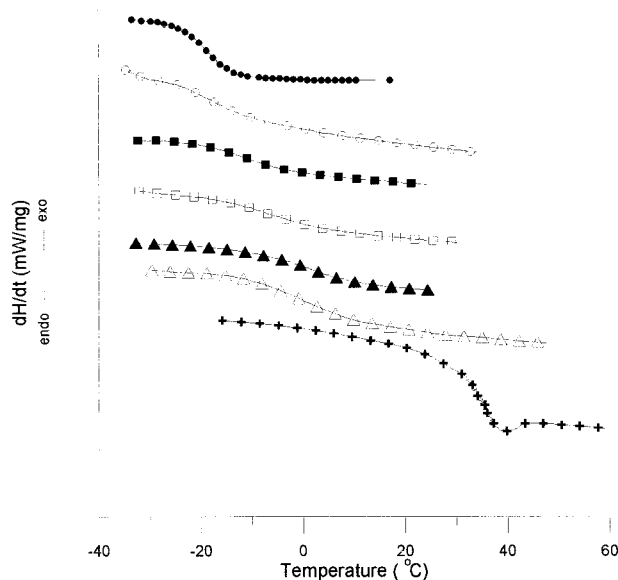
Figure 1   DSC traces of the synthesized SIPNs, PU, and EMBA: (●) PU; (○) S-1; (■) S-2; (□) S-3; (▲) S-4; (△) S-5; and (+) EMBA

the double bond from the EMBA polymer, gradually disappeared during heating. The disappearance of the double bonds pointed out that the EMBA crosslinked and passed to a network structure. As a result, a SIPN was formed, where linear PU chains interpenetrated the crosslinked EMBA polymer.

DSC Analysis

The DSC technique was used to examine the miscibility of the raw components within the synthesized SIPNs and to probe the intermolecular interactions that may be present between the component polymers.[20] Figure 1 shows the DSC traces for the synthesized SIPNs, including both the PU and the EMBA pure polymers, whereas the Table II lists the glass transition tempera-

Table II T_g's of the Studied Systems

Sample	T_g (°C)
PU	−19
S-1	−17
S-2	−11
S-3	−6
S-4	0
S-5	0
EMBA	32

Table III   Solvents with their δ_s Used for the Swelling Measurements[26]

| Number	Solvent	δ $(\text{cal/cm}^3)^{1/2}$
1.	*n*-Hexane	7.3
2.	Diethyl ether	7.4
3.	2-Ethyl, hexyl acrylate	7.8
4.	1,4-Dioxane	7.9
5.	Butyl methacrylate	8.2
6.	Butyl acetate	8.5
7.	Ethyl acrylate	8.6
8.	Toluene	8.9
9.	Ethyl acetate	9.1
10.	Benzene	9.2
11.	Carbon tetrachloride	9.2
12.	Chlorophorm	9.3
13.	Para-nonyl-phenol	9.4
14.	Acetone	9.9
15.	Cyclohexanone	9.9
16.	Ethylamine	10.0
17.	Pyridine	10.7
18.	Epichlorohydrin	11.0
19.	Isopropyl alcohol	11.5
20.	*N,N*-Dimethylformamide	12.1
21.	Ethyl alcohol	12.7
22.	Methanol	14.5
23.	Ethylene glycol	14.6

tures (T_g's) of the PU and SIPNs, respectively.

The examination of the curves in Figure 1 shows that the studied SIPNs present a single composition-dependent T_g. This behavior is evidence for good miscibility within the studied systems[20,21] and proves that the high degree of the intermolecular interactions exist between the component materials. These interactions include hydrogen bonding and van der Waals forces.[16–22] Figure 2 shows that the transition zone of EMBA is sharp, that of PU is broader, and those of SIPNs are of intermediate broadness. The peak broadening of SIPNs in Figure 2 means a good interpenetration between the two components of the mixtures.[18,23,24]

The variation of the T_g of the synthesized SIPNs against composition was examined by using the Fox eq. (1):[25]

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{1}$$

where W_1 and W_2 are the weight fractions, and T_{g1} and T_{g2} are T_g's of the two pure polymers.
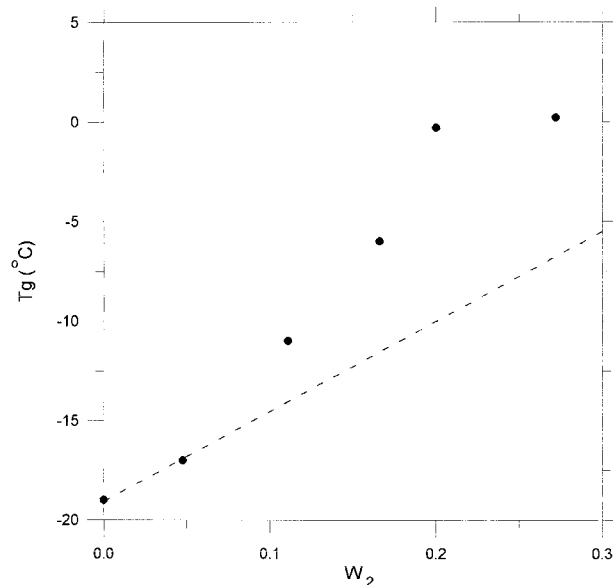

Figure 2   The T_g values (°C) of the synthesized SIPNs as a function of their composition: (●) experimental T_g values. The dotted line is a theoretical plot based on the Fox equation.

The positive deviation of T_g values from the Fox equation (Fig. 2) indicates a high degree of miscibility within the studied SIPNs and the presence of strong intermolecular interactions between the network components.[19]
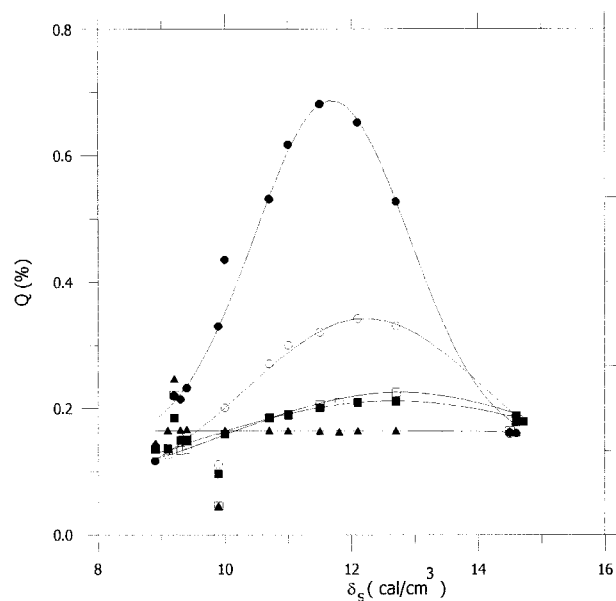
Figure 3   Variation of the swelling coefficient with the solubility parameter of the various solvents: (●) *S*-1; (○) *S*-2; (■) *S*-3; (□) *S*-4; and (▲) *S*-5.
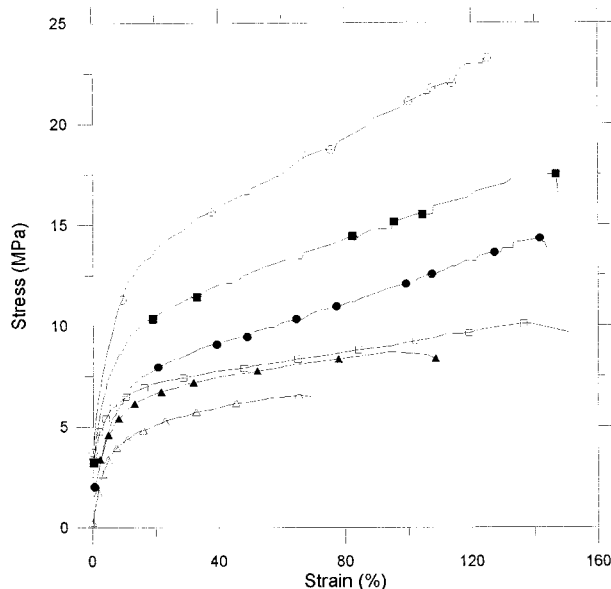
Figure 4   The stress of the synthesized SIPNs against the strain: (●) PU; (○) S-1; (■) S-2; (□) S-3; (▲) S-4; (△) S-5.

Swelling Measurements

The swelling behavior of the synthesized SIPNs was studied by using solvents with various solubility parameters (δ_s) (Table III) in accordance with the method described previously.[18]

The percentage swelling was calculated by a gravimetric method as follows[2]:

$$Q(\%) = \frac{(W_s - W_0)}{W_0} \, 100 \qquad (2)$$

where Q is the swelling coefficient, W_s is the weight of the swollen film, and W_0 is the weight of the dry film after swelling.

The results are expressed in terms of swelling coefficient, Q, as shown in Figure 3.

The maxima in the Q-δ plot give the solubility parameter of the synthesized SIPNs. The solubility parameters of the SIPNs increase with an increase of the EMBA content in the synthesized network. Simultaneously, the Q value strongly decreases with an increase of EMBA content. This behavior proves the existence of the strong interpenetrations among the PU and EMBA polymers in the formed networks.

Physicomechanical Analysis

The synthesized SIPNs were studied regarding their physicomechanical properties. As reported previously,[16] PU–EMBA blends show lower physicomechanical properties as against PU, taken alone. In contrast with the blends, the SIPNs on the basis of PU and EMBA exhibit excellent mechanical properties. Figure 4 shows the stress–strain curves recorded for both the PU and the synthesized SIPNs.

As compared to PU, the plots recorded for the synthesized SIPNs as against the EMBA content show differences in the stress values. The samples S-1 and S-2, with a content of EMBA up to 12 wt %, exhibit higher mechanical stress against PU. The stress decreases with important values for the samples having a content of EMBA higher than 12 wt %. In concordance with the stress, other mechanical properties of the synthesized samples show the same behavior in a large measure (Table IV).

The physicomechanical parameters determined for the samples S-1 and S-2, namely, the initial modulus of elasticity, the elongation at the limit of elasticity, the resistance at the limit of elasticity, the strain at the break, the resistance

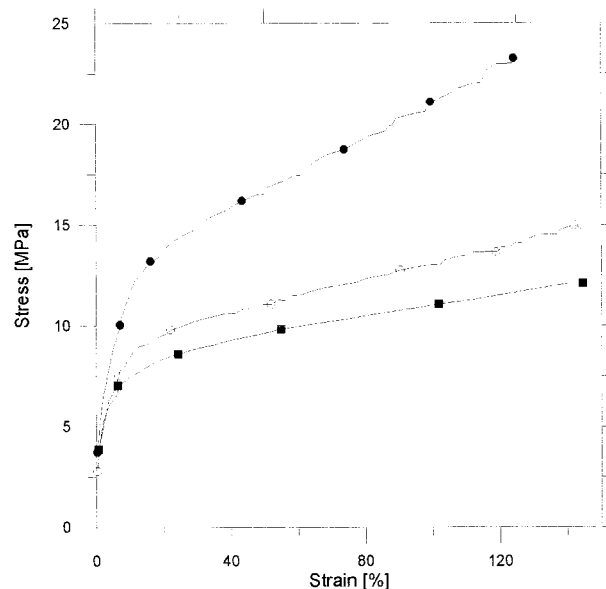**Table IV   Physicomechanical Properties of the Synthesized SIPNs**

Sample	Initial Modulus of Elasticity (MPa)	Elongation at the Limit of Elasticity (%)	Resistance at the Limit of Elasticity (MPa)	Strain at the Break (%)	Resistance at the Break (MPa)	Hardness (MPa)	Resilience (MPa)
PU	68.5	4.40	4.45	141.60	14.06	1497.4	14.875
S-1	107.8	9.60	11.30	126.00	23.14	2160.5	6.882
S-2	87.4	4.80	7.20	147.08	17.50	1984.2	4.559
S-3	75.7	3.11	5.09	149.80	9.87	903.7	5.304
S-4	50.1	5.12	4.60	106.39	8.68	803.9	5.458
S-5	84.9	2.35	2.64	69.42	6.59	374.5	5.043
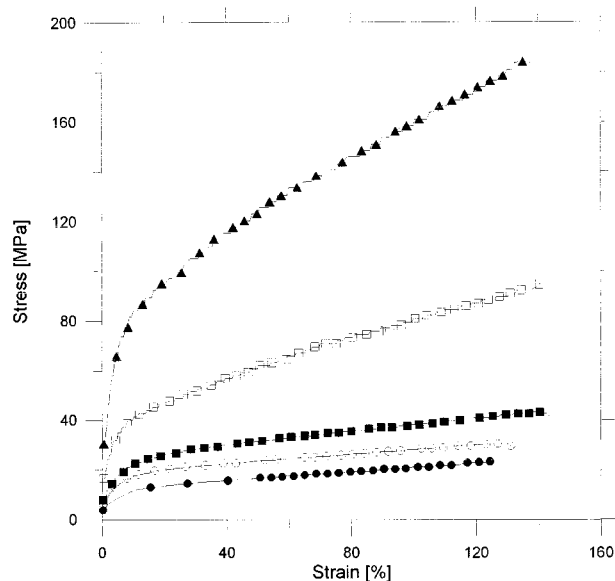
Figure 5   The stress of the sample S-1 against the strain in function of the duration of irradiation: (●) initial; (○) 2.5-h irradiation; (■) 5-h irradiation; (□) 7.5-h irradiation; and (▲) 10-h irradiation.

Figure 6   Modification of the physicomechanical properties of the sample S-1 with duration of the thermal treatment: (●) initial; (○) 5 h at 120°C; and (■) 12 h at 120°C.

at the break, and the hardness, show high values as against PU and low values for resilience. The resilience was measured by integration area under the stress–strain curve at the elastic limit stress.[27]

The change of the mechanical properties induced by irradiation was also studied. Figure 5 shows the stress–strain curves recorded for the sample S-1 by using various durations of irradiation, whereas Table V lists the mechanical properties determined for the same sample subjected to irradiation. The sample S-1 was taken for experiments with UV radiation because it has the higher initial mechanical properties against the other analyzed SIPNs.

Generally, with exception of the elongation at the limit of elasticity, the irradiated S-1 sample shows, as compared to the initial S-1 sample, a high increase in the initial modulus of elasticity (about nine times), the resistance at the break (eight times), and the hardness (eight times). This behavior suggests a high and permanent interpenetration of the PU and EMBA polymers in the networks due to some additional crosslinks generated by UV radiation.

The change of the mechanical properties with the thermal treatment can be observed in Figure 6, where the stress–strain curves are plotted for the sample S-1 at various duration of heating at 120°C.

Table V   Variation of the Physicomechanical Properties of the Sample S-1 with Duration of Irradiation

Duration of Irradiation (h)	Initial Modulus of Elasticity (MPa)	Elongation at the Limit of Elasticity (%)	Resistance at the Limit of Elasticity (MPa)	Strain at the Break (%)	Resistance at the Break (MPa)	Hardness (MPa)	Resilience (MPa)
0	107.9	9.60	11.30	126.00	23.14	2160.5	14.875
2.5	263.9	3.15	11.42	130.20	30.40	3215.0	16.550
5.0	209.7	4.99	17.62	143.33	43.30	4835.2	15.364
7.5	430.7	3.28	29.53	140.83	95.74	9491.87	15.771
10.0	945.3	3.56	58.08	139.55	184.04	18433.27	17.258

According to Figure 6, the thermal treatment of the S-1 sample leads to a decrease of the mechanical properties. This is probably due to some degradation process which starts at 120°C.

CONCLUSION

Some SIPNs based on PU and EMBA were prepared in DMF solvent and in the presence of benzoyl peroxide by heating the samples as films at 120°C for 3 h. The networks obtained by the thermal treatment include the crosslinked EMBA and the linear PU. The DSC technique showed that the synthesized SIPNs present a single composition-dependent T_g. This means good miscibility within the studied SIPNs. The existence of some strong intermolecular interactions between the network components were also emphasized. The SIPNs with EMBA content up to 12 wt % exhibit excellent mechanical properties as against PU. Under UV radiation, the mechanical properties were much improved.

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