

# A Study of Epoxy Resin–Acrylated Polyurethane Semi-Interpenetrating Polymer Networks

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**ABSTRACT:** Epoxy resin–acrylated polyurethane semi-interpenetrating polymer networks (semi-IPNs) were synthesized containing various ratios of the diglycidyl ether of bisphenol-A (DGEBA)-based epoxy resin and an acrylated aliphatic urethane oligomer. The synthesis was carried out in the presence of a mixture of triarylsulfonium hexafluoroantimonate salts as a dual photoinitiator that initiates both the cationic polymerization of the epoxy resin and the free-radical polymerization of the acrylated urethane oligomer simultaneously, upon irradiation with ultraviolet light. The simultaneous photopolymerization, followed by isothermal differential scanning calorimetry measurements, gave rise to simultaneous semi-interpenetrating polymer networks (semi-SINs). During polymerization, partial inhibition of the cationic polymerization was noticed. This was investigated by determination of the gel content and the infrared spectroscopy of the soluble fraction, after extraction of the synthesized polymer films in a Soxhlet apparatus, and by determination of the network density of investigated systems with thermal mechanical analysis. The compatibility of the components in the semi-IPNs was investigated by dynamic mechanical thermal analysis. It was found that glass transition temperatures are shifted inwardly, which indicated that the epoxy resin–acrylated polyurethane semi-IPNs were compatible. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 111–119, 1998

**Key words:** semi-interpenetrating polymer networks; ultraviolet curing; epoxy resin; acrylated urethane oligomer

## INTRODUCTION

Epoxy resins are well known for some unique properties, including outstanding adhesion to most surfaces, high mechanical strength, and chemical resistance. They have been used as adhesives, coatings, and resin matrices for advanced composites.<sup>1</sup> However, epoxy resins are too brittle

to be utilized alone, so it is useful to blend them with polyurethanes.<sup>2</sup> Polyurethanes have excellent elasticity and high impact strength; therefore, in proper ratio with epoxy resins, materials with desired mechanical and thermal properties can be produced. Hence, in this study, a blending technique is applied utilizing semi-interpenetrating polymer networks (semi-IPNs) of the two polymer components.

The objective of this study is to investigate the process of formation, thermomechanical properties, dynamic mechanical behavior, and compatibility of the components in semi-IPN systems.

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Interpenetrating polymer networks (IPNs) are a unique type of polyblend; they are defined as a combination of two or more polymers in network form that are synthesized in juxtaposition.<sup>3</sup> IPNs are therefore crosslinked polymer networks that are partially or totally physically interlocked.<sup>4</sup> IPNs can be made in many different ways.<sup>5</sup> One of them is simultaneous polymerization, which gives rise to simultaneous interpenetrating networks (SINs). SINs are generally believed to have a higher degree of intermixing compared with other IPNs since the compatibility of the starting mixture is much higher than that of a polymeric mixture.<sup>6</sup> It is known that IPNs have an important role in enhancing the miscibility of polymer blends since the physical interlocking prohibits phase separation during the IPNs polymerization process, and it is one of the methods to overcome the difficulty involved in mixing chemically incompatible polymers.<sup>7</sup>

In this study, the simultaneous polymerization method was used to synthesize epoxy resin–acrylated polyurethane semi-IPNs in the presence of a mixture of triarylsulfonium hexafluoroantimonate salts<sup>8–10</sup> as a dual photoinitiator.

## EXPERIMENTAL

### Materials

As a cationically polymerizable compound, a bisphenol-A diglycidyl based epoxy resin (Chemolepox 020 by Pevdi Ltd., Hungary) with a number-average molecular weight,  $M_n$ , equal to 1000 and an epoxy equivalent weight of 490 was selected [structure in Fig. 1(a), where  $n \cong 3$ ]. For a free-radically polymerizable compound an acrylated aliphatic urethane oligomer (Ebecryl 285, kindly supplied as a free sample by UCB Chemicals, Radcure Specialties s.a., Belgium) with  $M_n$  equal to 1200 was used. The photoinitiator was a mixture of triarylsulfonium hexafluoroantimonate salts (Cyracure UVI-6974 by Union Carbide, Belgium).

### Methods

#### Preparation

Epoxy resin–acrylated polyurethane semi-IPNs were obtained as follows. The epoxy resin was measured in a glass beaker and heated to melt. After melting of the epoxy resin, the acrylated

urethane oligomer and the photoinitiator were added into the beaker, and the reactants were homogenized by a stirrer. The homogeneous mixture was then poured into a polyester mold and irradiated by ultraviolet (UV) light from a 1500 W Fusion Systems UV source of the UV dose of  $0.1 \text{ J/cm}^2$ .

Five mixtures (semi-IPNs) were prepared with the following epoxy resin to acrylated urethane oligomer ratios: 8 : 2, 6 : 4, 5 : 5, 4 : 6, and 2 : 8. The above ratios were calculated taking into account the ratio of the functional groups of the epoxy resin (two epoxy end groups) and the acrylated urethane oligomer (two acrylate end groups). The concentration of the photoinitiator in each mixture was 1% (w/w).

#### Differential Scanning Calorimetry Measurements

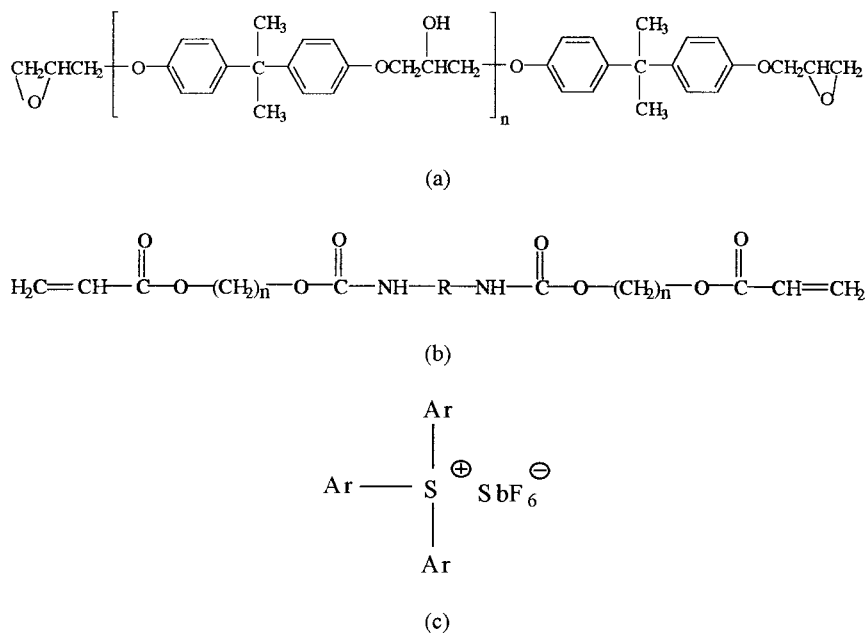
Polymerizations were performed in an aluminum crucible placed in the sample holder of the differential scanning calorimetry (DSC) apparatus under argon atmosphere (argon flow rate:  $30 \text{ dm}^3/\text{h}$ ) using 21 mg of mixture. The reference samples contained all components of the measured sample except for the photoinitiator. The samples were irradiated continuously during measurement from the distance of 30 mm by a Desaga UVIS irradiator equipped with an 8-W low-pressure mercury vapor tube with a maximum wavelength at 366 nm. The heat flux was measured by a Du Pont Instruments 910 type DSC calorimeter at  $36^\circ\text{C}$  in isothermal mode.

#### Gel Content

The insoluble fraction (gel content) of UV-cured polymers was determined by a 6-h extraction with acetone of a polymer foil in a Soxhlet apparatus. The extracted foil (gel) was dried for 16 h at room temperature and then for 4 h at  $70^\circ\text{C}$ . The gel was weighed and compared to the initial weight (before extraction) to give a gel fraction. The weight loss caused by extraction, expressed as a percent of the initial weight of the foil, was assumed as a degree of polymerization.

#### Infrared Measurements

Infrared (IR) spectroscopy was used to indicate the specific functional groups present in the soluble fraction remaining after acetone extraction of the investigated polymer films in a Soxhlet apparatus. IR measurements were carried out on a Perkin–Elmer Model 1600 FTIR with a resolution



**Figure 1** Structures of the used materials: (a) the diglycidyl ether of bisphenol-A; (b) the acrylated aliphatic urethane oligomer; (c) the general structure of triarylsulfonium salts.

of  $4 \text{ cm}^{-1}$ . A sample of the investigated extract was measured as a film between two sodium chloride ( $\text{NaCl}$ ) plates.

#### Thermal Mechanical Analysis Measurements

Thermal mechanical analysis (TMA) was used to obtain information on the network density by determination of the glass transition temperature ( $T_g$ ) of the investigated samples over the temperature range of  $-10$  to  $+100^\circ\text{C}$ , with a temperature scan of  $5^\circ\text{C}/\text{min}$ . For measurements, the Du Pont 943 TMA used was set in the penetrating mode, with a sample size of  $3 \times 3 \text{ mm}^2$ .

#### Dynamic Mechanical Thermal Analysis Measurements

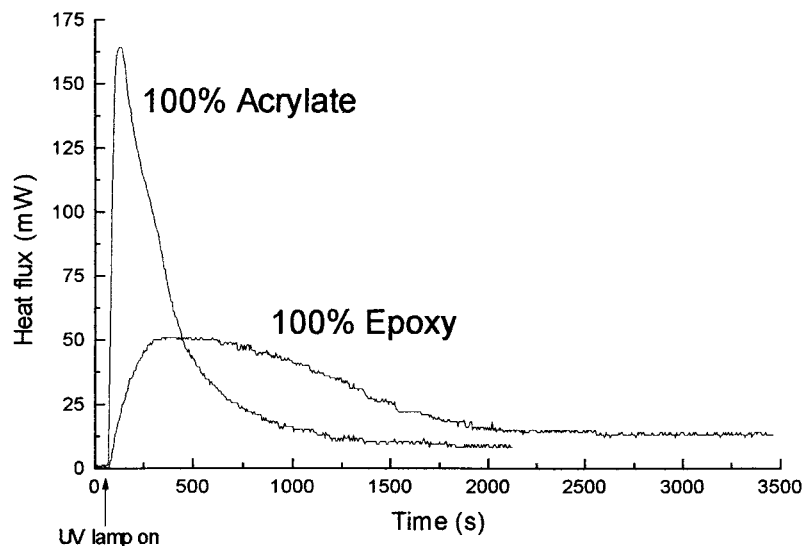
The dynamic mechanical thermal analyses (DMTA) were carried out by a Polymer Laboratories Dynamic Mechanical Thermal Analyzer Type Mk II in the bending mode over the temperature range from  $-40$  to  $+120^\circ\text{C}$ . Samples were cut from cast polymer films using an ASTM D1043 die. Measurements were carried out at a fixed frequency of  $1 \text{ Hz}$  with a temperature scan of  $2^\circ\text{C}/\text{min}$ . Data acquisition was via an IBM PC with Polymer Laboratories software.

## RESULTS AND DISCUSSION

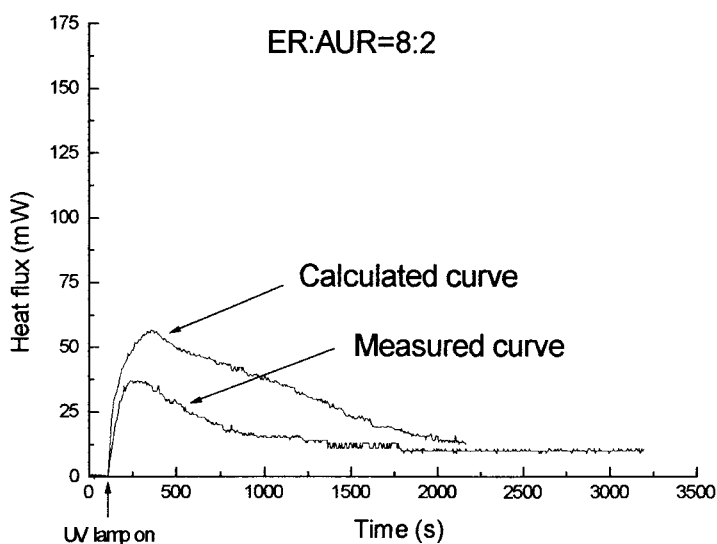
Isothermal DSC curves of the photoinduced polymerization of the investigated mixtures obtained under argon atmosphere were recorded. The measured DSC curves for the epoxy resin-acrylated urethane oligomer mixtures were then compared to the corresponding calculated ones, obtained by multiplying the individual DSC curves for pure epoxy resin and pure acrylated urethane oligomer with appropriate factors, corresponding to the proportion of the particular component in the mixture. These results are shown in Figure 2(a-f).

We have found a discrepancy comparing the measured DSC curves to the calculated ones. Namely, the areas under the measured DSC curves were always smaller than those under the calculated ones. In addition, a tendency for this discrepancy to decrease was noticed, as the proportion of the acrylated urethane oligomer increased in the mixtures. These observations are presented in Table I.

The difference of integrals of the calculated and measured DSC curves is considered as the efficiency of inhibition. As can be seen in Table I, the efficiency of inhibition shows a decreasing tendency with increasing acrylated urethane oligomer proportion. While at a ER : AUR of 8 : 2 ratio, the difference between the calculated and



(a)

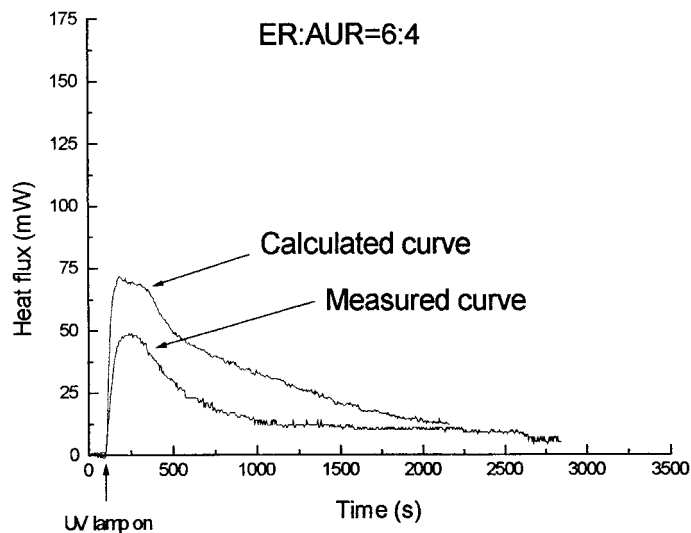


(b)

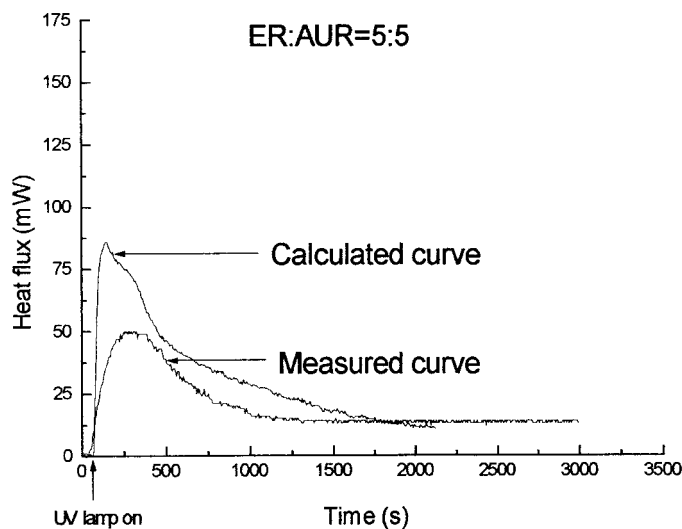
**Figure 2** Isothermal heat flux versus time DSC curves for (a) pure epoxy resin (ER) and pure acrylated urethane oligomer (AUR), (b) ER : AUR = 8 : 2, (c) ER : AUR = 6 : 4, (d), ER : AUR = 5 : 5, (e) ER : AUR = 4 : 6, and (f) ER : AUR = 2 : 8 mixtures of bisphenol-A–diglycidyl ether based epoxy resin and acrylated aliphatic urethane oligomer in the presence of a mixture of triarylsulfonium salts at 36°C irradiated continuously at a 366-nm wavelength with an 8-W low-pressure mercury vapor lamp under argon atmosphere.

measured areas was 48%; at a ratio of 2 : 8, that difference was only 4%. These results imply inhibition of cationic polymerization by the present

acrylated urethane oligomer. The acrylated urethane polymerizes via free-radical polymerization, which is much faster than the cationic poly-



(c)



(d)

**Figure 2** (Continued from the previous page)

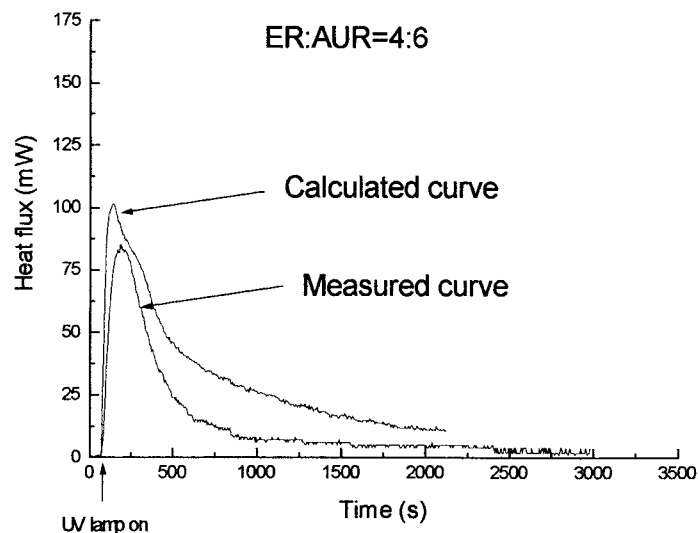
merization of the epoxy resin. Consequently, after initiation of the photopolymerization, the system quickly becomes very viscous. Due to very high viscosity, the chain mobility is hindered, so cationic polymerization cannot proceed to its full completion.

From the investigated hybrid systems, foils of the thickness of 20  $\mu\text{m}$  were prepared. All foils were optically transparent and showed no signs of

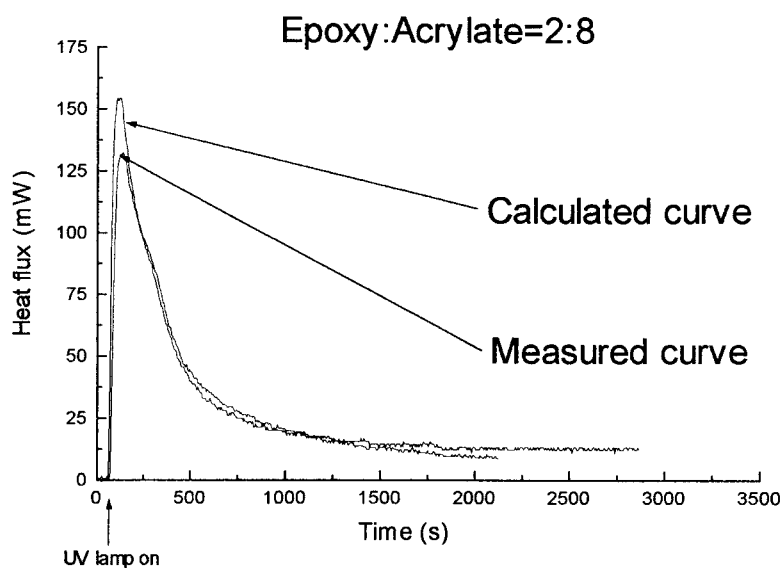
phase separation. The homogeneity of the hybrid foils indicates formation of IPNs or, in this case, SINs.

#### Inhibition Expressed Through Gel Content

Results obtained by isotherm DSC were correlated with an independent method, the determi-



(e)



(f)

**Figure 2** (Continued from the previous page)

nation of gel content. The results of gel content determination are presented in Figure 3.

The polymerizations of the two pure materials, the epoxy resin and the acrylated urethane oligomer, proceed almost to completion. The situation is, however, different with the mixtures of these two materials. The least gel content was mea-

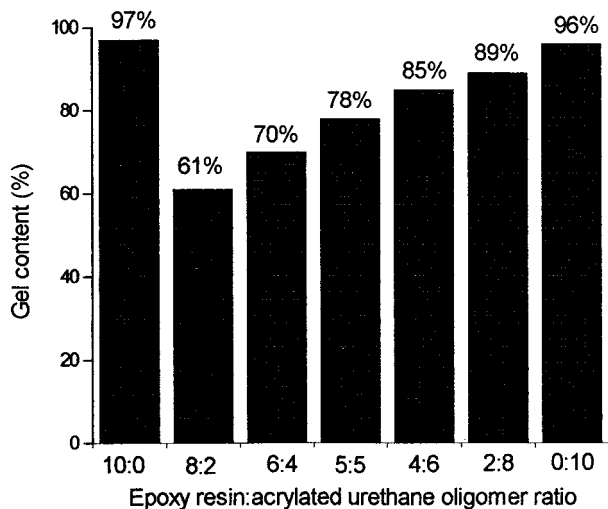
sured at a ratio of ER : AUR of 8 : 2, where the efficiency of inhibition was the largest, while at a ratio of 2 : 8, gel content was the largest among the mixtures and the efficiency of inhibition was the least. Between these two points, the gel content gradually increases with the increase of the proportion of acrylated urethane oligomer. These

**Table I Comparison of Integrals of Areas Under Calculated and Measured Isotherm DSC Curves of Various Epoxy Resin (ER): Acrylated Urethane Oligomer (AUR) Mixtures**

No.	ER : AUR Ratio	Integral of the Area Under the Measured Curves Compared to That of Calculated Curves <sup>a</sup>	Difference of Integrals of Areas Under Calculated and Measured Curves
1	8 : 2	52.0	48.0
2	6 : 4	55.3	44.7
3	5 : 5	61.2	38.8
4	4 : 6	73.4	26.6
5	2 : 8	95.6	4.4

<sup>a</sup> Integral of the area under each calculated curve was taken as 100.

results support the earlier statement that the acrylated urethane oligomer inhibits the polymerization of the epoxy resin. At a ratio of 8 : 2, the small quantity of the acrylated urethane oligomer present polymerizes upon UV irradiation, while the epoxy resin remains in the form of monomer as a soluble fraction that gets extracted by acetone. Contrary to this, at a ratio of 2 : 8, a small quantity of epoxy resin is present, so the soluble fraction is small too. This was proven by IR spectroscopy of the soluble fraction. By IR analysis, it was determined that the soluble fraction remained after a 6-h acetone extraction in a Soxhlet apparatus, consisting mainly of epoxy monomer and epoxy prepolymers with only traces of the acrylated urethane oligomer in each case, denoted by peaks at 1734 (C=O group), 2931 (R-CH<sub>2</sub>-R'), and 1460 (R-CH<sub>2</sub>-R') cm<sup>-1</sup>.

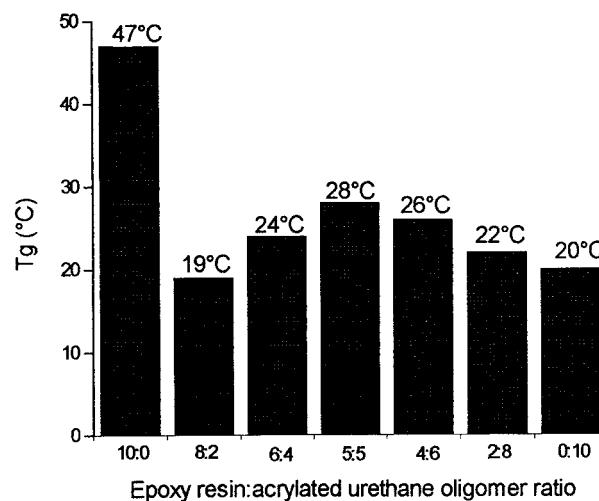


**Figure 3** Gel content of the epoxy resin-acrylated polyurethane mixtures.

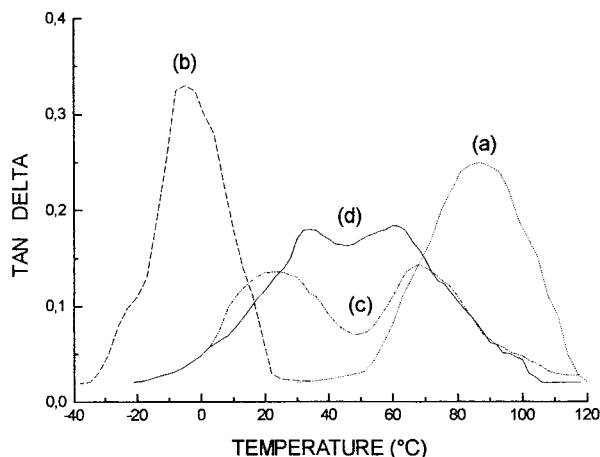
### Inhibition Expressed Through TMA Measurements

The network density of the epoxy resin-acrylated urethane semi-IPNs was characterized by their glass transition temperatures ( $T_g$ ), presented in Figure 4.

The network density is influenced by two factors. The first to be considered is the influence of the two homopolymers. The epoxy resin increases the network density, while the acrylated urethane decreases it. The second factor is the influence of inhibition, as a consequence of which semi-IPNs with high epoxy content possess a high monomer content, which plastifies the network, decreasing its density. At a ratio of 8 : 2, according to DSC and gel content data, the efficiency of inhibition and gel fraction are the largest, which indicates large quantities of monomer. Although the pro-



**Figure 4** Glass transition temperatures of the epoxy resin-acrylated polyurethane mixtures.



**Figure 5** Tan  $\delta$  versus temperature for semi-IPNs with epoxy resin-acrylated polyurethane: (a) 10 : 0, (b) 0 : 10; (c) 5 : 5; and (d) 6 : 4.

portion of the epoxy resin is the highest here, it is present mainly as a monomer and, thus, instead of increasing, it decreases the network density of this mixture. At ratios of 6 : 4 and 5 : 5, the epoxy resin proportion gradually drops, which decreases the network density and, at the same time, the efficiency of inhibition decreases, which increases the network density. At ratios of 4 : 6 and 2 : 8, the network density decreases because the epoxy resin proportion further drops, which, as it seems, has more influence on the network density than the decreasing efficiency of inhibition.

### Dynamic Mechanical Properties

The glass transition temperature ( $T_g$ ) was measured from the peak temperature of tan  $\delta$  curve. When two polymers are mixed, the dynamic mechanical behavior shows two distinct transitions, indicating the incompatibility between the two polymers. As the compatibility increases, the two  $T_g$ s shift toward each other and the damping curve (tan  $\delta$ ) becomes broader.<sup>11</sup> The dynamic mechanical behavior of the epoxy resin-acrylated polyurethane IPNs at various epoxy resin contents is shown in Figure 5. The peak temperatures of tan  $\delta$  curve of pure component epoxy resin and acrylated polyurethane were 87 and  $-5^\circ\text{C}$ , respectively [Fig. 5(a,b)].

Figure 5(c) indicates that when the epoxy resin-acrylated polyurethane system is at a ratio of 5 : 5, it shows two  $T_g$ s that are shifted inward by  $19^\circ\text{C}$  for the epoxy domain and by  $28^\circ\text{C}$  for the acrylated polyurethane domain starting from the

$T_g$ s of the pure components. In addition, Figure 5(d), shows that when the epoxy resin-acrylated polyurethane semi-IPNs system is at a ratio of 6 : 4, it shows two  $T_g$ s, shifted inward by  $27^\circ\text{C}$  for the epoxy domain, and by  $39^\circ\text{C}$  for the acrylated polyurethane domain. The inward shifting of the two  $T_g$ s in the epoxy resin-acrylated polyurethane semi-IPNs system implies that the compatibility between the epoxy resin and acrylated polyurethane would be improved due to the formation of epoxy resin-acrylated polyurethane semi-IPNs.

### CONCLUSION

The experimental findings based on isotherm DSC measurements imply that the IPN formation is followed by partial inhibition of cationic polymerization. On the basis of our analysis of heat flux changes and comparison of integrals under the isotherm DSC curves for various mixtures of the epoxy and the acrylated monomer, we concluded that the partial inhibition of cationic polymerization of the epoxy resin is caused by fast polymerization of the acrylated urethane oligomer. This was proven by gel content determination, IR spectroscopy of the soluble fraction after extraction of the synthesized polymer films in a Soxhlet apparatus, and determination of the network density of investigated systems with TMA. The compatibility of the components in the semi-IPNs was investigated by DMTA. It was found that glass transition temperatures are shifted inwardly, which indicated that the epoxy resin-acrylated polyurethane semi-IPNs were compatible.

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