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GRAFT COPOLYMER NETWORKS OF POLYURETHANE AND EPOXY STRUCTURES—I. DYNAMIC MECHANICAL PROPERTIES

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Abstract—The dynamic mechanical properties of polyurethane (PU) grafted epoxy polymer networks have been investigated. The glass transition region is successfully broadened on variation of the degree of phase separation. The tensile strength initially increases with increasing PU content and reaches its maximum value when the PU/epoxy ratio is about 20/80.

INTRODUCTION

Epoxy resins are important engineering polymeric materials that possess high elastic modulus and glass-transition temperatures. Many papers treat the modification of the epoxy structure to improve its fracture toughness, flexibility, impact strength and mechanical properties [1–3]. However, the dynamic mechanical behaviour of the modified epoxy resin has received less attention.

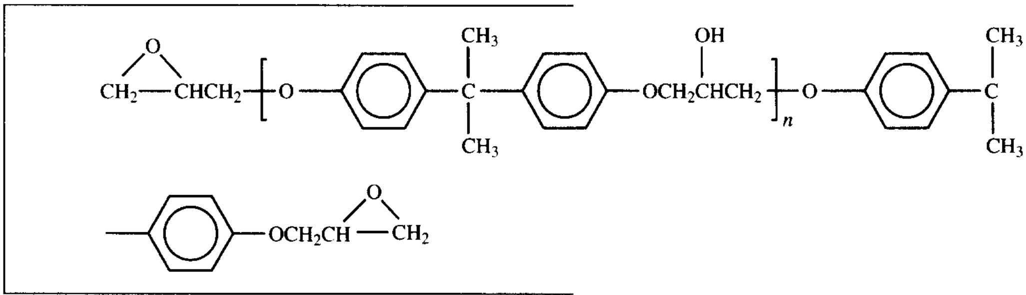
A homogeneous copolymer system shows a single T_g that can be predicted according to the Fox equation. A normal polyblend, due to thermodynamic incompatibility, shows two separate T_g. Both systems may contain a damping area slightly, but not significantly, broader than that of the individual components. For the past 20 yr, interpenetrating polymer networks, IPN, have been extensively studied [4, 5]. These may, but not invariably, broaden the damping peak corresponding to the degree of phase separation [6, 7].

We attempted to graft the epoxy resin matrix using poly(oxypropylene) glycol as the reactive reagent. The graft copolymers were then crosslinked with MDA (4,4′-methylene dianiline). The resulting materials were examined by dynamic mechanical analysis, scanning-electron microscopy, differential scanning calorimetry and tensile testing.

EXPERIMENTAL

Materials and synthesis

The epoxy resin is the diglycidyl ether of bisphenol A (DGEBA, Epon 828)



in which n is the number of repeat units in the resin chain. The polyol (PPG-400, Mn = 400 g/mol, Chiunglong Co.) and DGEBA were dried at 80 and 100°C under vacuum for 4 hr, respectively. The chain extender TDI (Toluylene-2,4-diisocyanate, Aldrich) and hardener MDA (Dow Chemical) were used as received.

To prepare graft copolymers, varying amounts of TDI were added to DGEBA (NCO/OH > 2). The temperature was maintained at 25° for 8 hr and then 70° for another 4 hr under nitrogen to allow urethane reaction between TDI and the secondary hydroxyl group of DGEBA to occur. Because excess TDI was used, unreacted NCO groups remained in the mixture. Then the polyol with stoichiometric equivalent of free TDI was mixed with the mixture at 25° for 8 hr and 70° for another 4 hr under nitrogen. The graft copolymer was then characterized by gel-permeation chromatography (GPC).

To synthesize graft PU/epoxy networks, MDA was melted at 120°, then mixed with the same equivalent (based on epoxide groups) of graft copolymer. After degassing for 10 min, the mixture was poured into a hot mould (120°) and cured for 2 hr. The specimens were then step-cured at 150° for 2 hr and 180° for another hour. The basic formulations for graft PU/epoxy networks are listed in Table 1.

Testing methods

The mechanical properties were determined on a Tensile Tester (Instron Model 1137) according to ASTM D-638 with a crosshead speed 5 cm/min.

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Table 1. Formulations of PU/epoxy graft copolymer

Designation	Epon 828	PPG-400	TDI	MDA
P0E100	100			26.20
P10.7E89.3	100	8.33	3.63	26.20
P23.0E77.0	100	20.83	9.06	26.20
P37.4E62.6	100	41.67	18.13	26.20
P47.3E52.7	100	62.50	27.19	26.20
P54.5E45.5	100	83.33	36.25	26.20
P60.2E39.8	100	105.25	45.78	26.20

A differential scanning calorimeter (DSC-2, Perkin–Elmer) was used to measure the glass transition temperature (T_g) of a specimen. The measurements were carried out from −60 to 200° under N_2 gas with a heating rate 10°/min.

The molecular weight of the graft copolymer was analysed using a Gel Permeation Chromatograph (Millipore/Waters Model 150 C). The instrument contains a combination of four columns of microstyragel with pore sizes 10^5, 10^4, 10^3, and 500 Å. All measurements were carried out at 30°, with THF as solvent. The flow rate was 1.0 ml/min.

The dynamic properties were measured on a Rheometrics Dynamic Spectrometer Model 7700. The measurements were made at temperatures in the range −140 to 210° with a heating rate 5°/min and a frequency 1 Hz. The morphology of the graft copolymers was examined by scanning-electron microscopy.

RESULTS AND DISCUSSION

Epon resin 828 is a resinous blend with approximate 86 mol.% of small molecular weight species ($n = 0$) and 14 mol.% of medium molecular weight species ($n = 1$). A typical gel-permeation chromatography result for P0E100 (without diamine) is shown in Fig. 1. The distribution curve has two peaks: the first peak eluting about 38 min is the medium molecular weight species, whereas the other peak at 40 min is the small molecular weight species. As copolymerization was carried out utilizing the secondary hydroxyl groups in the medium molecular weight species, the peak eluting at 38 min can be used as a reference of the extent of the reaction. As an example of P54.5E45.5 (without diamine) (Fig. 2), the first peak diminished but the second peak remained the same. A broad peak in the range 26–38 min was observed in the graft copolymer; this feature indicates that the reaction increases the molecular weight of the medium molecular weight species. Combined with the above observations, the increase in viscosity of the reaction mixture after graft copolymerization and molecular weight obtained from GPC (Table 2) confirmed that the polyol was grafted to the epoxy resin.

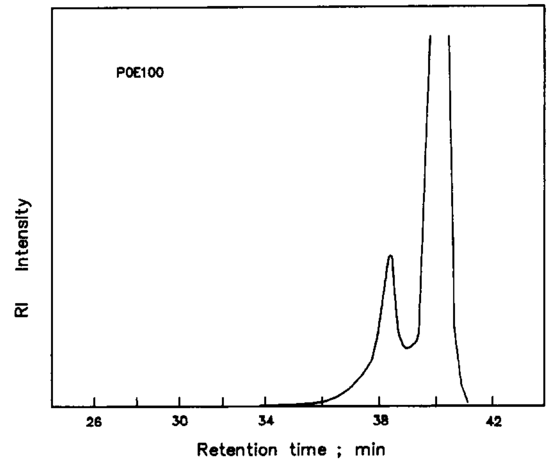

Fig. 1. Gel permeation chromatogram of DGEBA resin.

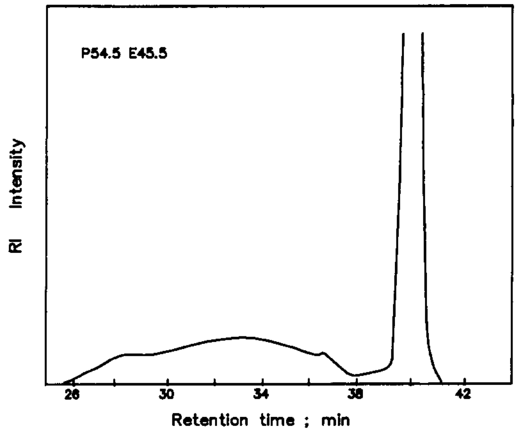

Fig. 2. Gel permeation chromatogram of P54.5E45.5 graft copolymer.

Table 2. Viscosity and molecular weight of the reaction mixture before and after graft copolymerization

Sample	Viscosity (Brookfield) (poise) at 70°	$\overline{Mn}$ (g/mole)	$\overline{Mw}$ (g/mole)
P0E100	2.4	359	428
P10.7E89.3	6.4	425	2323
P23.0E77.0	12.0	447	5819
P37.4E62.6	17.0	497	5446
P47.3P52.7	32.0	580	7447
P54.5E45.5	113.6	658	12623
P60.2E39.8	192.0	768	6527

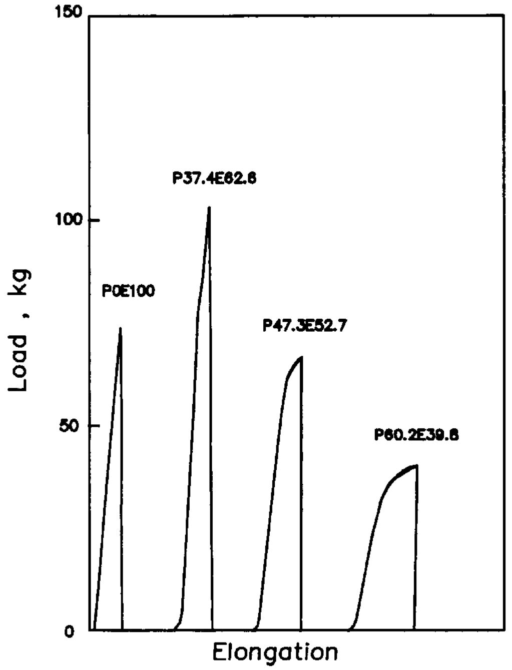

Fig. 3. The characteristic stress–strain diagrams for PU/epoxy graft copolymer.

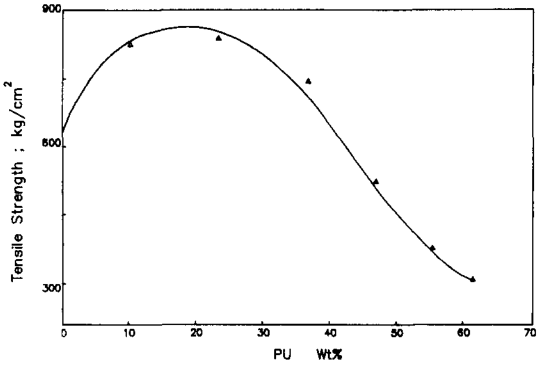

Fig. 4. Tensile strength of PU/epoxy graft copolymer.

Figure 3 shows characteristic stress–strain diagrams for various graft copolymer networks. The initial modulus and elongation gradually changed according to the PU content. The tensile strength of the graft copolymer networks is shown in Fig. 4. The value increased with PU content and reached its maximum value when the PU/epoxy ratio was about 20/80. This improvement may possibly result from the fact that the long grafted chains served as a plasticizer that may increase the flexibility of the polymer network. A similar result was observed by Frisch and coworkers from IPN samples [6, 8, 9]. However, too long grafted PU chains or ungrafted chains greatly decreased the crosslinking density; the tensile strength was then decreased.

DSC curves for DGEBA and the graft copolymers appear in Fig. 5. For the pure epoxy resin, the glass transition temperature is 154°. For the graft copolymers, the glass transition region is gradually broadened corresponding to the PU content. In most cases, except P60.2E39.8, only one T_g was observed.

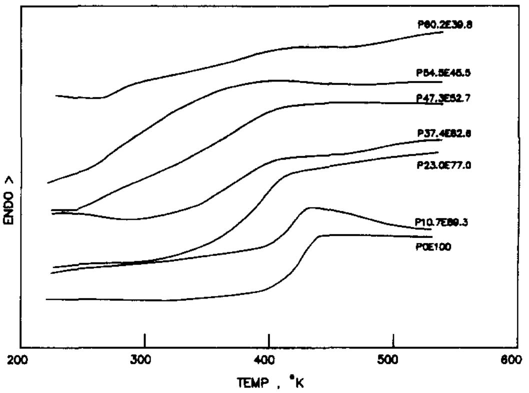

Fig. 5. DSC curves of PU/epoxy graft copolymer.

Table 3. Glass transition temperature of PU/epoxy graft copolymer

Sample	T_gIII	T_gII (RDS), °C	T_gI	T_g (DSC), °C	
P0E100	−67	69	164	154	—
P10.7E89.3	−70	58	154	146	—
P23.0E77.0	−72	—	128	113	—
P37.4E62.6	−80	7	118	97	—
P47.3E52.7	−75	8	121	54	—
P54.5E45.5	−78	6	122	34	—
P60.2E39.8	−76	8	122	3	75

The polyblends with phase separation invariably have two distinct transition peaks. Thus the components appear to have some mutual solubility (or the second phase has a small domain). The measured T_g (midpoint of the transition region) are listed in Table 3.

Plots of tan δ vs temperature for DGEBA and the PU/epoxy graft copolymers appear in Fig. 6. Our result agrees with those of previous research [10] except that an extra medium temperature transition

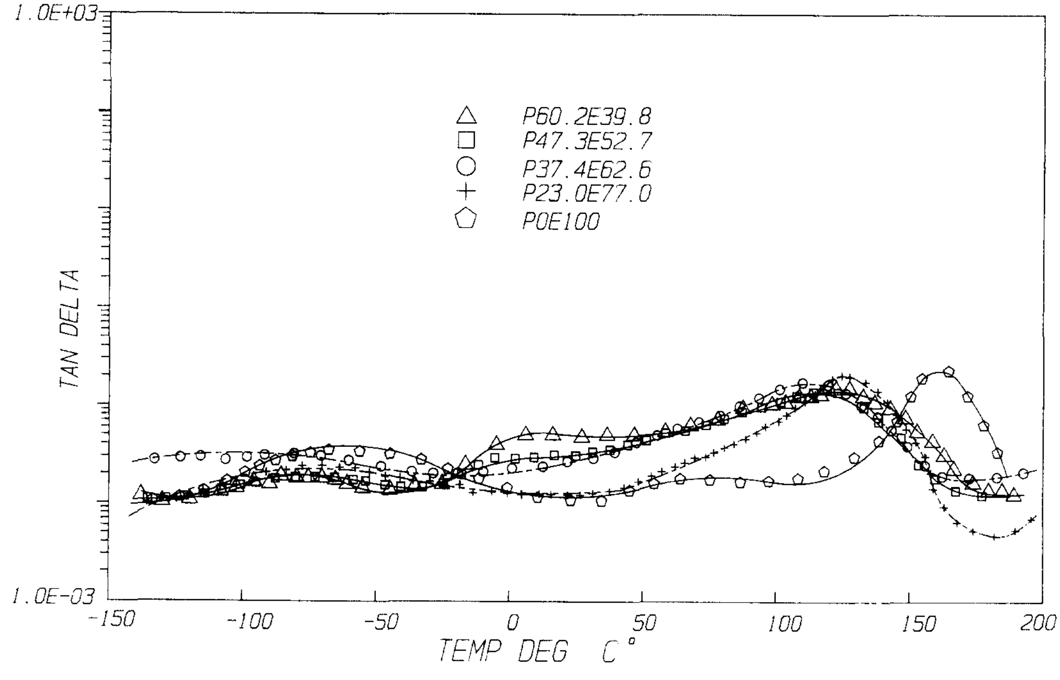

Fig. 6. Loss tangent as a function of temperature.

region was observed near 70°. The three peaks occur at -65 (T_gIII), 69 (T_gII) and 164° (T_gI), respectively. An extension to the dynamic mechanical plots of epoxy cured with MDA was made by Murayama and Beli, who noted that the low-temperature transition was related to the diglycidyl ether portion of the molecule, and the high-temperature transition was influenced by substituents on the central carbon bridge of the bisphenol portion of the molecule [11]. Incorporation of PU in the DGEBA decreased the glass transition temperature. (The data are also summarized in Table 3.) This result also indicates the mutual compatibility of PU and epoxy resin. It is interesting to note that the intensity of the medium temperature transition region increased and overlapped with the T_gI transition region corresponding to the PU content. The detailed mechanism will be evaluated and discussed by solid-state NMR in our next paper. In addition, all glass transition temperatures reach a minimum value at the PU/epoxy ratio

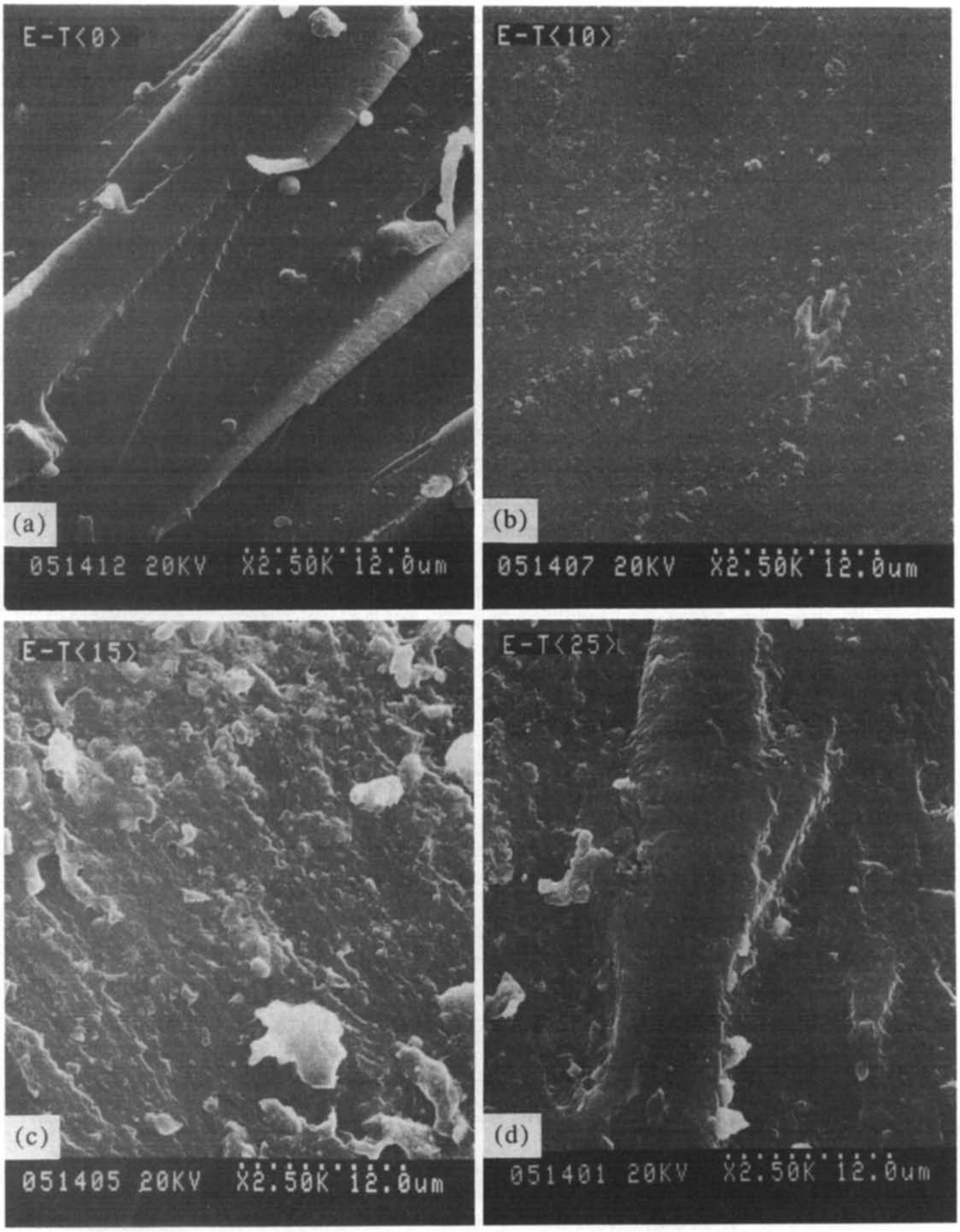

Fig. 7. SEM micrographs of PU/epoxy graft copolymer. (a) P0E100; (b) P37.4E62.6; (c) P47.3E52.7; (d) P60.2E39.8.

37.4/62.6. Continued increase of PU in the graft polymer could not change the glass transition temperature any further. This result indicates that the graft polymer forms a homogeneous system when the PU/epoxy ratio was less than 37.4/62.6. On further increase of PU content, the extra portion of PU gradually separated from the matrix and formed microdomains. Scanning-electron micrographs of the fractured surfaces appears in Fig. 7; phase separation is clearly seen in samples with PU/epoxy ratio graeter than 37.4/62.6 [Fig. 7(c) and 7(d)]. The observations are in good agreement with the above results.

CONCLUSION

Polymer systems with broad and high glass transition temperature regions are effective absorbing materials, because they cover a wide temperature/frequency range of high energy absorption during vibration. Our study of PU/epoxy graft copolymers has shown various degrees of phase separation which can successfully broaden the glass transition region without sacrificing its peak height.

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