

# Polyurethane Acrylate/Epoxy–Amine Acrylate Hybrid Polymer Networks

M. R. JEAN, I. HENRY, M. TAHA

Laboratoire des Matériaux Macromoléculaires, UMR CNRS No. 5627, Institut National des Sciences Appliquées de Lyon, Bât 403, 20, Avenue A. Einstein, 69621 Villeurbanne Cedex, France

Received 13 January 1999; accepted 14 April 1999

**ABSTRACT:** New classes of hybrid polymer networks (HPNs), having variable polyurethane acrylate (PUA) and epoxy–amine acrylate (EAA) compositions, were prepared using initially miscible systems in methyl methacrylate (MMA). The initial systems were based on PUA prepolymer and EAA monomer solutions in MMA. HPNs were a result of epoxy–amine and radical polymerization competition. Phase separation occurred during the course of HPN formation. Mechanical dynamic analysis of the prepared HPNs showed good affinity between the PUA and PMMA phases and lower affinity between the EAA and PMMA phases. Mechanical property evolution and transmission electronic microscopy showed that, for all the composition ranges used in this study (PUA/EAA/PMMA 15/45/40–45/15/40 wt %), the PUA-rich phase was the continuous phase. EAA-rich phases, 20–50 nm, in the PUA-rich matrix were obtained for HPNs containing up to 30 wt % EAA. For higher EAA concentration (45 wt %), 2  $\mu$ m EAA-rich phases were obtained in the PUA-rich matrix. A substructure was also observed in each phase. PUA/EAA copolymers were prepared and used successfully for the compatibilization of the different phases of the HPNs. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2711–2717, 2000

**Key words:** hybrid polymer networks; polyurethane acrylate (PUA); epoxy–amine acrylate; synthesis; mechanical properties

## INTRODUCTION

To improve the performance properties of polymeric materials and to satisfy the chemical and physical properties required in various applications, multiphase polymeric systems have been extensively used for more than three decades.<sup>1–4</sup> The particular type of polymer blend, concerning two or more polymer networks, that polymerizes and/or crosslinks in the presence of one another is usually called an interpenetrating polymer net-

work (IPN).<sup>5,6</sup> IPNs have received much attention in both scientific and industrial studies. In these systems, a permanent entanglement as well as chemical bonding can occur between the different phases of the system, which can play a significant role in the modification of the structure and interfacial adhesion phase of separated IPN materials. Many investigations on their morphology, mechanical properties, and transitional behavior have been published. When the IPN is composed of a backbone polymer containing two types of reactive groups that can take part in crosslinking reactions with different mechanisms, a hybrid polymer network (HPN) is obtained. Acrylated polyurethane (PUA) and acrylated epoxy–amine (EAA) prepolymers can be prepared using a one-step method.<sup>7–10</sup> For PUA synthesis, a polyalco-

Correspondence to: M. Taha, Laboratoire de Rhéologie des matières plastiques, Université Jean Monnet, Faculté des Sciences et Technique, 23 rue P. Michelon, 42023 Saint-Etienne Cédex 2, France.

*Journal of Applied Polymer Science*, Vol. 77, 2711–2717 (2000)  
© 2000 John Wiley & Sons, Inc.

hol reacts with a diisocyanate in the presence of a monoalcohol acrylate, that is, hydroxyethyl acrylate (HEA). HEA, acting as a chain-termination agent, prevents gelation and introduces double bonds that can react in a subsequent step by free-radical polymerization, leading to a network. Equivalent reactions based on a diepoxy, diglycidyl ether of bisphenol A (DGEBA), a diamine, and an acrylated epoxy glycidyl methacrylate (GMA) lead to an EAA. An HPN based on EAA and PUA can take advantage of the high modulus and tensile strength of EAA and the high impact strength of PUA-based networks.

This article concerns the synthesis of a PUA/EAA-based HPN. The influence of the HPN composition on the morphology evolution and on the thermal and mechanical properties was examined. Since PUA and EAA are very viscous prepolymers, methyl methacrylate (MMA) was used as a reactive diluent to reduce the viscosity of the initial blends.

## EXPERIMENTAL

### Materials

The hydroxy-terminated polybutadiene (HTPB) used was Elf-Atochem (France) R45HT,  $\overline{M}_n = 2830 \text{ g mol}^{-1}$ ,  $\overline{M}_w = 7190 \text{ g mol}^{-1}$ ,  $f_n = 2.5$ ,  $f_w = 2.93$ . The DGEBA used was Ciba (France) LY 556 with an epoxy equivalent of 188 g. The 4,4'-diaminodicyclohexyl methane (PACM) used was Anchor (France) Amicure. *m*-Tetramethyl xylene diisocyanate (TMxDI) was supplied by Cyanamid (France). The other reactants and monomer were from Fluka (France). When not specified in the text, the reactants were used as received without any further purification.

### Apparatus

Fourier transform infrared spectroscopy was performed using a Nicolet Magna-IR 550 spectrometer. An Ever-Glo source was used along with a KBr beamsplitter and a DTGS-KBR detector. For liquid reactants, the windows for the transmission cell were KBr discs. No spacer was used because of the need for a very small sample path length. For network analysis, specimens were ground up (cryogenic milling) and mixed with KBr. Cells were then prepared and analyzed. A Mettler TA3000 was used for DSC analysis at a 10°C/min heating rate under nitrogen. Size-exclusion

chromatography (SEC) was performed using a Waters 510 device equipped with UV and refractive index detectors. The solvent was THF at a 1 mL/min flow rate and a pressure of  $3 \times 10^3 \text{ Pa}$ . Three Millipore microStyragel HR1, HR2, and HR3 columns were used. Number- and weight-average molar mass were calculated using calibration from polystyrene standards. Transmission electron microscopy (TEM) was done with a Philips CM 120 apparatus. Specimens with 30 wt % or more PUA were microtomed at  $-80^\circ\text{C}$ . The others were microtomed at room temperature. Specimens were stained with osmium tetroxide before analysis.

The dynamic mechanical spectra of networks were recorded in the tension mode using an RSA II viscoelasticimeter (from Rheometrics) at 1 Hz. The storage ( $E'$ ) moduli, loss moduli ( $E''$ ), and the loss factor ( $\tan \delta$ ) were recorded as a function of the temperature. Specimen geometry was typically  $35 \times 5 \times 2 \text{ mm}^3$ .

The stress-strain properties were tested at  $25^\circ\text{C}$  on a J. J. Loyd M30K tensile tester equipped with a Laserscan laser extensometer. Test specimens were prepared in the form of microtensile test specimens according to the ISO 60 standard.

### PUA Synthesis

Reactions were processed in a four-neck flask equipped with a mechanical stirring apparatus and heated in an oil bath at  $70^\circ\text{C}$ . The HTPB (2 mol) was first introduced into the flask and degassed for 5 h under a vacuum ( $10^{-1} \text{ mmHg}$ ). The vacuum was then stopped and HEA (5 mol), dibutyltin dilaurate ( $5 \times 10^{-3} \text{ mol}$ ), hydroquinone ( $10^{-3} \text{ mol}$ ), and MMA (40 wt %) were then introduced. When the temperature was completely stabilized, TMxDI (5 mol) was added. The reaction was then conducted under argon for 7 h.

### PUA/EAA Hybrid Synthesis

To the PUA prepared as mentioned above, DGEBA (1 mol), GMA (6 mol), hydroquinone ( $10^{-3} \text{ mol}$ ), and MMA (40 wt %) were introduced. The system was stirred at room temperature until complete homogenization was achieved. *para*-Toluene sulfonic acid (EAA condensation catalyst; APTS, 0.6 wt %) and then PACM (2 mol) were introduced. As soon as the reactive system was homogeneous (1 min), it was transferred to molds ( $10 \times 10 \times 2 \text{ mm}$ ) and allowed to react at  $130^\circ\text{C}$  at 50 bar pressure for 8 h.

### Emulsifier Synthesis

Two methods were used for the synthesis of the emulsifier. In the first one, PUA was prepared as mentioned above using an excess of isocyanate (10%). EAA monomers were then added with an amine excess (10%). The reaction was carried out for 8 h at 50°C, leading to copolymer 1. In the second method, the EAA monomers were allowed to react at 50°C for 1 h (epoxy conversion 0.5), then added to the PUA prepolymer. The reaction was then conducted for 7 h at 50°C, leading to copolymer 2. The same stoichiometry was used in both syntheses. MMA concentration was 40 wt %.

## RESULTS AND DISCUSSION

### Reactive System

Details concerning the different syntheses are given in the Experimental part.

### PUA and EAA Synthesis

TMxDI-based PUA was prepared in 40 wt % MMA. The HTPB/TMxDI/HEA stoichiometry used was 0.5/1/0.5. The reaction was conducted at 80°C using dibutyltin dilaurate as a catalyst and hydroquinone as a radical polymerization inhibitor. The SEC of this prepolymer showed that 5 wt % of the HEA/TMxDI/HEA diadduct was obtained (elution time = 26.1 min). The obtained product characteristics were  $\overline{M}_n = 5700 \text{ g mol}^{-1}$  and  $\overline{M}_w = 33300 \text{ g mol}^{-1}$ . The FTIR analysis showed also the existence of 5% residual isocyanate functions at  $2250 \text{ cm}^{-1}$ .

The EAA was also prepared in 40 wt % MMA. The DGEBA/PACM/GMA stoichiometry used was 2/8/6. The reaction was conducted at 60°C using hydroquinone as radical polymerization inhibitor. A complete epoxy conversion was obtained after 18 h of reaction. A viscous prepolymer with  $\overline{M}_n = 2400 \text{ g mol}^{-1}$  and  $\overline{M}_w = 6800 \text{ g mol}^{-1}$  was obtained.

### Initial Solubility

Solubility tests were first made for the choice of the reactive system to be used for the HPN synthesis. It was found that even if each of the acrylates (PUA or EAA) is soluble in MMA, PUA/EAA/MMA blends were heterogeneous. The use of such reactive systems for the synthesis of the HPN can lead to very heterogeneous blends (macrophase

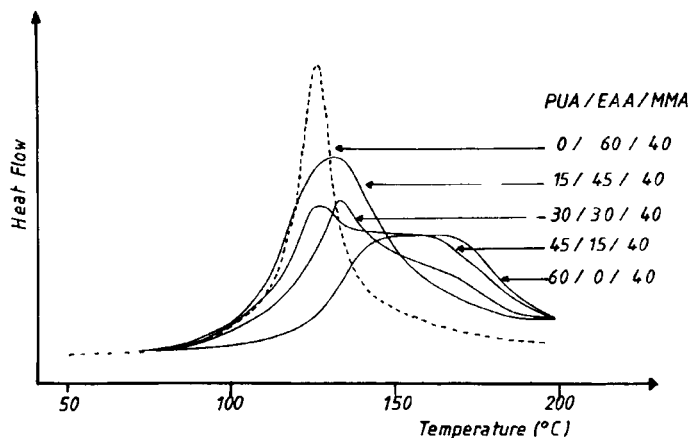
separation). In addition, since the initial morphology of the ternary blend will depend on several parameters (sedimentation, effectiveness of the mixing operation, temperature, etc.), the reproducibility of the experiments is expected to be insufficient. For these reasons, initially homogeneous systems were preferred in this study for which phase separation should occur only during the course of HPN formation. Such systems can be based on a PUA solution in the EAA monomers (DGEBA-GMA-PACM) and MMA. For PUA/EAA/MMA with a composition range from 15/45/40 to 45/15/40 wt %, limp and time-stable solutions were obtained. This system also takes advantage of the residual isocyanate in the PUA synthesis that can react easily with amine functions, leading to chemical bonding and to better interfacial adhesion.

### Free-radical and Condensation Reactions

Since two reactions are involved in the hybrid synthesis, and if the free-radical reaction takes place before the condensation reaction, the latter may be slowed down, so reaction conditions were chosen so that an almost complete epoxy-amine reaction was achieved before the radical polymerization. In preceding studies concerning EAA synthesis,<sup>7,8</sup> kinetic studies showed that, for the EAA synthesis catalyzed using 1 wt % APTS, complete reaction at 130°C is obtained within 5 min. Since  $t_{1/2}$  of TBP is around 40 min at 130°C, the EAA condensation reaction should occur more readily than does the radical polymerization. In Figure 1, DSC runs in the temperature sweep mode corresponding to the above-mentioned system are given. A clear separation of the two reactions is obtained. From this observation, one can reasonably assume that EAA condensation takes place before radical polymerization. This was also confirmed by an FTIR kinetic study at 130°C (Fig. 2). The epoxy band at  $863 \text{ cm}^{-1}$  and the acrylate band at  $810 \text{ cm}^{-1}$  evolution was analyzed using the C-H band at  $2870\text{--}2970 \text{ cm}^{-1}$  as the reference band. Here, also, it can be seen that EAA condensation occurs before the radical polymerization. This shows that the reactive system reaction temperature is coherent with the above-mentioned HPN elaboration strategy.

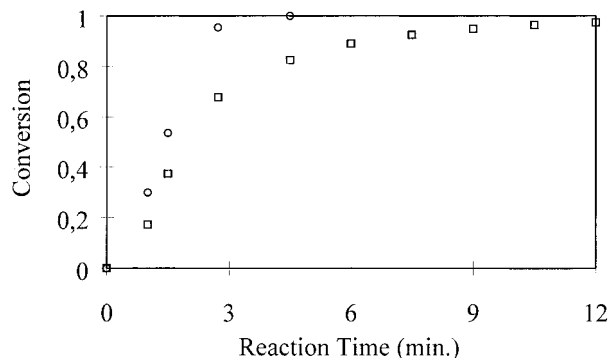
### HPNs

HPNs with different compositions were prepared. DSC analysis of these networks did not present

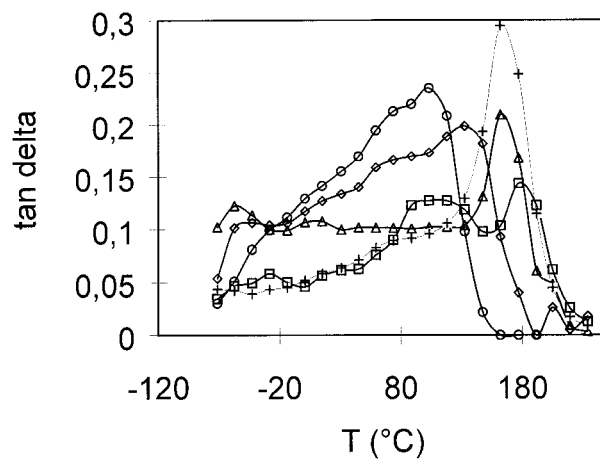


**Figure 1** DSC runs, scanning mode at  $10^{\circ}\text{C}/\text{min}$ , corresponding to HPN synthesis with variable PUA/EAA/MMA compositions using 0.5 wt % *ortho-para*-toluene sulfonic acid and *tert*-butyl perbenzoate. The initiator-to-double-bond molar ratio was  $10^{-3}$ .

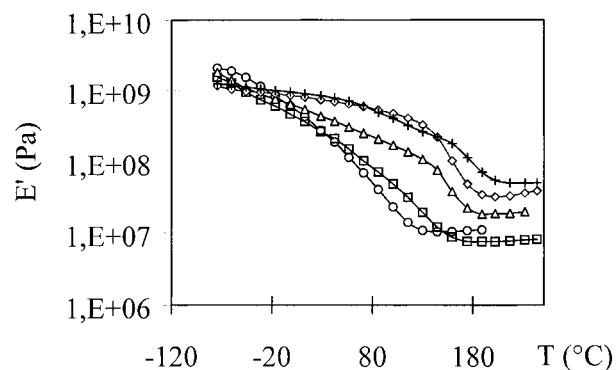
any residual reaction heat, showing that reactions were completed. FTIR analysis also showed complete conversions of epoxy and acrylate functions. Mechanical dynamic analyses were performed on these materials. Shown in Figure 3(a,b) are the storage modulus ( $E'$ ) and the loss factors ( $\tan \delta$ ). For the PUA/MMA network, a regular decrease of  $E'$  with the temperature was obtained and only one large  $\tan \delta$  peak was observed. This shows high interlocking of PUA and PMMA networks. For PEAA/MMA networks,  $E'$  shows two clear transitions and  $\tan \delta$  shows two distinct peaks corresponding to a PMMA-rich phase (maximum  $\tan \delta$   $\approx 100^{\circ}\text{C}$ ) and a PEAA-rich phase (max.  $\tan \delta$   $\approx 160$ – $170^{\circ}\text{C}$ ). This shows that the



**Figure 2** FTIR kinetics of PUA/EAA/MMA 30/30/40 wt % HPN elaboration using 0.5 wt % *ortho-para*-toluene sulfonic acid and *tert*-butyl perbenzoate. The initiator-to-double-bond molar ratio was  $10^{-3}$ . (○) Epoxy and (□) double-bond conversion versus reaction time.



(a)



(b)

**Figure 3** (a) Loss tangent ( $\tan \delta$ ) versus temperature for HPNs with variable PUA/EAA/MMA composition: (○) 60/0/40; (□) 45/15/40; (△) 30/30/40; (◇) 15/45/40; (+) 0/60/40. (b) Dynamic shear modulus ( $E'$ ) versus temperature for HPN with variable PUA/EAA/MMA composition: (○) 60/0/40; (□) 45/15/40; (△) 30/30/40; (◇) 15/45/40; (+) 0/60/40.

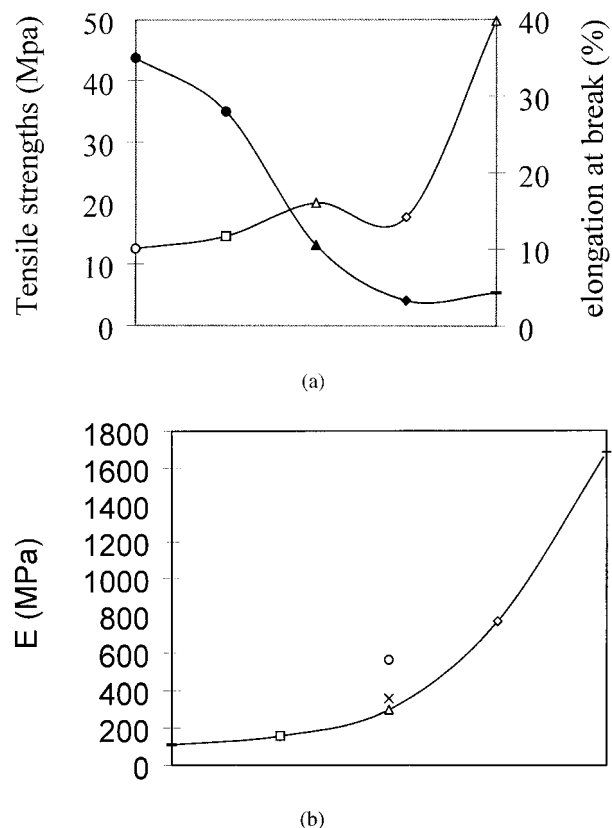
interactions between these distinct phases are poor. By increasing EAA concentration,  $\tan \delta$  peaks corresponding to the PUA-rich phase become more and more perceptible and are shifted to lower temperature. For the HPN based on PUA/EAA/MMA 15/45/40 wt %, a  $\tan \delta$  peak equivalent to a nearly pure PUA network was obtained (max.  $\tan \delta$  at  $-70^\circ\text{C}$ ). This clearly shows that the addition of EAA results in a decrease of PUA and PMMA network interactions. Equivalent remarks can be made concerning the evolution of  $E'$ . In this case, the transition corresponding to the PUA network became more visible and shifted to a lower temperature. The examination of max.  $\tan \delta$ , corresponding to the PEAA-rich phase, shows that an increase of PUA concentration results in a small shift to low temperature; this shift becomes greater for the HPN based on PUA/EAA/MMA 45/15/40 wt %, showing that the addition of PUA increases the interactions between the phases present in the system. Here, also, similar remarks can be made when examining the  $E'$  evolution.

### Stress-Strain Properties

Three types of modulus evolution behavior could be obtained corresponding to a rubber-phase matrix and a glassy-phase dispersion, a glassy-phase matrix, and a rubber-phase dispersion and two cocontinuous phases. In the first two cases, negative and positive deviations from the additivity rule are expected<sup>11</sup>; in the third one, the modulus can be calculated as a function of the sample composition.<sup>12</sup> Mechanical properties, corresponding to the different HPNs, are given in Figure 4(a,b). For the HPNs studied here, a modulus negative deviation was obtained, showing that the PUA-rich phase is the continuous one with the EAA-rich-phase dispersion. The strength-at-break ( $\sigma$ ) and elongation-at-break ( $\epsilon$ ) plots versus the HPN composition confirm that the elastomeric phase is the continuous one. Nevertheless, the HPN based on PUA/EAA/MMA 15/45/40 wt % has a singular behavior and the values are particularly low. This shows that a particular morphological change occurred in this HPN. This will be examined in the next part.

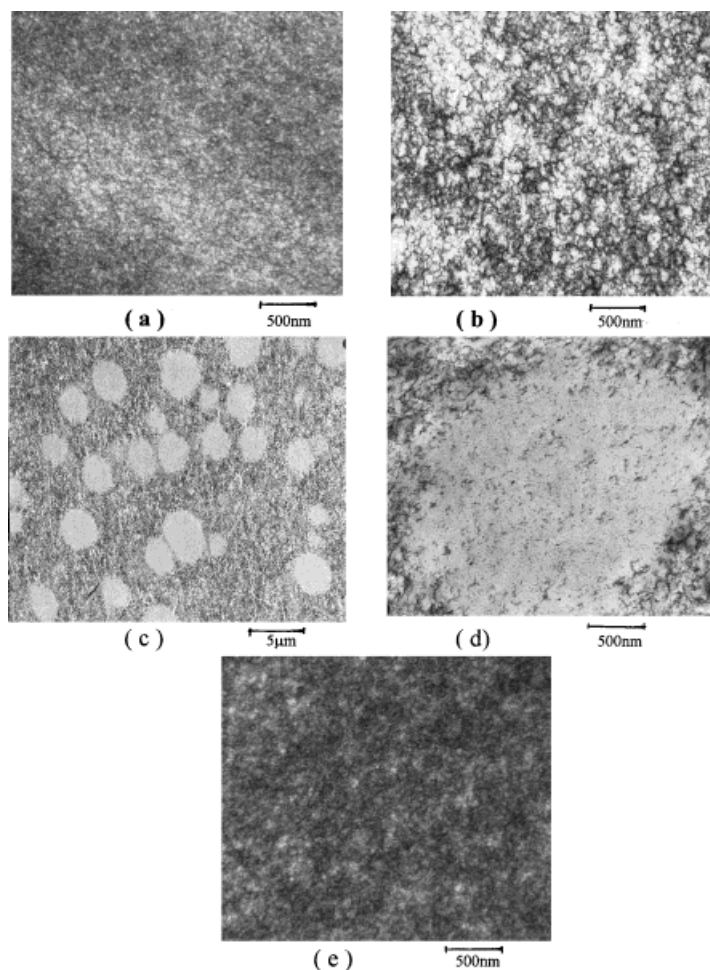
### Morphology of the HPNs

The morphology of the HPNs as observed by TEM are shown in Figure 5(a-c). In these pictures, the dark areas ( $\text{OsO}_4$ -stained) represent the PUA-



**Figure 4** (a) (Unfilled symbols) Ultimate tensile strengths and (filled symbols) elongation at break for HPNs with variable PUA/EAA/MMA composition: 60/0/40 (○); 45/15/40 (□); 30/30/40 (△); 15/45/40 (◇); 0/60/40 (+). (b) Young's modulus for noncompatibilized HPN with variable PUA/EAA/MMA composition: (○) 60/0/40; (□) 45/15/40; (△) 30/30/40; (◇) 15/45/40; (+) 0/60/40; 30/30/40 compatibilized using 5 wt % (X) copolymer 1 and (○) copolymer 2.

rich phase and the bright areas represent the EAA-rich phases. Even if clearly shown from the mechanical dynamic analysis the PUA/MMA and EAA/MMA networks are phase-separated, it was not possible to discern these phases from the TEM pictures corresponding to these materials under the experimental conditions used. For all other HPNs, the first examination showed continuous dark PUA-rich phases and bright EAA-rich-phase dispersions. In the PUA/EAA/MMA 45/15/40 wt %, these dispersion diameters were 30 nm [Fig. 5(a)]. Increasing the EAA concentration increased the dispersion diameters up to 100 nm for the PUA/EAA/MMA 30/30/40 wt % HPN [Fig. 5(b)]. The structure of the PUA/EAA/MMA 15/45/40 wt % HPN is quite different: First, the EAA-rich phase, having a relatively high diame-



**Figure 5** TEM image for HPN with variable PUA/EAA/MMA composition: (a) 45/15/40; (b) 30/30/40; (c,d) 15/45/40; (e) 30/30/40 with 5 % copolymer 2.

ter ( $2.5 \mu\text{m}$ ), was discerned in a PUA-rich matrix [Fig. 5(c)]. For higher magnifications [Fig. 5(d)], PUA subdomains are observed in EAA-dispersion nodules and the interphase is not well defined. A composition gradient was discerned going from the PUA matrix containing finely dispersed EAA to a cocontinuous structure, then to an EAA matrix with PUA dispersions. These observations concerning the poor dispersion in the PUA/EAA/MMA 15/45/40 wt % HPN explain the singular mechanical properties and thermal behavior of this HPN. (Low  $E$ ,  $\varepsilon$ ,  $\sigma$ , and a particularly well-defined and separated  $\tan \delta$  corresponding to the different phases are shown in Figs. 3 and 4.)

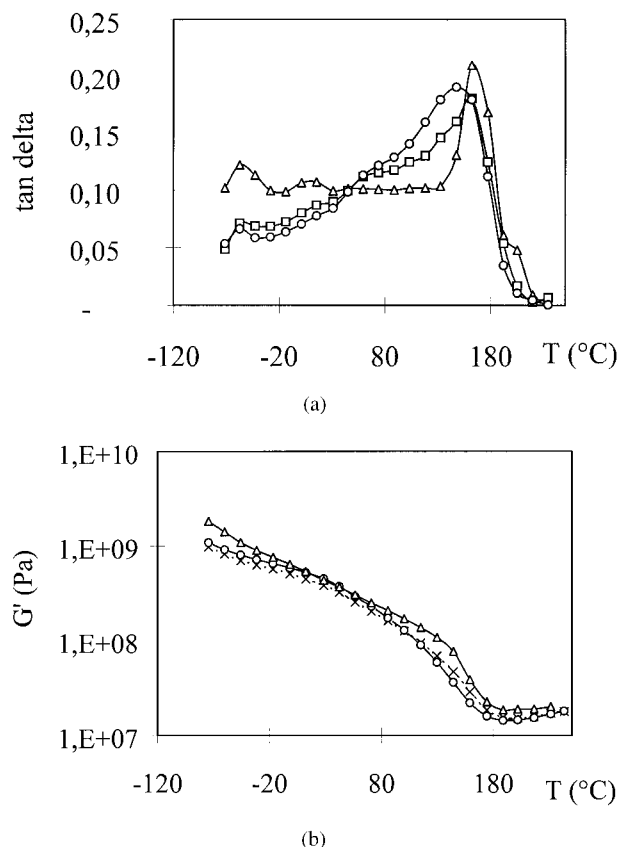
#### Compatibilization of the HPN

Multiphase networks were obtained over all the studied composition ranges. Finer and more ho-

mogeneous dispersions can be obtained using a copolymer as a compatibilizer.

The effect of such additives were examined for the PUA/EAA/MMA 30/30/40 wt % HPN.

Two copolymers were prepared using isocyanate/amine reactions: Details are given in the Experimental part. Five weight percent of these copolymers was added in the reactive system, leading to a PUA/EAA/MMA 30/30/40 wt % HPN. The  $E'$  and  $\tan \delta$  evolutions are given in Figs. 6a,b. Note that the addition of these copolymers resulted in a broader evolution of  $\tan \delta$  and a shift to lower temperatures. Also,  $E'$  showed a less pronounced evolution corresponding to the different phases present in the materials. This shows that finer dispersions with increased interfacial cohesion resulted from the addition of the two copolymers. TEM of the 30/30/40 wt % HPN com-



**Figure 6** (a) Loss tangent  $\tan \delta$  versus temperature for HPN PUA/EAA/MMA 30/30/40 ( $\Delta$ ) noncompatibilized and with 5 wt % ( $\square$ ) copolymer 1 and ( $\circ$ ) copolymer 2. (b) Dynamic shear modulus ( $E'$ ) versus temperature for HPN PUA/EAA/MMA 30/30/40 ( $\Delta$ ) noncompatibilized and with 5 wt % ( $\square$ ) copolymer 1 and ( $\circ$ ) copolymer 2.

patibilized by the addition of 5% of copolymer 2 is given in Figure 5(e).

The addition of the copolymers led to an increase in the Young's modulus (+20 % with copolymer 1 and +95% with copolymer 2). In both cases, the  $E$  value was lower than the one expected with the logarithmic additivity law, showing that even if the dispersions became finer a continuous PUA-rich phase was still present in the HPN. These effects are characteristic of a

compatibilizer effect, leading to a rigid interphase. These analyses clearly show the compatibilization effect of the two copolymers used in this study.

## CONCLUSIONS

HPNs with finely dispersed phases were prepared using PUA and EAA monomer solutions in MMA. Increasing the EAA concentration resulted in a decrease in the homogeneity of the HPNs. PUA-EAA copolymers were used as effective compatibilizers. With the composition range used, PUA-rich matrices were obtained. For higher EAA concentration, phase inversion should occur. Our next studies will concern these HPNs.

## REFERENCES

1. Manson, J. A.; Sperling, L. H. *Polymer Blends and Composites*; Plenum: New York, 1976.
2. *Polymer Blends*; Paul, D. R.; Newman, S., Eds.; Academic: San Diego, 1978.
3. *Multicomponent Polymer Materials*; Paul, D. R.; Sperling, L. H., Eds.; American Chemical Society: Washington, DC, 1986.
4. Utracki, L. A. *Polymer Alloys and Blends*; Hanser: New York, 1989.
5. Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum: New York, 1981.
6. Klemperer, D.; Berkowski, L. In *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1987; Vol. 8, p 279.
7. Titier, C.; Pascault, J. P.; Taha, M.; Rozenberg, B. *J Polym Sci Part A Polym Chem* 1995, 33, 175.
8. Titier, C.; Pascault, J. P.; Taha, M. *J Appl Polym Sci* 1996, 59, 415.
9. Coudray, S.; Pascault, J. P.; Taha, M. *Polym Bull* 1994, 32, 605.
10. Chen, J.; Pascault, J. P.; Taha, J. *J Polym Sci Part A Polym Chem* 1996, 34, 2889.
11. Takayanagi, M.; Vermura, S.; Minami, S. *J Polym Sci Part C* 1964, 5, 113.
12. Davies, W. E. A. *J Phys D* 1971, 4, 1176, 1325.