Semi-IPNs formed from poly(ethylene glycol monomethyl ether acrylate) and an epoxy thermoset

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Abstract: Poly(ethylene glycol monomethyl ether acrylate) (PEGMEA) was synthesized from the reaction of poly(ethylene glycol monomethyl ether) (PEGME) with acryloyl chloride. Semi-IPNs based on various weight ratios of diglycidyl ether of bisphenol A (DGEBA)/PEGMEA were prepared, using isophronediamine (IPDA) and 2,2′-azo-bis(isobutyronitrile) (AIBN) as curing agents. The glass transition temperature and exothermic peak shifts were studied with differential scanning calorimetry (DSC). Viscosity changes during semi-IPN formation were measured with a Brookfield viscometer. Dynamic mechanical properties were investigated by rheometric dynamic spectroscopy (RDS). Stress–strain curves were obtained with an Instron tensile tester, while impact resistance was measured with a computer aided falling dart impact tester.

Experimental results revealed retarded curing rates for all semi-IPNs, as evidenced from the shifts of curing exothermic peaks to higher temperatures, together with retarded viscosity increases during semi-IPN formation. These phenomena were interpreted in terms of chain entanglement between epoxy and PEGMEA. Nevertheless, the semi-IPNs indicated good compatibility as inferred from a single T_g in DSC and a single damping peak in RDS for each semi-IPN. Improved tensile stress and strain along with toughness improvements were noticed for this semi-IPN system. Shear band yielding was proposed to interpret this result.

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Keywords: semi-IPNs; toughness improvements; shear band yielding

INTRODUCTION

Both thermal and dimensional stabilities and material strength have led to the widespread use of commercial epoxy resins in applications of composites, coatings, adhesives and electronics. However, many attempts have been made to improve the drawback of their relative hardness and brittleness.[1–5] Recent efforts have been made to mix thermoplastic polymers with epoxy resins in order to improve toughness.[6–14] These thermoplastic modified thermosetting polymers indeed show significant improvements in mechanical properties. For easy processing, our present study deals with chemical mixing of monomer with liquid epoxy resin, followed by curing of DGEBA and polymerizing of PEGMEA simultaneously to form semi-IPNs. Toughness improvement of this semi-IPN system was proposed to occur via a shear banding yield mechanism.

EXPERIMENTAL

Materials

Poly(ethylene glycol monomethyl ether) with a number-average molecular weight of 350 was purchased from the Janssen Co., and a diglycidyl ether of bisphenol-A epoxy (DGEBA, Epon 815) with an EEW of 194.5 was obtained from the Shell Co. Acryloyl chloride was bought from TCI. Isophronediamine (IPDA) and 2,2′-*azo*-bis(isobutyronitrile) (AIBN) were received from the Merck Co. AIBN was recrystallized from 95% ethanol. Poly(ethylene glycol monomethyl ether acrylate) was obtained by the reaction of PEGME with acryloyl chloride in 1:1 molar ratio by the same procedure as reported elsewhere.[15]

Preparation of semi-IPNs

Semi-IPNs based on weight ratios of DGEBA/PEGMEA = 100/0, 87.5/12.5, 75/25, 62.5/37.5, 50/50, 25/75 and 0/100 were obtained by simultaneously polymerizing PEGMEA with AIBN (1 phr on PEGMEA) and curing DGEBA with IPDA (in stoichiometric balance with DGEBA). Samples were prepared by pouring mixtures into Teflon™ moulds, and were pre-cured at 60°C for 4h, followed by curing at 80°C for 8h, and finally post-cured at 120°C for an additional 10h.

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Instruments

All DSC thermograms were recorded with a Seiko model 100 instrument at a heating rate of $10 \, K \, min^{-1}$ under a nitrogen atmosphere. Viscosity increases during semi-IPN formation were measured with a Brookfield LVT viscometer. Gel fractions were measured after 3 days of continuous extraction with a Soxhlet extractor using acetone as solvent. Dynamic mechanical properties were measured on a rheometric dynamic spectrometer (RDS, Rheometric II) at $31.4 \, rad \, s^{-1}$, temperature sweeping from -100 to $200°C$; the heating rate was set at $5 \, K \, min^{-1}$. The sample size was $50 \times 10 \times 2.5 \, mm.^3$ The stress–strain procedure was followed as described in ASTM-D638, with a crosshead speed of $10 \, mm \, min^{-1}$ and at least five specimens were used for each test. Impact resistance tests were done at room temperature with a computer aided falling dart impact tester with a dart weight of $3.68 \, kg.$ Scanning electron micrographs were obtained from the fractured surfaces of the impact-tested specimen.

RESULTS AND DISCUSSIONS

Poly(ethylene glycol monomethyl ether acrylate) (PEGMEA) and isophronediamine (IPDA), the curing agent for DGEBA, have the following structures:

$$CH_3O-(CH_2CH_2O)_n-\underset{\underset{O}{\|}}{C}-CH=CH_2$$

(PEGMEA)

$$H_2N-\text{(cyclohexane ring with } CH_3, CH_3 \text{ and } CH_3, CH_2NH_2)$$

(IPDA)
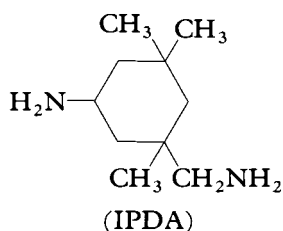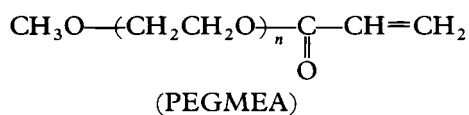
Shifts of exothermic peaks during semi-IPN formation in the dynamic DSC are given in Fig. 1. Curve A (pure epoxy) exhibits a maximum peak at $104°C$ with a shoulder at $132°C$. The $104°C$ peak is due to the reaction of the less sterically hindered NH_2 and the second peak at $132°C$ to the reaction of the NH_2 near the methyl group.[16] Curve G shows a sharp and narrow exothermic peak of pure PEGMEA, due to free radical polymerization of the $C=C$ bonds. The other semi-IPNs show exothermic peaks at higher and broader temperature ranges. This phenomenon appears quite similar to the curing behaviour of full IPNs.[17] The entanglement of chains, one epoxy network and the other PEGMEA linear polymer, presumably gave extra steric hindrance to the curing and/or polymerization reactions. In addition, chain mobilities were restrained, and higher activation energies might be expected,[18] resulting in a difficult cure.[17] An increase in temperature would compensate for this difficulty, and subsequently be reflected
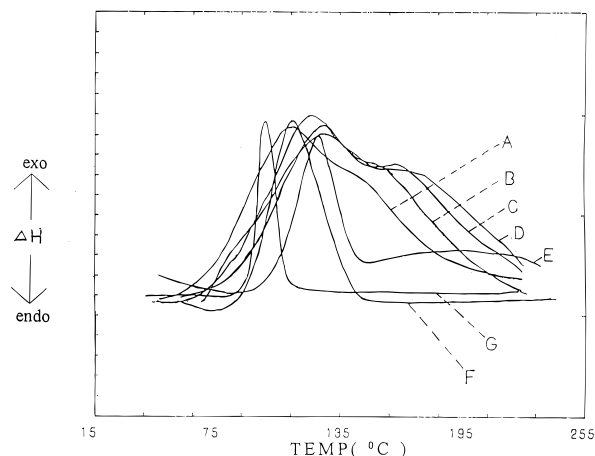

Figure 1. Dynamic DSC thermograms showing the exothermic peak shifts for various semi-IPNs: DGEBA/PEGMEA = (A) 100/0, (B) 87.5/12.5, (C) 75/25, (D) 62.5/37.5, (E) 50/50, (F) 25/75 and (G) 0/100.

in shift of the peak to higher temperature. Similar phenomena have been reported in the literature.[17]

The extensive chain entanglements would be reflected by retarded cure rate, leading to slow viscosity increases.[17] Figure 2 shows this result. Pure epoxy (curve A) cured fairly quickly at $70°C$ with a pot-life of approximately 15 min. Upon incorporating small portions of PEGMEA, the semi-IPNs show retarded viscosity increases (curves B and C). As more PEGMEA is incorporated, the semi-IPNs exhibit even slower viscosity increases (curves D and E). However, composition E (DGEBA/PEGMEA = 50/50) shows a much slower viscosity increase than composition D (DGEBA/PEGMEA = 62.5/37.5), presumably because composition E contained more portions of chain entanglement on the molecular scale. A similar phenomenon was found elsewhere.[17] Of course, the
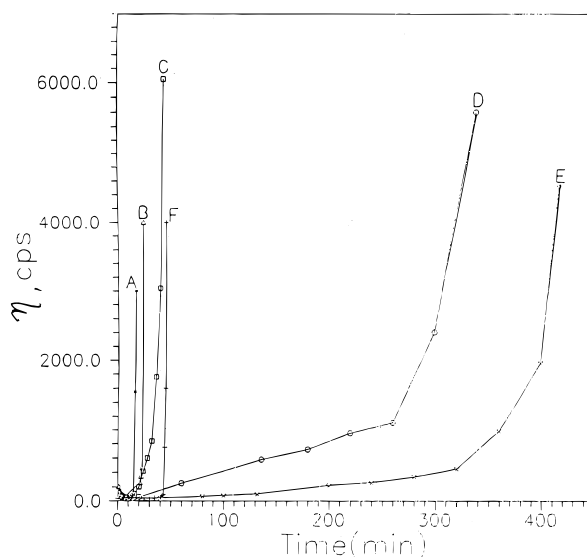

Figure 2. Viscosity increases during semi-IPN formation at $70°C$. DGEBA/PEGMEA = (A) 100/0, (B) 87.5/12.5, (C) 75/25, (D) 62.5/37.5, (E) 50/50, (F) 25/75 and (G) 0/100.

entanglement of the system may be affected by the constant agitation of the paddle. This may lead not only to concentration of some species, but also disruption of the incipient network. The retarded cure rates may also possibly be due to the dilution of acrylate and AIBN by addition of the epoxy components, and possible chemical interaction between the radical and the amine. A full explanation, however, would require data on the isothermal kinetics. Nevertheless, our previous kinetic studies reveal a decreased rate constant and an increased activation energy during IPN formation.[18,19] and strongly support the participation of chain entanglement. The chain entanglement not only provided an additional sterically hindered environment during network formation, but also restrained the chain mobilities of species, thus accounting for the observed phenomena. This inference appears reasonable when one checks the compatibility of DGEBA/PEGMEA semi-IPNs. The DSC thermogram in Fig 3 shows a single T_g for each composition. This compatibility can be confirmed from the single damping peak in the RDS curves (Fig 4). It is generally known that a single glass transition is a good indication of compatibility. Data for compositions with higher PEGMEA content have not been collected because those semi-IPNs containing higher PEGMEA are quite brittle.

Figure 5 plots the gel fractions versus compositions. As expected, the gel fraction decreases linearly with compositions[17] (ie the more PEGMEA incorporated in a semi-IPN, the lower the gel fraction), because PEGMEA is a linear polymer and is extractable. It is interesting to note that the percentage of gel is higher than the weight percentage of PEGMEA, suggesting that some of it is incorporated into the network structure. This linear relationship of gel fraction versus composition in semi-IPNs is quite different from the U-shape in the full IPNs.[17] Because PEGMEA is also a soft component, a semi-IPN with more PEGMEA content would have a lower T_g (Fig 3).

Figure 4. RDS curves showing the damping peak of each semi-IPN: DGEBA/PEGMEA = (A) 100/0, (B) 87.5/12.5, (C) 75/25 and (D) 62.5/37.5.

Figure 6 shows the storage modulus E' and Fig 7 shows the loss modulus E'' versus temperature for various semi-IPNs. It is noted that near the transition temperature, semi-IPNs with more PEGMEA have lower E' but higher E'' values. Figure 8 shows

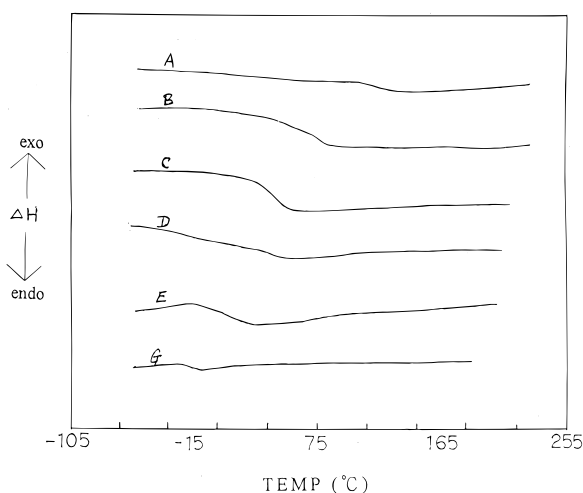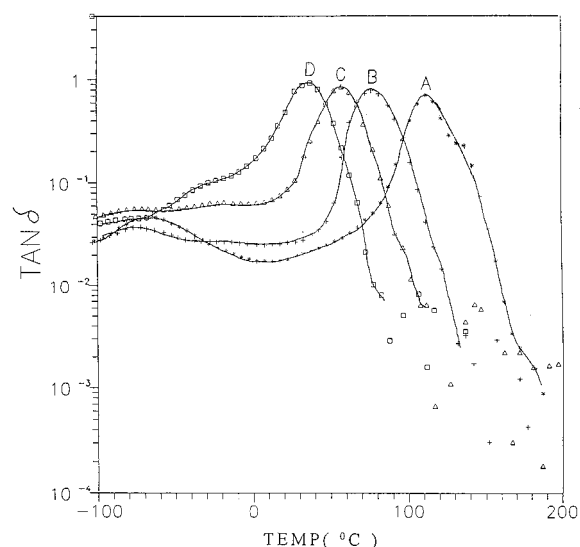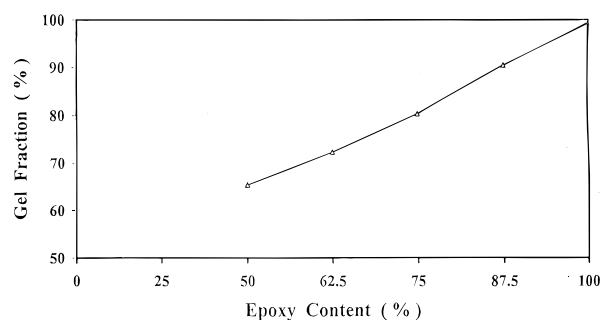**Figure 5.** Plot of gel fraction versus composition.

Figure 3. DSC thermograms showing the T_g values for various semi-IPNs. DGEBA/PEGMEA = (A) 100/0, (B) 87.5/12.5, (C) 75/25, (D) 62.5/37.5, (E) 50/50 and (G) 0/100.
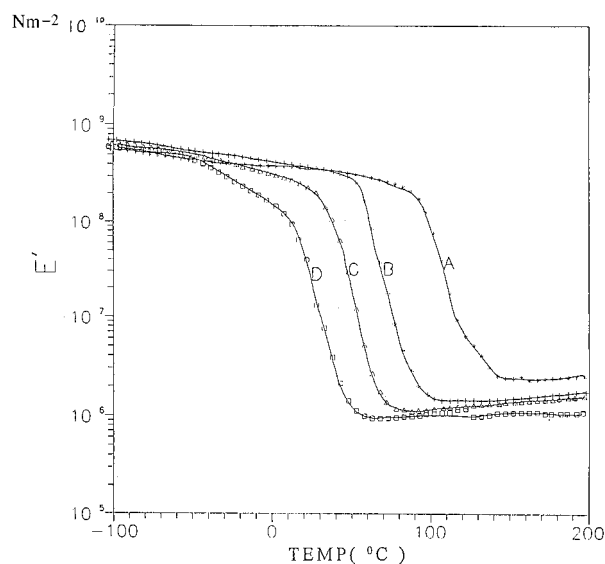

Figure 6. RDS curves showing the storage modulus E' for each semi-IPN: DGEBA/PEGMEA = (A) 100/0, (B) 87.5/12.5, (C) 75/25 and (D) 62.5/37.5.
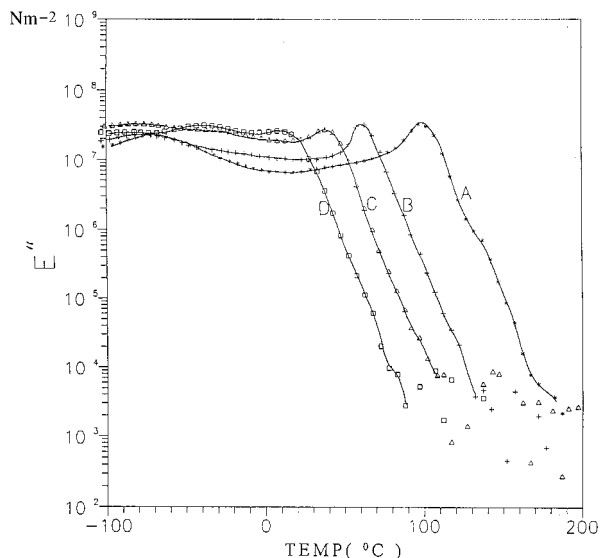
Figure 7. RDS curves showing the loss modulus E'' for each semi-IPN. DGEBA/PEGMEA = (A) 100/0, (B) 87.5/12.5, (C) 75/25 and (D) 62.5/37.5.
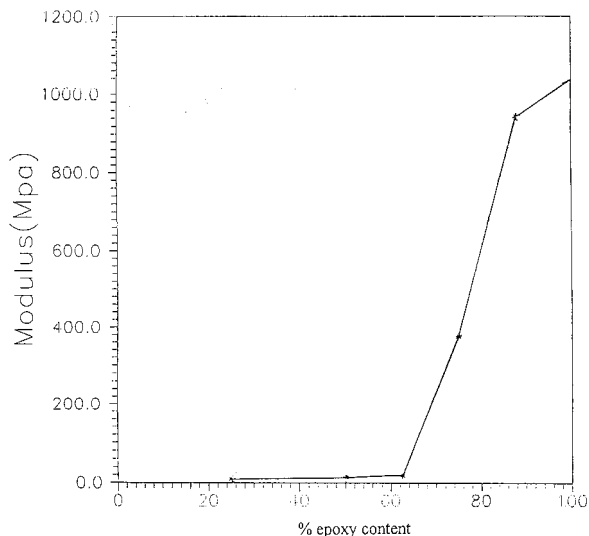

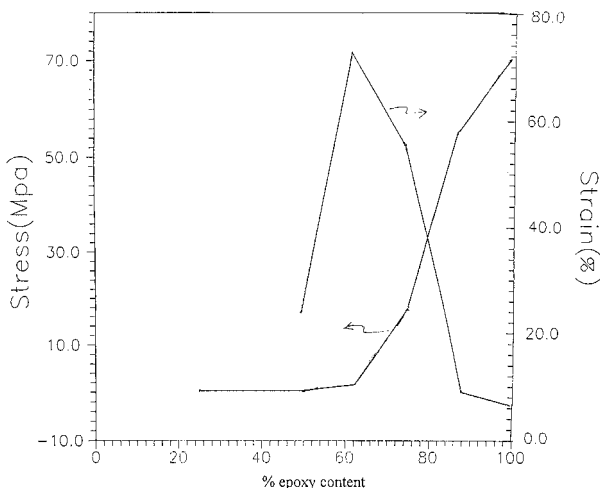**Figure 8.** Plot of modulus versus composition.

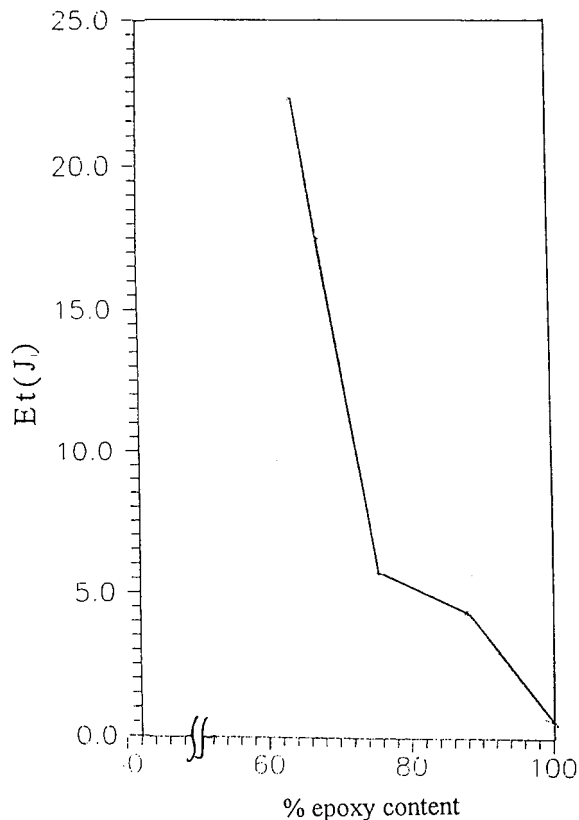**Figure 9.** Plots of stress and percentage strain at break versus composition.

Figure 10. Plot of cracking energy versus composition.

the modulus versus composition; Fig 9 shows the stress and strain at break versus composition. Improvements in modulus, stress and strain were generally observed with epoxy contents higher than approximately 60%. This improvement is most likely due to chain entanglement. Similar results are reported in the literature.[20] Another possible explanation for the improvement of properties above 60 wt% PEGMEA is that the semi-IPN is in a leathery state at the testing temperature, which would enhance deformation and viscoelastic energy loss. Figure 10 plots the cracking energy of fractured sample during impact testing against composition. It is noted that semi-IPNs with 62.5% of epoxy show a high energy-absorbing capability. This toughness improvement appears to be due to the newly produced internal shear surfaces, ie the shear banding yield mechanism,[21–23] as observed from the scanning electron micrographs of fractured surfaces (Fig 11).

CONCLUSIONS

During semi-IPN formation, retarded cure rates with retarded viscosity increases were observed. This retardation is believed to be due to chain entanglements between the linear PEGMEA polymer and the epoxy network, which strain the chain mobility. Improved mechanical properties, such as modulus, stress, strain and toughness, were found for this compatible semi-IPN system.
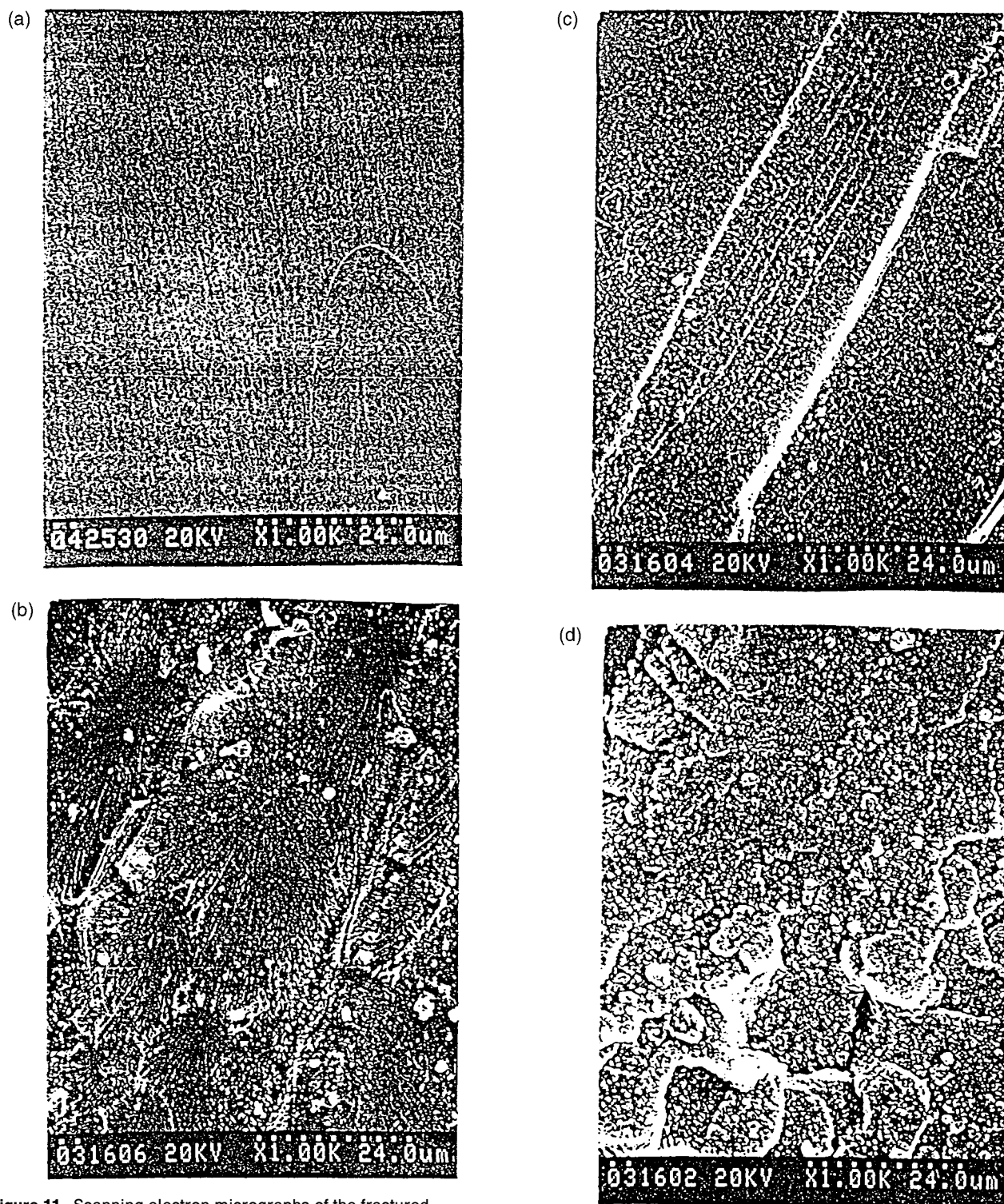
(a)

(c)

(b)

(d)

Figure 11. Scanning electron micrographs of the fractured surfaces: a (a) DGEBA; DGEBA/PEGMEA = 87.5/12.5 (b), 75/25 (c), 62.5/37.5 (d) and 50/50 (e).
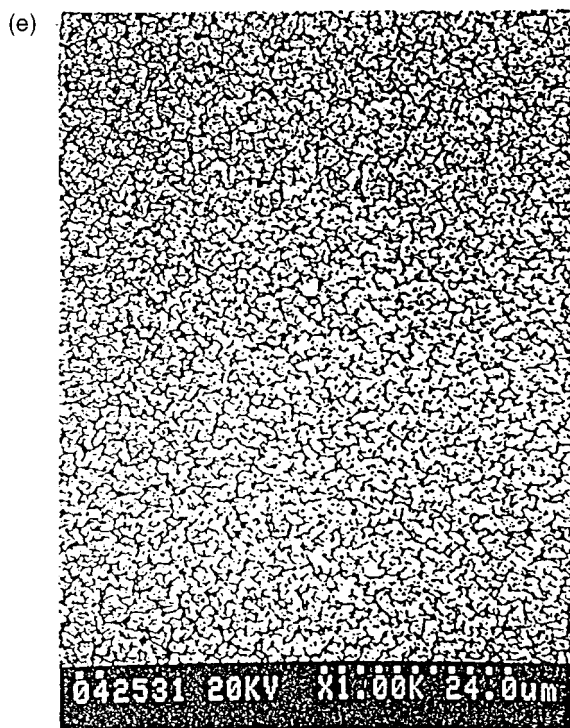
Figure 11. (*Continued*)

(e)

Figure 11. (*Continued*)

ACKNOWLEDGEMENT

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