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Morphological variations in PMMA-modified epoxy mixtures by PEO addition

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Abstract

Thermoplastic epoxy blends are successfully used commercially. The thermoplastic may serve as a toughening agent although other properties may also be improved. In the present study, microscopy and mechanical testing techniques were used to study morphology and ultimate properties of ternary epoxy/Poly(methyl methacrylate) (PMMA)–Poly(ethylene oxide) (PEO) blends. PEO is functioning like a compatibilizer by which the morphology of the resulting polymer mixture may be changed dramatically by only small amounts of PEO. Whilst stiffness was controled by the corresponding matrix of the ternary mixture, both strength and fracture toughness were a function of the defined morphology. However, the most efficient toughening agent was PMMA, in particular when present as a co-continuous PMMA-rich phase within the epoxy-rich matrix. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy modification; Poly(methyl methacrylate); Poly(ethylene oxide)

1. Introduction

Addition of thermoplastics to thermosetting epoxy resins is a common way for improving fracture toughness [1–6]. Phase separation through epoxy curing is advantageous in this context. In order to reach significant toughness enhancement, strong polymer–polymer interfacial adhesion between the separated phases has been claimed necessary in earlier studies [7]. Polymers containing reactive end groups have been investigated by several authors [8]. One difficulty is that although we may devise routes to increased polymer–polymer adhesion, better miscibility does not always lead to improved mechanical behavior.

Morphology is a significant factor influencing the mechanical properties of modified epoxy mixtures [9–12]. Modifier level and chemical features as well as curing conditions are key factors controlling the final morphology. Both rubber and thermoplastics toughening agents are used in commercial carbon fiber composite materials. Another possibility which has only been considered to a limited extent [13,14] is the simultaneous addition of two polymers to the epoxy resin before curing. In this way, many different morphologies may result depending on the miscibility between the modifiers and between the modifiers and the epoxy matrix.

Poly(ethylene oxide) (PEO)/Poly(methyl methacrylate) (PMMA) blends form a single phase-mixture in the melt [15–17]. Phase segregation is often observed in solid mixtures. The extent of miscibility depends on the molecular mass of both polymers [18,19] and also on the blend composition [17,20].

We have previously demonstrated [10,21,22] that the morphologies of PMMA-modified epoxy matrices is strongly dependent on PMMA content but also on curing conditions. From an initially homogeneous solution, this allows us to tailor polymer mixtures ranging from opaque to transparent with different mechanical properties. The curing agent also has a great influence on the morphology, since it influences the thermodynamics of the mixtures [22–27].

As for other epoxy matrix blends, PEO addition can also lead to phase-separated systems as a consequence of variations in physico-chemical interactions when the curing agent is changed. Thus, miscibility has been reported for PEO-modified epoxy networks for curing agents as amines and anhydrides [28–31]. Also immiscibility is found in the literature survey for epoxies cured with aliphatic amines as

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tetraethylenepentamine (TEPA) or diethylenetriamine [30,32].

The present study is intended to discuss the morphological variations in immiscible PMMA-modified epoxy matrices by the incorporation of a typical crystalline polymer as PEO. 4,4′-diaminodiphenylmethane (DDM) has been chosen as curing agent in order to have PEO as a miscible polymer diluent for the epoxy resin. Morphologies have been investigated by both scanning electron (SEM) and atomic force (AFM) microscopy, and results compared with those obtained from dynamic mechanical analysis (DMA). Finally, the effects of morphological variations on the mechanical properties have also been analyzed.

2. Experimental

The epoxy resin, DER 332, kindly supplied by Dow Chemical, was a diglycidyl ether of bisphenol-A (DGEBA). It has an epoxy equivalent weight of around 175. DDM curing agent (HT-972, gift from Ciba) was used in a stoichiometric amine/epoxy ratio for all mixtures. PMMA, Lucryl G77 from Basf, was added in percentages ranging from 5 to 20 wt% of the overall mixture. PEO, Aldrich quality, with a M_v of around 200,000, was added in amounts of 2 or 5 wt%.

Mixing was carried out by using the following procedure. First, a weighed amount of PMMA was dissolved in dichloromethane to give an approximately 10 wt% solution. On the other hand, the corresponding amount of PEO was added into the epoxy resin heated to 110 °C. After mixing both solutions, the solvent was removed by heating to 110 °C for 8 h and further overnight degassing in vacuo. Then, DDM in a stoichiometric amine/epoxy ratio was added while stirring the mixture for 5 min. At this stage, all mixtures were transparent, thus indicating complete miscibility. These mixtures were poured into a preheated mold at 110 °C and cured for 2 h degassing with vacuum during the early stage of curing. They were then post-cured at 200 °C for 2 h and thereafter allowed to cool gradually to room temperature.

The dynamic mechanical behavior of the neat and modified epoxy mixtures was studied in a Metravib viscoanalyser from 20 to 250 °C at 3 °C/min and 10 Hz using $60 \times 12 \times 5\ mm^3$ samples with a bending device. The temperature corresponding to the maximum for the α relaxation in the loss factor was recorded as the glass transition temperature, T_g. The rubber modulus, E'_r, taken as the modulus at $T_g + 40$ °C, was used to compare the cross link densities of the networks. The comparison was based on the theory of rubber elasticity where rubbery modulus is inversely proportional to the average molecular weight between crosslinks, $M_c(E'_r = \rho RT/M_c)$, ρ being the density of the network and T the absolute temperature.

Dynamic DSC measurements were performed with a DSC-7 Perkin Elmer instrument from 30 to 250 °C at a rate of 20 °C/min.

For morphological analysis both AFM and SEM techniques were used. The AFM examinations were performed using a Nanoscope IIIa (Digital Instruments) operating in contact mode (the tip was always touching the surface when the feedback loop was on) in air, using commercial silicon nitride probes with V-shaped cantilevers of length 200 nm and spring constant 0.12 N/m. Images are presented without any image processing except horizontal leveling. SEM measurements were performed in a Jeol JSM 35 CF instrument.

Mechanical tests were performed in an Instron 4206 test machine equipped with a 5 kN load cell. Flexural properties were measured according to the ASTM D230 standard at a crosshead rate of 1.7 mm/min using $80 \times 12 \times 5\ mm^3$ specimens. Fracture toughness tests were performed following the European Structural Integrity Society's (ESIS) protocol [33,34] using single-edge-notched type samples ($60 \times 12 \times 5\ mm^3$) in a three point bending geometry. Both critical stress intensity factor, K_{Ic}, and critical strain energy release rate, G_{Ic}, were measured. For both tests a minimum of five specimens were used. Poisson's ratio was taken as 0.35 for all matrices.

3. Results and discussion

In order to understand the morphological evolution in epoxy matrices modified with both PMMA and PEO, analyses of the mixtures containing only one of these polymers was carried out. Fig. 1 presents the loss modulus, E'', variation with temperature for mixtures containing different amounts of PMMA. For all compositions the T_g of the epoxy-rich phase and that for the PMMA-rich phase are, respectively, slightly lower and higher than those corresponding to the neat materials. This is due to partial miscibility, each phase contains a small amount of the other

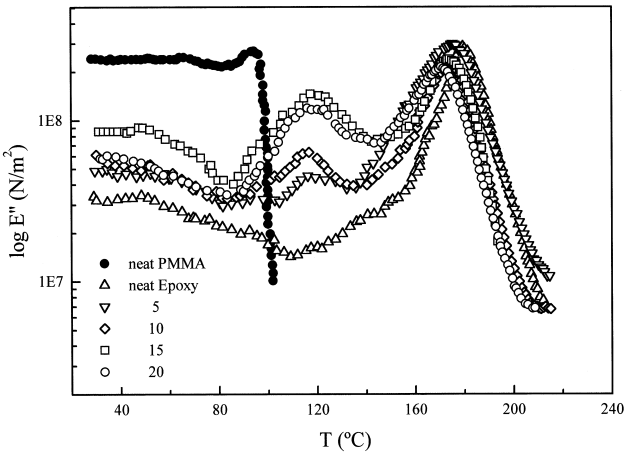

Fig. 1. Loss modulus vs. temperature plots of epoxy mixtures with different contents (wt%) of PMMA.

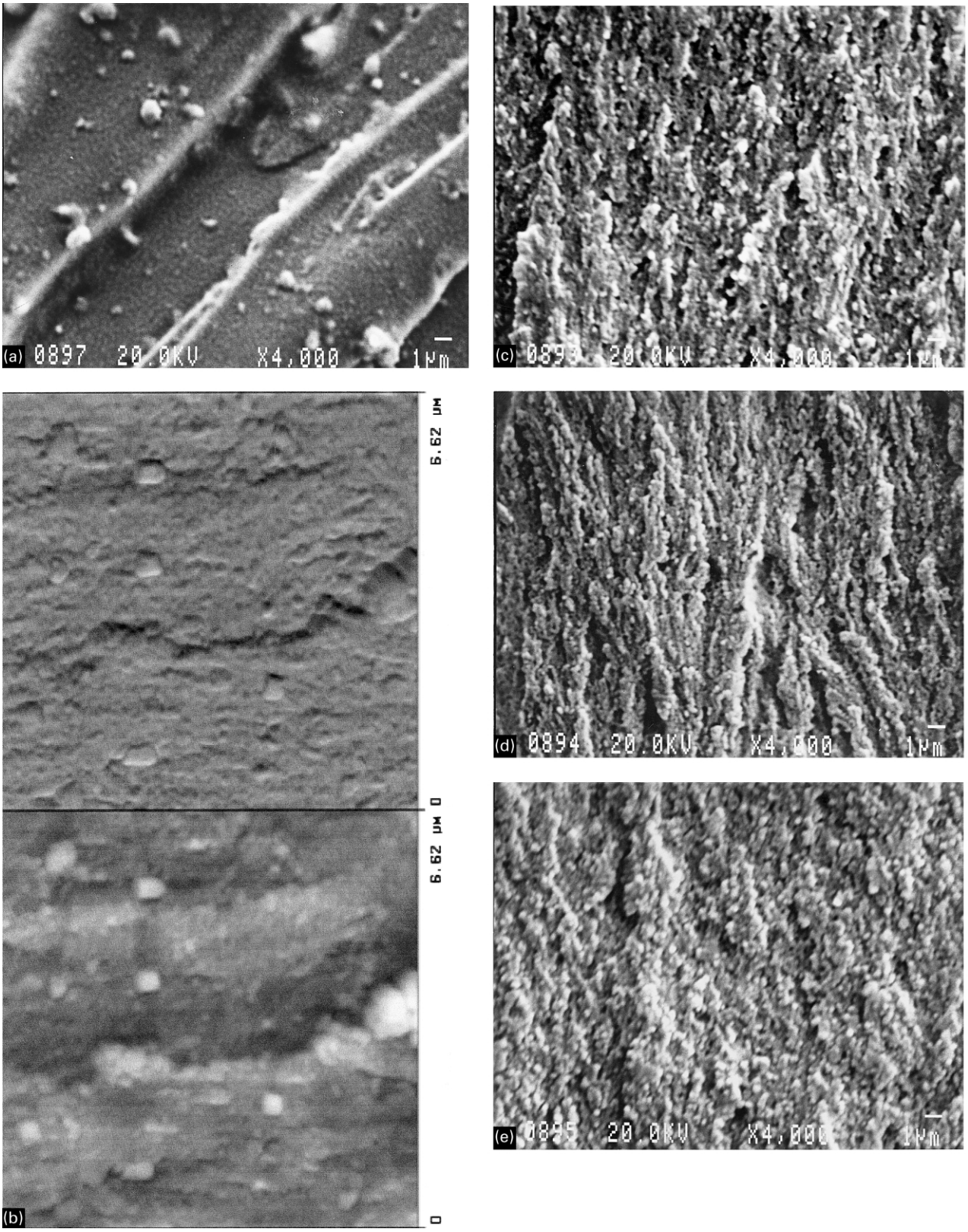

Fig. 2. Morphologies (SEM) of PMMA-modified epoxy mixtures with different contents (wt%) of PMMA: (a) 5, and (b) 10 AFM, (c) 15 unetched, (d) 15 etched, and (e) 20.

component of the mixture. The increase in the height of the α-relaxation of the PMMA-rich phase as PMMA content is higher in the mixture is a clear indication of a change in the morphology from particulate to phase-inverted. These trends are corroborated by microscopy studies. Thus, as inferred from Fig. 2a–e, small dispersed particles are observed up to 10 wt% PMMA. The morphology becomes coarser at higher contents. When co-continuity or phase-inversion takes place, the PMMA-rich phase provides very little contrast. The morphological features of the unetched and etched 15 wt% PMMA-modified mixtures, Fig. 2c and d, are very similar.

Thereafter, the influence of PEO addition was analyzed. As inferred from Fig 3, PEO is miscible with the epoxy matrix since T_g of the modified epoxy matrix decreased proportionally to the amount of PEO in the mixture. A PMMA/PEO (80:20 wt%) mixture showed a T_g clearly lower than that for neat PMMA. This indicates that also this mixture is basically miscible.

The epoxy mixtures modified with both thermoplastics were investigated subsequently. Fig. 4 presents the dynamic mechanical results for mixtures containing 5 wt% PMMA and different amounts of PEO. Though the T_g of the epoxy phase slightly decreased, the addition of PEO clearly lowered the T_g of the PMMA-rich phase with respect to the modified matrix without PEO. This indicates that PEO migrates preferentially to the PMMA-rich phase. AFM images, Fig. 5a and b, show that the size and volume fraction of the particulate morphology increased as the PEO content was increased. Moreover, some interconnection between dispersed particles can be also observed for the 5 wt% PEO containing mixture.

Concerning to the mixtures modified with 10 wt% PMMA, Fig. 6 again indicates that PEO migrates to the PMMA-rich phase. However, PEO also is present in the epoxy-rich phase as its T_g is also lowered. We may note that the height of the α-relaxation for the PMMA-rich

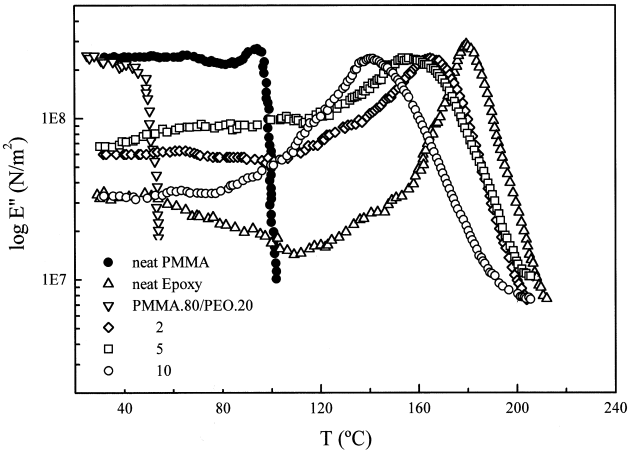

Fig. 3. Loss modulus vs. temperature plots of epoxy mixtures with different contents (wt%) of PEO including the PMMA/PEO (80:20 wt%) mixture.

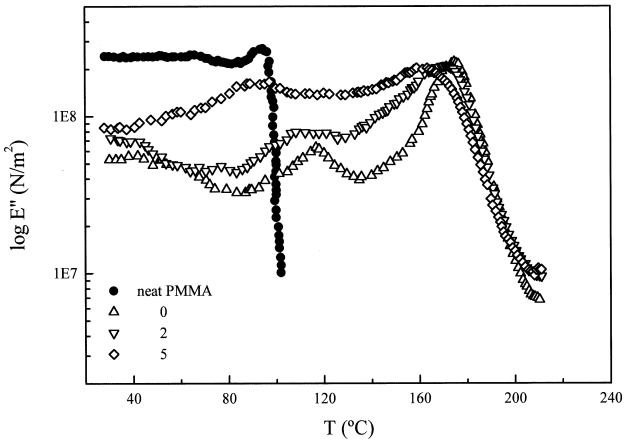

Fig. 4. Effect of PEO content (wt%) on loss modulus of 5 wt% PMMA-modified epoxy mixtures.

phase increases as the PEO content increases. This is possibly because of an increasing interconnectivity in the dispersed phase. Also, the low-temperature side of the α-relaxation in the epoxy-rich phase becomes broader because of an increasing amount of PEO in this phase. DSC results shown below confirm this assumption. SEM micrographs permit observations of the changes in morphology by PEO addition. Thus, as shown in Fig. 7a, a 2 wt% PEO addition leads to a coarser morphology similar to the one for the 15 wt% PMMA-modified matrix. A complete change in morphology occurs at 5 wt% PEO addition, see Fig. 7b. Epoxy becomes the dispersed phase formed by 1–5 μm ϕ domains.

The influence of PEO addition on the morphology of the non-particulate PMMA-modified epoxy mixtures was also investigated. In the case of 15 wt% PMMA mixtures, Fig. 8 indicates that phase inversion occurred for the 2 and 5 wt% PEO mixtures. The peak corresponding to the PMMA-rich phase shows up as the most dominating one in the E'' spectrum. Microscopy studies with SEM and AFM, Fig. 9a and b, respectively, confirm this since discrete epoxy-rich particles with a diameter smaller than 1 μm appeared for 2 wt% PEO addition. For the 5 wt% PEO mixture, the particle size was clearly larger.

For the 20 wt% PMMA-modified epoxy mixtures containing PEO, Fig. 10, phase inversion was clearly detected from dynamic mechanical measurements since only the α-relaxation corresponding to the PMMA-rich phase was prominent. In the same way as previously shown in E'' vs. T curves for other PMMA contents, T_g of the PMMA-rich phase decreased more strongly as more PEO was added to the material. This indicates that a significant amount of PEO remained in the PMMA-rich phase. According to the SEM images, PEO addition led to a slight increase in size of the epoxy-rich particles, see the phase-inverted morphology in Fig. 11a and b.

DSC measurements where also carried in order to investigate if some PEO was present in the epoxy-rich

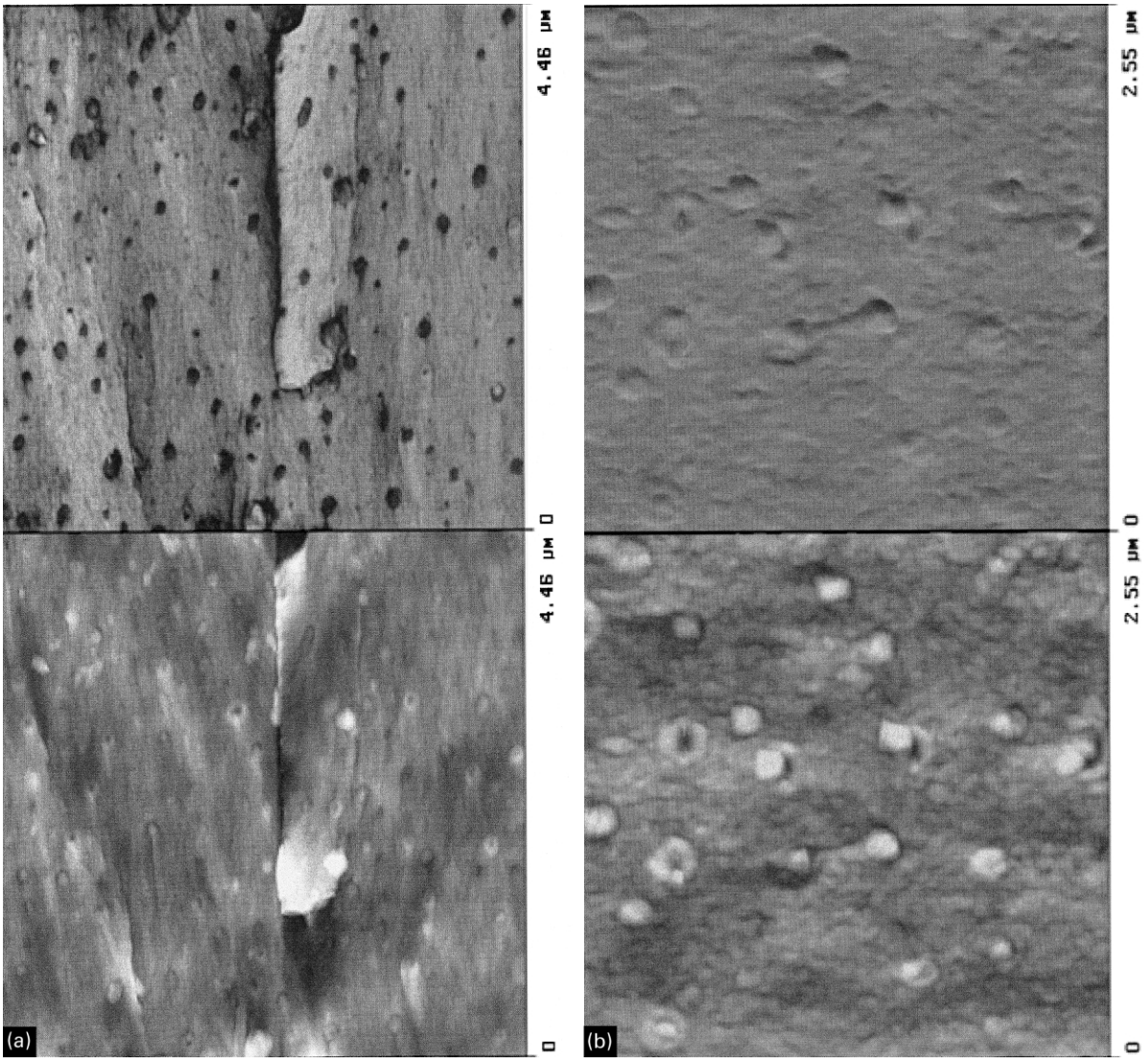

Fig. 5. AFM images of 5 wt% PMMA-modified epoxy mixtures containing different PEO contents (wt%): (a) 2, and (b) 5.

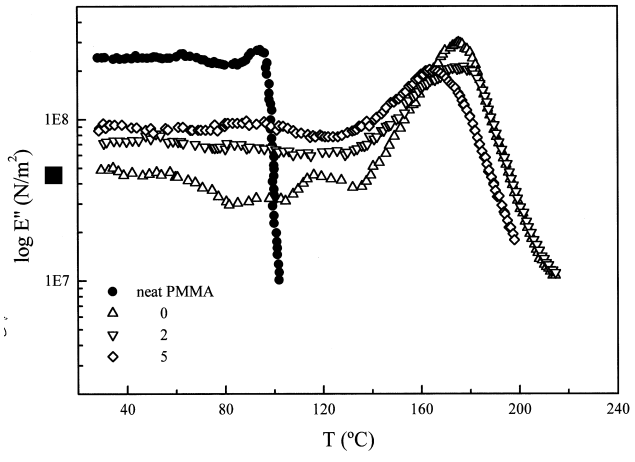

Fig. 6. Effect of PEO content (wt%) on loss modulus of 10 wt% PMMA-modified epoxy mixtures.

phase of the modified mixtures. Scans are presented in Fig. 12 for 20 wt% PMMA-modified epoxy mixtures. The increase in PEO content clearly lowered the temperature of the transition corresponding to T_g. We may therefore conclude that some PEO was also present in the epoxy-rich phase.

Finally, the influence of morphology on the mechanical behavior, including fracture toughness, was also investigated. Results are reported in Table 1. PMMA-modified epoxy mixtures presented higher flexural modulus, E, and strength, σ, with higher PMMA content. The 15 wt% PMMA-content mixture showed the highest values. The fracture toughness was significantly improved at 10 wt% PMMA-content and then stayed fairly constant with further increase in PMMA-content.

As 2–5 wt% PEO was added to the PMMA-modified mixtures, both strength and fracture toughness decreased. This decrease was particularly more evident for the mixtures

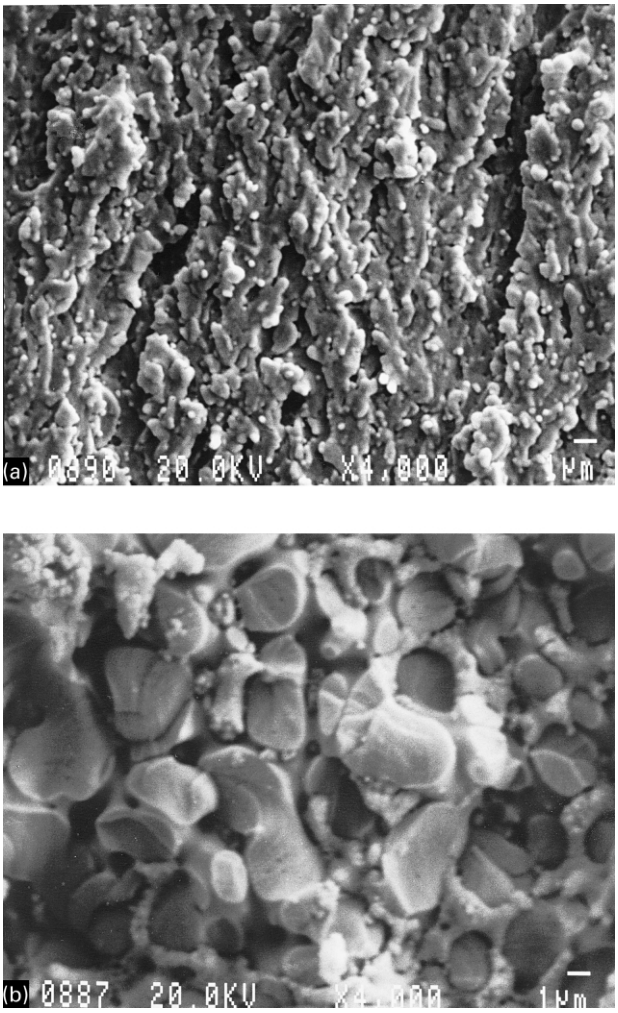

Fig. 7. SEM micrographs of 10 wt% PMMA-modified epoxy mixtures containing: (a) 2 wt% PEO, and (b) 5 wt% PEO.

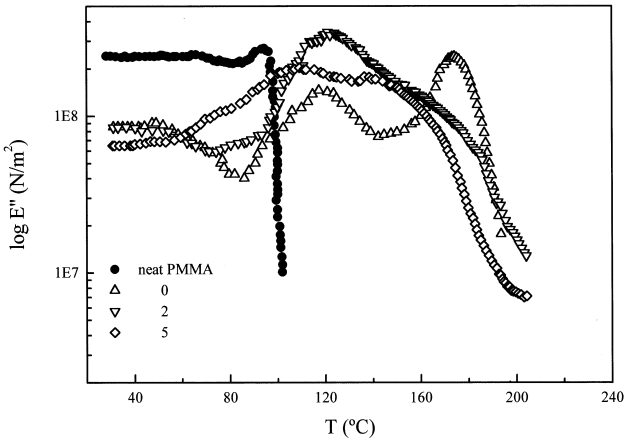

Fig. 8. Effect of PEO content (wt%) on loss modulus of 15 wt% PMMA-modified epoxy mixtures.

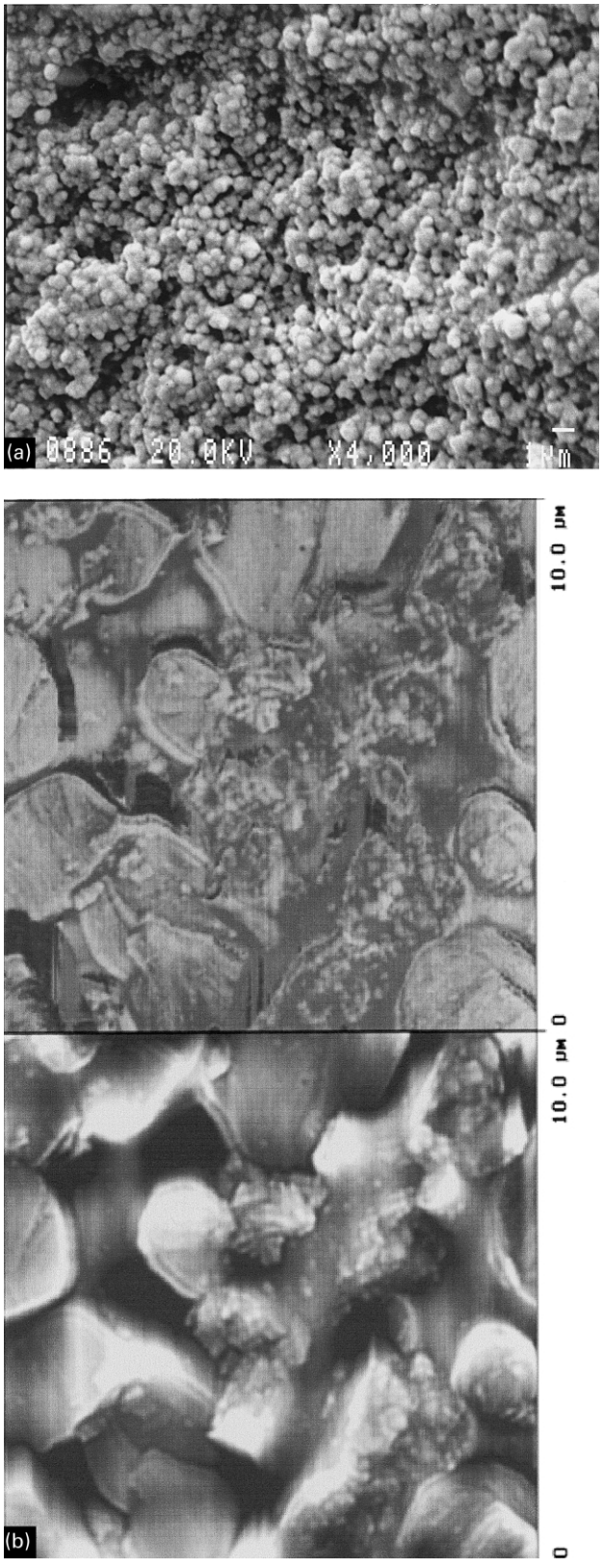

Fig. 9. Morphologies of 15 wt% PMMA-modified epoxy mixtures containing: (a) 2 wt% PEO (SEM), and (b) 5 wt% PEO (AFM).

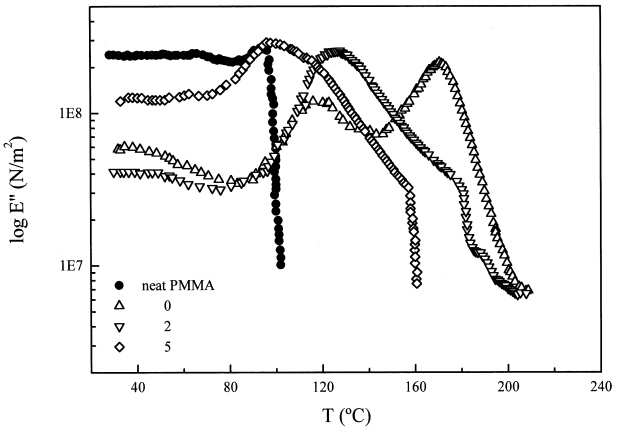

Fig. 10. Effect of PEO content (wt%) on loss modulus of 20 wt% PMMA-modified epoxy mixtures.

defined by co-continuous or phase inverted morphologies than for those containing PMMA-rich particles as dispersed phase. We may therefore conclude that the beneficial toughness increase in PMMA-modified epoxy seems to be linked

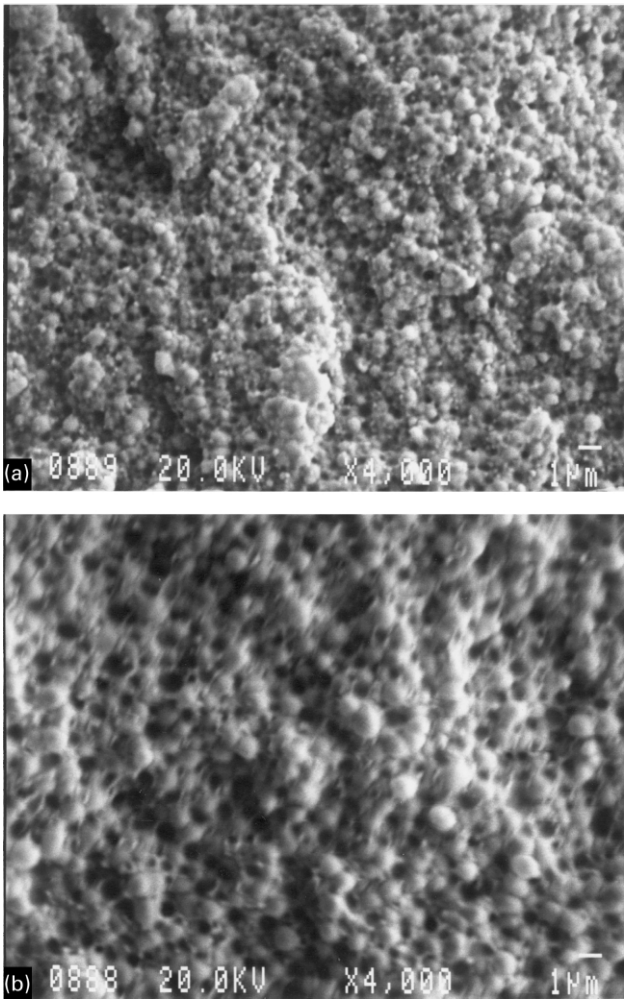

Fig. 11. SEM micrographs of 20 wt% PMMA-modified epoxy mixtures containing: (a) 2 wt% PEO, and (b) 5 wt% PEO.

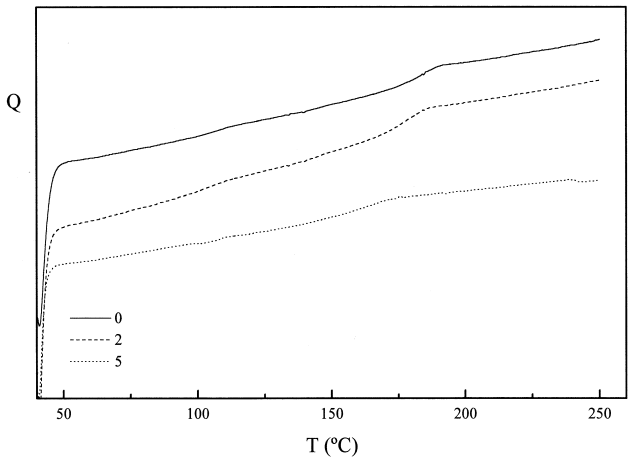

Fig. 12. DSC scans of 20 wt% PMMA-modified epoxy mixtures with different contents (wt%) of PEO.

with the particle morphology. As PEO is added, increased miscibility leads to unfavorable changes in morphology and this leads to lowered fracture toughness as well as strength. The values of the elastic modulus were a function of the phase acting as matrix in the mixture. Thus, for low PMMA contents at which dispersed PMMA-rich particles appeared, the stiffness was similar to that for the neat epoxy matrix. Otherwise, when co-continuity or phase inversion was observed, the elastic modulus approached to that for PMMA.

Addition of only PEO slightly increased the fracture toughness of the epoxy mixture. Since the effect is also associated with decreased T_g, this seems analogous to a plasticizing or flexibilising effect on the epoxy matrix.

4. Conclusions

The morphology and mechanical properties of epoxy-PMMA–PEO blends were investigated. The application of PEO as a compatibilizer in thermoplastic-epoxy blends can be of great interest. The binary mixtures between PEO and epoxy/amine or PMMA were miscible. In the ternary mixtures PEO is functioning like a compatibilizer by which the morphology of the resulting polymer mixture may be changed dramatically.

For each content of the thermoplastic PMMA/PEO mixture, the elastic modulus of the ternary epoxy mixtures was dependent upon matrix composition, its value clearly increasing as the PMMA-rich phase turned to be the main phase. However, both flexural strength and fracture toughness decreased as epoxy became the dispersed phase. The most efficient toughening agent was PMMA, in particular when present as PMMA-rich particles in epoxy-rich matrix. Addition of only PEO also increased fracture toughness although here the mechanism seemed to be analogous to a plasticizing effect.

Table 1
Mechanical properties and fracture toughness of the PMMA/PEO modified epoxy mixtures

PEO (%)	PMMA (%)	E (MPa)	Flexural strength (MPa)	K_{Ic} (MPa $m^{1/2}$)	G_{Ic} (J/m^2)
0	0	2353	93.5	0.880	279
0	5	2348	103.5	1.140	488
0	10	2636	104.0	1.730	1008
0	15	2938	116.0	1.700	825
0	20	2756	112.5	1.780	1026
2	5	2300	101.0	1.200	554
2	10	2613	91.0	0.915	655
2	15	2810	68.0	0.310	31
2	20	2698	69.5	0.420	60
5	0	2405	100.5	1.140	720
5	5	2192	94.0	1.175	556
5	10	2684	95.0	0.860	244
5	15	2711	75.5	0.750	187
5	20	2818	60.0	0.320	33
10	0	2375	95.0	1.075	480

Acknowledgements

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