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The miscibility and morphology of epoxy resin/poly(ethylene oxide) blends

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Poly(ethylene oxide) (PEO) was found to be miscible with uncured epoxy resin, diglycidyl ether of bisphenol A (DGEBA), as shown by the existence of a single glass transition temperature (T_g) in each blend. However, PEO with $M_n = 20\,000$ was judged to be immiscible with the highly amine-crosslinked epoxy resin (ER). The miscibility and morphology of the ER/PEO blends was remarkably affected by crosslinking. It was observed that phase separation in the ER/PEO blends occurred as the crosslinking progressed. This is considered to be due to the dramatic change in the chemical and physical nature of ER during the crosslinking.

(Keywords: poly(ethylene oxide); epoxy resin; polymer blends; miscibility; morphology)

INTRODUCTION

The study of miscibility for polymer blends where one component is crystallizable and another is highly crosslinked has received relatively little attention. Noshay and Robeson examined the miscibility of a range of anhydride-cured epoxy resins with poly(ε-caprolactone) (PCL) of various molecular weights and with different end-groups[1]. They concluded that above a critical molecular weight (3000–5000) of PCL, the blends had a two-phase structure and that the PCL end-groups reacted with the anhydride curing agent to produce a type of block copolymer. In another work by Clark *et al.*[2], PCL blends with amine-cured epoxy resins were examined with attention being paid to the opportunity that existed for hydrogen bonding in amine-cured epoxy resin/PCL blends. They found that PCL with average molecular weight about 20 000 was partially miscible with amine-cured epoxy resins although it was largely immiscible with the anhydride-cured epoxy resins reported by Noshay and Robeson. The different miscibility with PCL between amine-cured and anhydride-cured systems was considered to be due to the presence of hydroxyl groups in the amine-cured system, which offer an excellent potential for hydrogen-bonding interaction with ester groups of PCL in blends.

From the point of view of thermodynamics, an increase in molecular weight for either of the components of a miscible blend would decrease the cloud-point temperature. Therefore, the occurrence of even partial miscibility in such polymer blends containing one component with an infinite molecular weight (i.e. highly crosslinked) is surprising and requires further comment. The complex interrelationship between morphology and composition is not yet clarified and is the subject of a research programme in this laboratory. The present paper describes the results of a study on epoxy resin (ER)/poly(ethylene oxide) (PEO) blends and, in particular, the role of degree of crosslinking in influencing the miscibility of ER with PEO and the phase structure of the resulting blends. The ER/PEO blend system was used to form complexes with inorganic salts as promising solid electrolytes, with PEO salts yielding the advantage of higher ion conductivity while cured ER offers suitable strength[3,4]. Investigation of the miscibility and morphology of this blend system, therefore, is also of practical significance.

EXPERIMENTAL

Materials and preparation of samples

The poly(ethylene oxide) ($M_n = 20\,000$) was supplied by Polysciences Inc., Warrington, PA, USA. The bisphenol A type epoxy resin E-51 with epoxide equivalent weight 185–210, i.e. diglycidyl ether of bisphenol A (DGEBA), was obtained from Wuxi Resin Factory, Wuxi, China. Tetraethylenepentamine (TEPA) was chemically pure and used as crosslinking agent. DGEBA and PEO were mixed at a temperature above the melting point of PEO for a sufficiently long time and then slowly cooled to room temperature. To prepare ER/PEO blends with various crosslinking degrees, the DGEBA/PEO blend so obtained was heated to be just molten, and the curing agent was rapidly added with continuous stirring until a clear mixture was obtained (in approximately 2 min), which was then cured at 110°C for 4 h.

Differential scanning calorimetry

The calorimetric measurements were made on a Perkin-Elmer DSC-2C differential scanning calorimeter. All samples were first heated to 97°C to remove any

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crystallinity followed by quenching to −133°C. A heating rate of 20°C min^{-1} was used in all cases. The glass transition temperature (T_g) and the crystallization temperature (T_c) were taken as the midpoint of the transition and the minimum of the exothermic peak, respectively, while the melting-point temperature (T_m) was taken as the maximum of the endothermic transition.

Morphological observation

The overall morphology of pure PEO, the DGEBA/PEO blends and the various cured ER/PEO blends was investigated by optical microscopy using an Opton-Universal R Pol microscope.

SAXS measurements

SAXS study was carried out using a Kratky small-angle X-ray scattering system. A Kratky copper target X-ray tube was used with a Philips Norelco generator operating at 45 kV and 40 mA. Samples were of uniform thickness and approximately 1 mm thick.

RESULTS AND DISCUSSION

All the DGEBA/PEO blends were transparent just above the melting point of PEO. Optical micrographs for the blends are shown in *Figure 1*. In the optical microscope with crossed polars the spherulites display a 'Maltese cross' birefringence pattern and have regular shape with defined borders. The following observations can be made: first, there is no evidence that the non-crystallizable component segregates in large domains in intraspherulitic regions or in interspherulitic contact zones exceeding the dimensions corresponding to the resolving power of the technique used. Secondly, the DGEBA/PEO blend samples are always completely volume-filled with PEO spherulites up to a composition of 90/10. Finally, spherulites of 90/10 DGEBA/PEO blends show a less regular texture; this may be caused by the coarseness of the crystalline lamellae due to the presence of uncrystallized material in interlamellar regions. All these observations suggest that PEO is miscible with DGEBA in the molten state; and during the crystallizing process of the blends, the DGEBA is incorporated in the interlamellar regions of PEO spherulites.

The d.s.c. thermograms (second heat) are shown in *Figure 2*, and the results are summarized in *Figure 3*. *Figure 2* reveals a single glass transition temperature, which varied with overall blend composition as indicated by the full circles in *Figure 3*. The appearance of a single glass transition temperature strongly suggests that the blend presents a homogeneous single amorphous phase, i.e. the two components are miscible in the amorphous phase.

Several theoretical and empirical equations have been used to describe the T_g–composition dependence of miscible blends. One of these, the Fox equation[5], is written as:

$$1/T_g(\text{blend}) = W(\text{DGEBA})/T_g(\text{DGEBA}) + W(\text{PEO})/T_g(\text{PEO}) \quad (1)$$

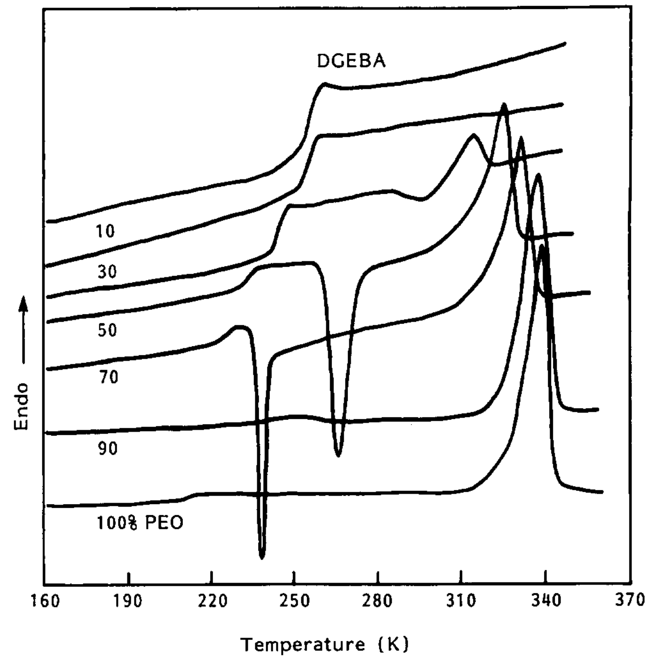

Figure 2 The d.s.c. thermograms of the DGEBA/PEO blends

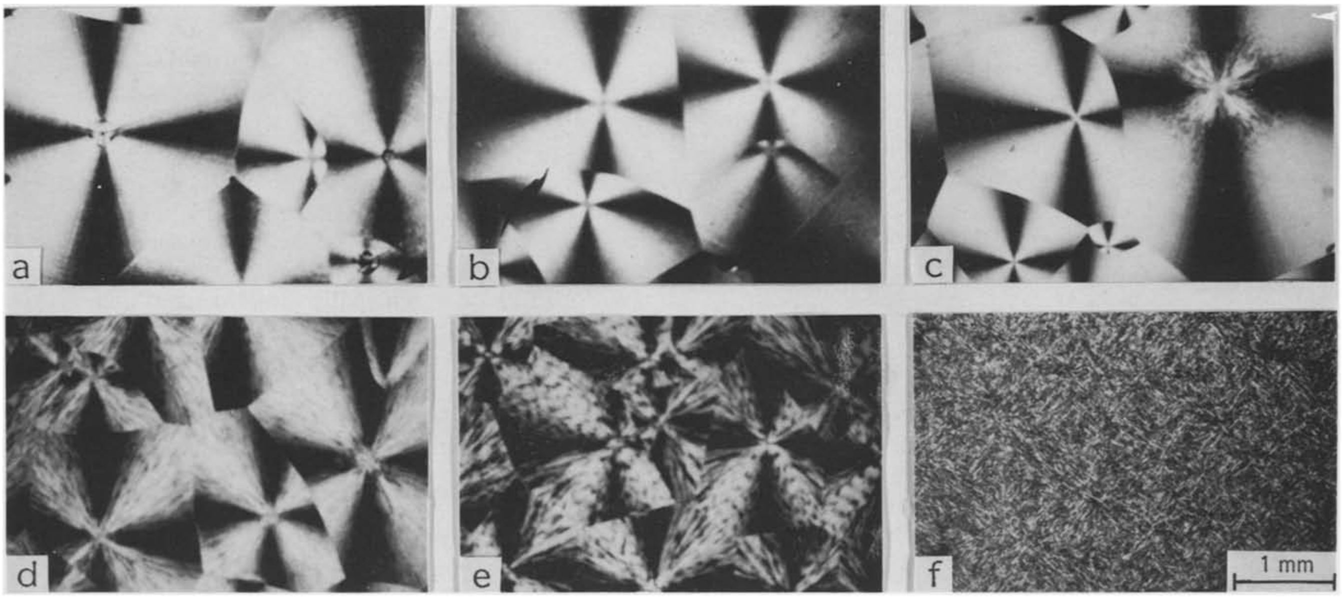

Figure 1 Optical micrographs for the thin films of (a) 0/100, (b) 10/90, (c) 30/70, (d) 50/50, (e) 70/30 and (f) 90/10 DGEBA/PEO blends

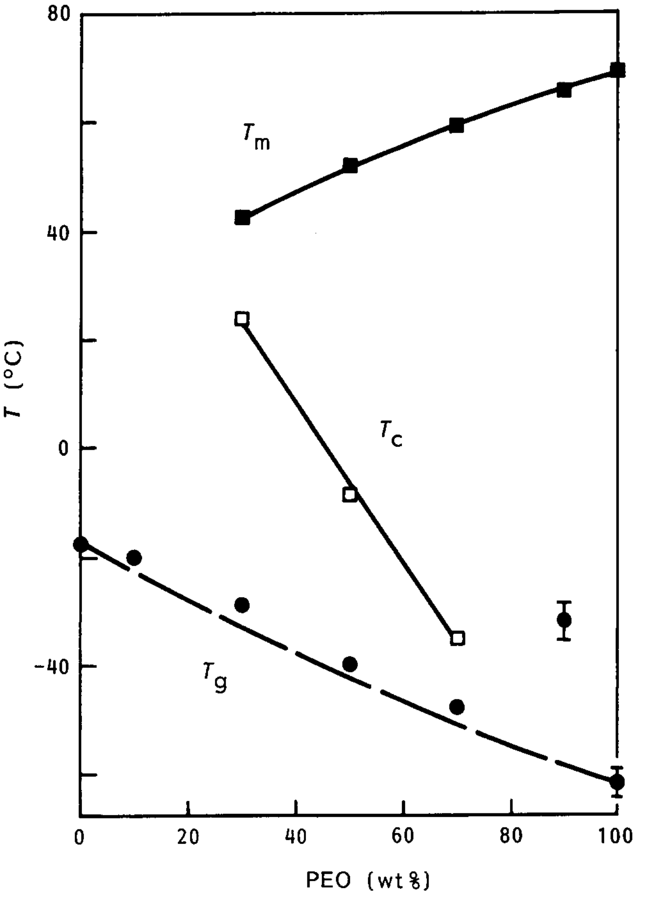

Figure 3 Dependence of T_g (●), T_c (□) and T_m (■) of the quenched DGEBA/PEO blends on the weight per cent of PEO. (———) Fox equation prediction

where T_g(blend) is the glass transition temperature of the blend, T_g(DGEBA) and T_g(PEO) are those of plain DGEBA and PEO, and W(DGEBA) and W(PEO) are the corresponding weight fractions.

Equation (1), as shown by *Figure 3*, fits the experimental T_g data quite well.The deviation of experimentally obtained T_g data from the Fox equation at high PEO content (90 wt% PEO) is because of the crystallization of PEO in the blend during quenching.

Figure 3 shows also the T_c and T_m of the quenched samples as functions of blend composition. For the pure PEO and 10/90 DGEBA/PEO blend, no crystallization exotherm was observed since crystallization was sufficiently rapid to occur completely during the quenching. However, for the blends with a higher DGEBA content up to 70 wt%, T_c increases with increase of DGEBA content. This phenomenon indicates that crystallization of PEO in the blend becomes progressively difficult with increase of DGEBA content. Furthermore, the blend containing 90 wt% DGEBA did not show any crystallization exotherm. These results support the idea that DGEBA is completely miscible with PEO over the entire composition range in the melt. The decrease in the crystallinity of PEO with increase of DGEBA content is attributed both to the higher T_g of DGEBA than that of PEO and to the interactions between these two components.

The T_m depression with increase of DGEBA content shown in *Figure 3* is more substantial than those usually observed for miscible blends having one crystallizable component. This is because both enthalpic and entropic effects contribute to the melting-point depression in the DGEBA/PEO blends owing to the small molecular weight of the DGEBA. In the case when the molecular weights of both components are adequately large, only the enthalpic contribution to the melting-point depression is not negligible^6.

Each of the DGEBA/PEO blends was optically homogeneous and fluid enough at temperatures just above the melting point of PEO and remained so after TEPA was added for a few minutes. As the temperature was raised to 110°C, the blend began gradually to become opaque and distinctly hazy, indicating that phase separation occurred as crosslinking progressed.

Figure 4 shows the d.s.c. thermograms of the ER/PEO blends containing 50 wt% PEO and cured with different TEPA contents. A crystallization exotherm occurred for blends with TEPA/DGEBA $\leqslant 0.08$, while no exotherm occurred for those with TEPA/DGEBA $\geqslant 0.12$, which implies that crystallization was rapid and had been completed during the quenching. The greater the TEPA content of the blend, the more rapidly the crystallization occurred and the higher the crystallinity of PEO. For the blend without TEPA, i.e. 50/50 DGEBA blend, the crystallization exotherm equalled the melting endotherm, which means that no crystallization occurred during the quenching. In the blends of low TEPA content (TEPA/DGEBA $\leqslant 0.08$), the T_g is observed to shift to lower temperature with increasing TEPA content. This is because the greater the TEPA content of the blend, the more the cured ER separated out and the more PEO in the uncured phase the blend had. For the blends with TEPA/DGEBA $\geqslant 0.12$, two T_g values are observed as shown in *Figure 4*. One (T_{g_1}) around 108°C is attributed

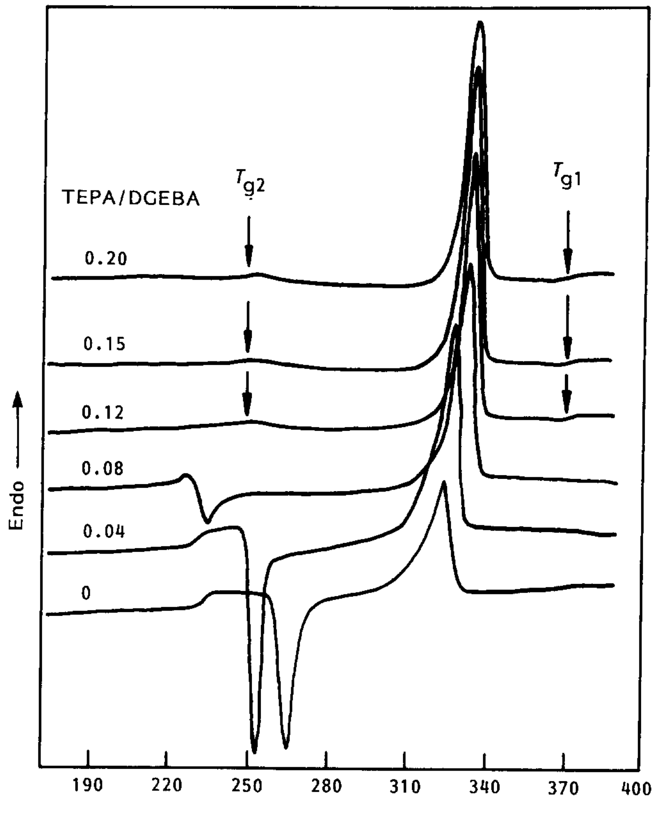

Figure 4 The d.s.c. thermograms of the ER/PEO blends containing 50 wt% PEO and cured with various amounts of TEPA

to the crosslinked ER remaining almost invariant. That is to say, a highly crosslinked ER was formed and separated out during the crosslinking. The other one (T_{g_2}) is higher than that of the 50/50 DGEBA/PEO blend and keeps almost constant, indicating that the related phase might be composed of PEO and partially cured ER. Additionally, the melting point of PEO is shifted to higher temperature and approaches the T_m of the pure PEO as a result of increasing crosslink density (*Figure 5*). It can be seen that PEO is miscible or partially miscible with insufficiently crosslinked ER but immiscible with highly crosslinked ER. The higher the crosslinking degree, the more completely the phase separation occurred. The degree of crystallinity, X_c, of the PEO phase of the crosslinked 50/50 ER/PEO blends, as shown in *Figure 5*, increases with TEPA content. The X_c was calculated from:

$$X_c = \Delta H_f(\text{PEO})/\Delta H_f^\circ(\text{PEO}) \qquad (2)$$

where $\Delta H_f^\circ(\text{PEO}) = 205 \text{ J g}^{-1}$ is the heat of fusion for 100% crystalline PEO[7] and $\Delta H_f(\text{PEO})$ is the heat of fusion for PEO in the blend.

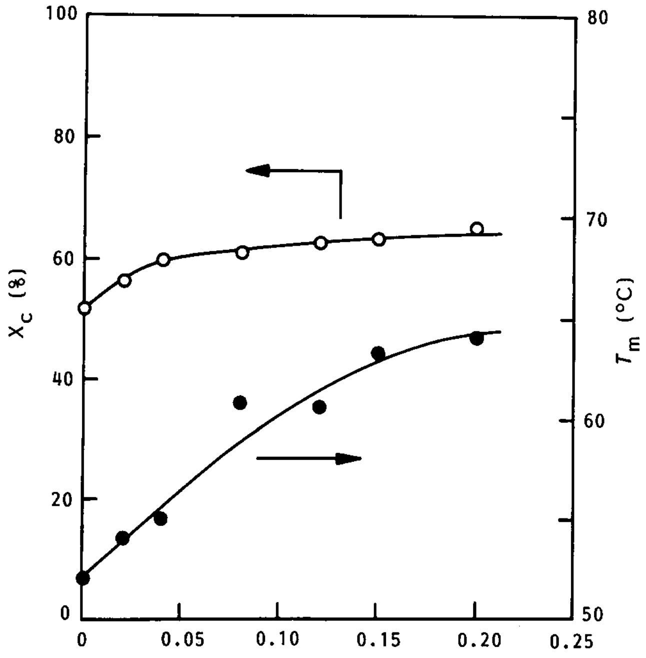

Figure 5 Crystallinity and melting point of PEO in the blend as functions of TEPA content for the crosslinked ER/PEO blends containing 50 wt% PEO

Optical micrographs for the ER/PEO blends containing 50 wt% PEO and cured with various amounts of TEPA are shown in *Figure 6*. The spherulites first become smaller, which may be attributed to the enhanced nucleation rate owing to the crosslinked ER phase, and then gradually become larger again and clearer as a result of increasing crosslink density. The spherulites of the highly crosslinked blends tend to become like those of plain PEO as the crosslink density increases.

All the ER/PEO blends cured with TEPA/DGEBA = 0.12 were quite opaque at room temperature and did not become clear above the T_m of PEO. The previously mentioned DGEBA/PEO blends exhibited opacity or were hazy at low temperature owing to PEO crystallinity, but all become fully transparent above T_m. The thermal properties of the cured ER/PEO blends are presented in *Table 1*. T_{g_1} is attributed to the cured ER phase, which was separated out in high ER-content blends. T_{g_2} is somewhat higher than that of the pure PEO, indicating

Table 1 Thermal properties of the ER/PEO blends cured with TEPA/DGEBA = 0.12

ER/PEO	T_{g_1} (°C)	T_{g_2} (°C)	T_m (°C)	ΔH_f (PEO) (J/g PEO)	X_c (%)
0/100		−62	69.0	147	72
10/90		−52	68.0	144	70
30/70		−35	62.5	141	69
50/50	106	−33	60.5	128	63
70/30	110	−34	62.5	113	55
90/10	104	−40	55.3	78	38
100/0	109				

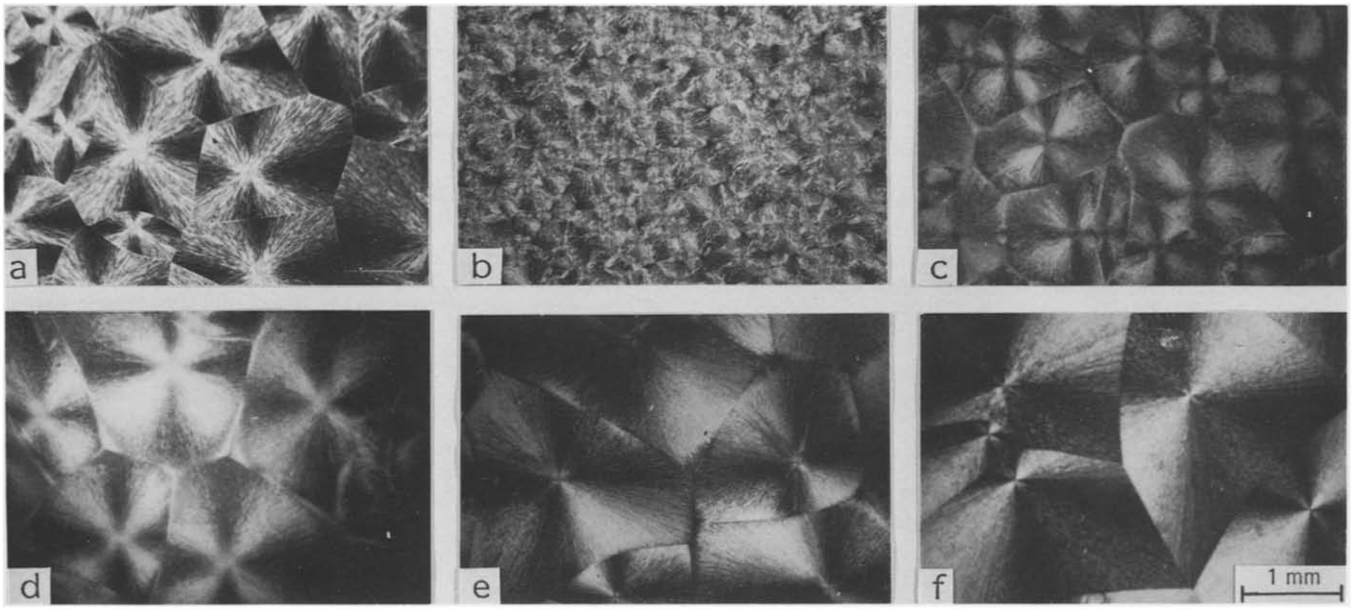

Figure 6 Optical micrographs of the ER/PEO blends containing 50 wt% PEO and cured with various amounts of TEPA. TEPA/DGEBA = (a) 0, (b) 0.04, (c) 0.08, (d) 0.12, (e) 0.15 and (f) 0.20

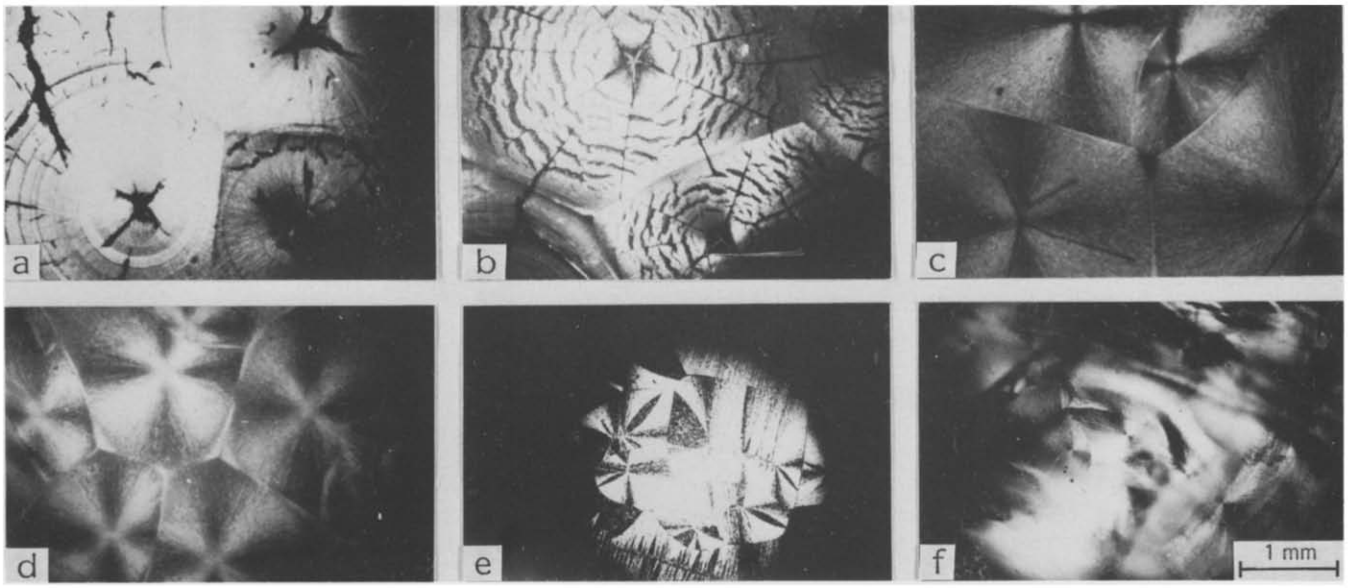

Figure 7 Optical micrographs of (a) 0/100, (b) 10/90, (c) 30/70, (d) 50/50, (e) 70/30 and (f) 90/10 ER/PEO blends crosslinked with TEPA/DGEBA = 0.12

Table 2 Values for the long period *L* of the ER/PEO blends cured with TEPA/DGEBA = 0.12

ER/PEO	*L* (Å)
0/100	206
10/90	201
20/80	207
30/70	211
40/60	209
50/50	209

the existence of another amorphous phase, which was composed of PEO and some uncured and/or insufficiently cured ER. The T_m for PEO lies between these two T_g values, and the melting-point depression is rather slight. It is quite evident that PEO is immiscible with the highly crosslinked ER in spite of the fact that it may be miscible with the partially cured ER.

Figure 7 shows the optical micrographs of the crosslinked ER/PEO blends. It is noted that the spherulites of pure PEO (*Figure 7a*) and 10/90 ER/PEO blend (*Figure 7b*) are cracked and the others are not. This may be because of the volume shrinkage in a thicker film during the crystallization process due to high degree of crystallinity. The thicker films were used for the micrograph since thin films of the cured ER/PEO blends are difficult to prepare. For low PEO-content blends (30 and 10 wt% PEO), a dark background was observed in the polarizing microscope. However, some discrete clusters of PEO spherulites (*Figure 7e*) or some discrete PEO spherulites (*Figure 7f*) could be found; they might be formed from the separated phase of PEO.

Using Bragg's law, long periods *L* were calculated from the peak positions of Lorentz corrected and desmeared SAXS patterns for the pure PEO and the crosslinked ER/PEO blends crystallized at room temperature. The results obtained are listed in *Table 2*. *L* remains almost invariant with increasing ER content. This indicates that no crosslinked ER is present in interfibrillar and interlamellar regions of PEO crystals. PEO is immiscible with the crosslinked ER.

CONCLUDING REMARKS

It can be concluded that PEO is immiscible with the highly crosslinked ER, although it is miscible with both uncured ER, i.e. DGEBA, and poly(hydroxy ether of bisphenol A)[8,9], which may be considered to be a model epoxy resin. However, it can be seen that PEO may be miscible with partially cured ER or partially miscible with more completely but not yet sufficiently cured ER. This result is similar to that for the amine-cured PCL/ER blends reported by Clark *et al.*[2], except that phase separation began to occur at a lower crosslinking degree in the ER/PEO blends than in the ER/PCL blends. The crosslinking reaction between DGEBA and TEPA resulted in the formation of crosslinked ER network, which was then separated out. The 'network effect' makes the crosslinked ER more stable in the isolated state than in the form of a homogeneous blend. This must imply that the exotherm of the crosslinking reaction was more than the endotherm of the demixing of the blend, leading to an overall decrease in the free energy of the system. Also the chemical and physical nature of ER changed dramatically as the crosslinking progressed.

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