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Phase separation during crosslinking of epoxy resin/poly(ethylene oxide) blends

Guo Qipeng[1],*, Peng Xinsheng[1], and Wang Zhiji[2]

[1]Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, People's Republic of China
[2]Jilin Institute of Technology, Changchun 130022, People's Republic of China

SUMMARY

Poly(ethylene oxide) (PEO) was found to be miscible with uncured epoxy resin of DGEBA type (ER) as shown by the existence of a single glass transition temperature (Tg) in each blend. However, PEO with $\overline{M}n$ = 20,000 was judged to be immiscible with the highly amine-crosslinked ER. It was observed that the phase separation in the ER/PEO blends occurred as the crosslinking progressed. This is considered to be due to the dramatical change in the chemical and physical nature of ER during the crosslinking.

INTRODUCTION

The study of miscibility for polymer blends where one component is crystallizable and another highly crosslinked has recieved relatively very little attention. Only two works concerning this aspect were reported (1,2). One is by Noshay and Robeson (1), who examined the miscibility of a range of anhydride-cured epoxy resins with poly(ε-caprolactone) (PCL) of different molecular weights and with different end groups. They concluded that above a critical molecular weight (3,000-5,000) 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 to the opportunity which 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 anhydride-cured epoxy resins reported by Noshay and Robeson. The different miscibility with PCL between amine-cured and anhydride-cured systems is 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. However, the occurence of even partial miscibility in such a polymer blend containing one component with an infinite molecular weight (i.e., highly crosslinked) is surprising and requires further comment. The complex interrelationship between morphology, composition is not yet clarified and is the subject of a research

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*To whom correspondence should be addressed program in this laboratory. In the present communication, we describe here a preliminary study of epoxy resin (ER)/poly(ethylene oxide) (PEO) blends and, in particular, the role of crosslinking degree in influencing the miscibility of ER with PEO and the phase structure of the resulted blends.

EXPERIMENTAL

Materials and Preparation of Samples

Poly(ethylene oxide) ($\bar{M}n$ = 20,000) were supplied by Polysciences, Inc. DGEBA Epoxy resin E-51 with epoxide equivalent weight 185-210 was obtained from Wuxi Resin Factory (China). Tetraethylenepentamine (TEPA) was used as crosslinking agent. ER and PEO were mixed at the 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 different crosslinking degrees, the ER/PEO blend so obtained was heated just to be molten, and the curing agent was rapidly added with continuously stirring until a clear mixture was obtained (in approximately 2 min), which was then cured at 110°C for 4 hours.

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 melt any crystallinity followed by quenching to -133°C. A heating rate of 20°C/min was used in all cases. The glass transition temperature (Tg) and the crystallization temperature (Tc) were taken as the onsets of the endothermic and exothermic transitions, respectively, while the melting point temperature (Tm) as the maximum of the endothermic transition.

RESULTS AND DISCUSSION

All the ER/PEO blends without TEPA were transparent just above the melting point of PEO. The results on Tg of the blends as a function of composition are given in Fig. 1. The appearance of a single glass transition temperature strongly suggests the blend presents a homogeneous single amorphous phase, i.e. the two components are miscible in the amorphous phase and in the melt. In the same figure the Fox relationship (3) is also drawn. The deviation of experimentally obtained Tg's data from Fox equation at high PEO content (90 wt.% PEO) is because of the crystallization during the quenching.

The Fig. 1 also shows the Tc and Tm of the quenched samples as functions of blend composition. For the pure PEO and 10/90 ER/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 ER content up to 70 wt.%, Tc increases with increase of ER content. This phenomenom indicates the crystallization of PEO in the blend become progressively difficult with increase of ER content. Furthermore, the blend containing 90 wt.% ER did not show any crystallization exotherm. These results support the idea that ER is completely miscible with PEO over the entire composition range in the melt. The decrease in the crystallinity of PEO with increase of ER content is attributed to the higher Tg of ER than that of PEO and the interactions between these two components.

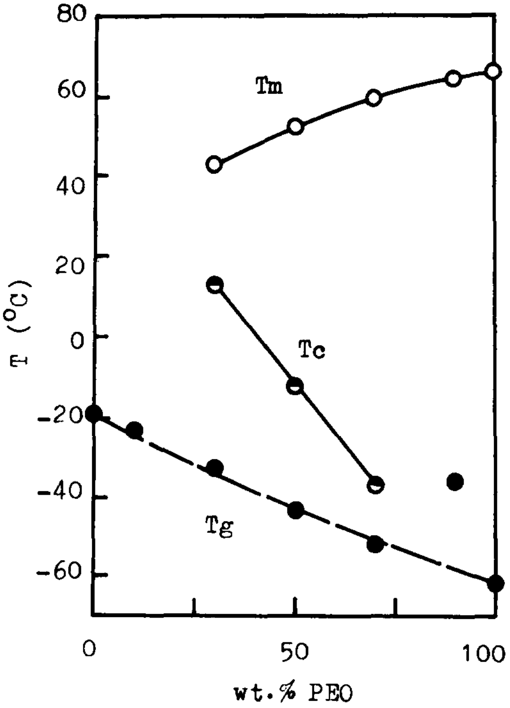

Fig.1. Dependence of Tg (●), Tc (●), and Tm (○) of the quenched ER/PEO blends on the weight percent of PEO. (— — —) Fox equation prediction.

The Tm depression with increase of ER content shown in Fig. 1 is much more substantial than those usually observed for miscible blends having one crystallizable component. This is because of both enthalpic and entropic effects contribute to the melting point depression in the ER/PEO blends owing to the small molecular weight of the ER, whereas in the case that the molecular weights of both components are adequately large, only enthalpic contribution to the melting point depression is not negligible (4).

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

Fig. 2 shows DSC thermograms of the ER/PEO blends containing 50 wt.% PEO and cured with different TEPA contents. A crystallization exotherm was occurred for blends with TEPA/ER $\leqslant$ 0.08, while no exotherm for those with TEPA/ER $\geqslant$ 0.12 implies that crystallization was so rapid and had been completed during the quenching. The more TEPA content the blend had, the more rapidly the crystallization occurred and the higher the crystallinity of PEO. For the blend without TEPA the crystallization exotherm equaled the melting endotherm, this means that no crystallization occurred during the quenching. In the low TEPA content blends (TEPA/ER $\leqslant$ 0.08) the Tg is

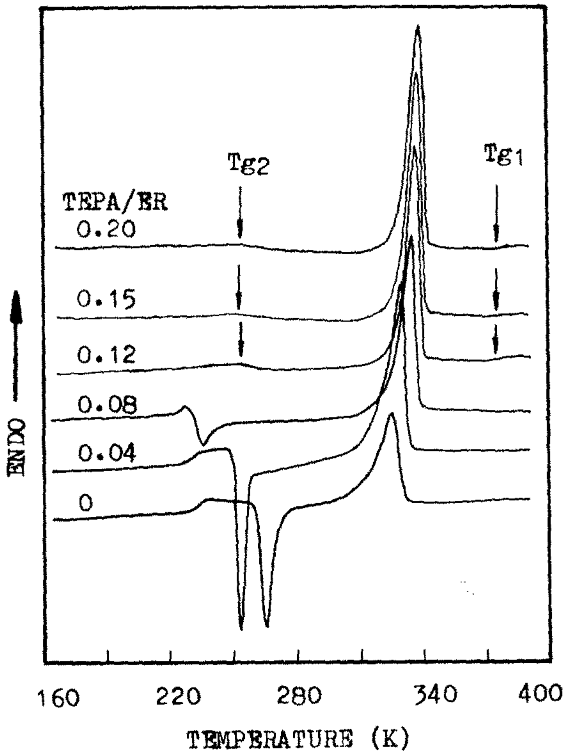

Fig. 2. DSC thermograms of the ER/PEO blends containing 50 wt.% PEO and cured with different amount of TEPA.

observed to shift to lower temperature with increasing of TEPA content. This is because the more TEPA content the blend had, the more the cured ER separated out and the more PEO in the uncured phase the blend had. For the blends with TEPA/ER $\geqslant$ 0.12, two Tg's are observed as shown in the figure. One (Tg1) around 105 C is attributed 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 (Tg2) is higher than that of the 50/50 ER/PEO blend without TEPA and keeps almost constant indicating the related phase might be composed of PEO and partially cured ER. Additionally, the melting point of PEO is shifted to higher temperature and to approach the Tm of the pure PEO as a result of increasing crosslinked density. It can be seen that PEO is miscible or partially miscible with unsufficiently crosslinked ER but immiscible with highly crosslinked ER. The higher the crosslinking degree, the more compoletely the phase separation occurred.

All the ER/PEO blends cured with TEPA/ER = 0.12 were quite opaque at room temperature and did not become clear above the Tm of PEO. The previously mentioned uncured ER/PEO blends exhibited opacity or hazy at low temperature owing to PEO crystallinity, but all become fully transparent above Tm. Fig. 3 shows the transition behaviour observed for these cured ER/PEO blends by DSC. At the high ER contents, glass transtions for the cured ER (Tg1) are evident with only minor shifts in

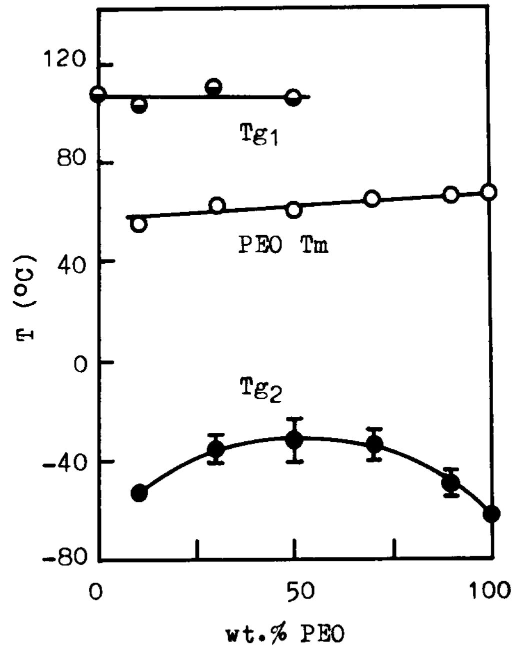

Fig. 3. Transition behaviour for the cured ER/PEO blends.

temperature locations suggesting that the cured ER was separated out. A lower glass transition (Tg2) also found in the figure is somewhat higher than that of the pure PEO indicating the existence of another amorphous phase which was composed of PEO and some uncured and/or unsufficiently cured ER. The Tm for PEO lies between these two Tg's. The crystallization seemed to occur unaffected by the presence of cured ER. The melting point depression is rather slight. It is quite evident that PEO is immiscible with the highly crosslinked ER in spite of it may be miscible with the partially cured ER.

It is noted that PEO is immiscible with the highly crosslinked ER although it is miscible with both uncured ER and poly(hydroxy ether of bisphenol A) (5,6) 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 compoletely 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 ER and PEO 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 homogeneous blend. This must imply that 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. And the chemical and physical nature of ER changed dramatically as the crosslinking progressed.

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