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STUDIES ON THE PHASE SEPARATION OF POLYETHERIMIDE MODIFIED TETRAFUNCTIONAL EPOXY RESIN. III. MORPHOLOGY DEVELOPMENT OF THE BLEND DURING CURING

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Key Words: TGDDM, Polyetherimide, Blend, Morphology Development, SEM, DSC, TRLS

ABSTRACT

Using scanning electron microscope (SEM), differential scanning calorimetry (DSC) and time-resolved light scattering (TRLS) methods, the morphology development of novel polyetherimide modified tetreglycidyl-4,4'-diaminodiphenylmethane (TGDDM) epoxy resin was investigated. The phase separation took place early in the blend and morphology was fixed in the first 10 minutes of curing. Then, the diffusion of the epoxy and the polyetherimide molecules still existed till the final stage of curing.

INTRODUCTION

In our previous work [1-3], the novel synthesized polyetherimide with different molecular weight has been used to modified epoxy resin. The obtained morphology of the blends exhibit variety from PEI dispersed particle domains to large co-continuous morphology as the increase of the PEI molecular weight. It

draws more attention to the development of blend morphology due to the relationship between morphology and the mechanical properties of the blend.

There is much in the literature [4-6] reporting that the morphology affects the mechanical properties. Yamanaka and Inoue [7] have already presented the phase separation scheme of thermoplastics-modified epoxy resin, where the homogeneous mixture starts to phase separate by spinodal decomposition after the temperature jump to the curing temperature, resulting in the development of a co-continuous structure in the early stage. Cho *et al.* [6] studied Ultem 1000 (G. E. Co.) polyetherimide modified four functional epoxy resin and found that through different curing programs a variety of phase structures are obtained. The morphology changes from the PEI spherical domain dispersed in the epoxy resin to the co-continuous structure, and finally the phase-invested morphology with PEI matrix. However, the reality of the formation of phase structure is little reported [8]. Especially, the co-continuous structure is somewhat larger than that of expected in our previous work [9], which is not easy to understand based on the spinodal decomposition mechanism.

In this work, a scanning electron micrograph (SEM) has been used to trace the morphological change of blend under curing. Combining the results of time-resolved light scattering and differential scanning calorimetry (DSC), the process of the blend phase formation is observed and discussed based on the spinodal decomposition mechanism.

EXPERIMENTAL

The epoxy resin used was supplied by Shanghai Institute of Synthesis Resin, which is tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM). The resin was cured with 40 phr of diaminodiphenyl sulfone (DDS) (Shanghai Third Regent Factory) which was used without further purification. The polyetherimide was synthesized in our laboratory and described in reference [1]. The used polyetherimide is phenyl-terminated and the inherent viscosity is 0.61 which was characterized at 0.5 g/dL concentration in 1-methyl-2-pyrrolidinoene solvent at 30°C. The polymer is designated as P-PEI (0.61).

An epoxy blend containing 20 phr of P-PEI was prepared by dissolving the P-PEI in TGDDM at 150°C. Until a homogenous, clear solution was obtained, the mixture was cooled to 130°C and 40 phr of DDS was added while the mixture was stirred. After the cure agent was dissolved, the blend was cooled to room temperature rapidly to avoid further curing reaction.

The phase separation process during curing reaction was observed at real time and in situ on the self-made Time-resolved Light Scattering (TRLS) with a controllable hot chamber and TRLS technique was described elsewhere [10]. The change of the light scattering profiles was recorded at appropriate time intervals during isothermal curing. The blend of epoxy resin with P-PEI for TRLS observation was prepared by solvent-casting film in 1,4-dioxane solution. The thin film of blend was degassed for two days at room temperature to remove the solvent.

The morphology of the blend cured for different time at curing temperature was observed under Scanning Electron Microscope (SEM) (HITACHI S-520). The samples were fractured in liquid nitrogen.

The change of the glass transition temperature of blends cured for different time at curing temperature was characterized with Setaram Differential Scanning Calorimetry (DSC) instrument from -20°C to 300°C at $20^{\circ}\text{C}/\text{min}$ heating rate.

RESULTS AND DISCUSSION

Morphological Development

The phase morphology of the E/P-PEI (0.61) blend was monitored by the scanning electron microscopy as a function of the cure time when conducted at a temperature of 150°C . Figure 1 shows the morphologies of the blend cured at 150°C for 2, 4, 6.5, 10, 15, 20 minutes, and 5 hours. In the initial curing time (Figure 1a), the blend appears just like a piece of silk with creases on it. This prologue is the common phenomenon in the curing procedure of pure epoxy resin and the blends. In our previous publication, the same phenomenon was also observed in the diglycidyl ether of bisphenol A (Epon-828) resin and the polyetherimide modified systems [11]. In Figure 1b, the blend cured for 4 minutes shows the evidence of phase separation. The creases become shorter and more crooked. At the same time, in the magnification of 3000, there are some white regions that appeared in the dark, smooth region (Figure 1b). But, the boundary between the two regions is not clear. After curing for 6.5 minutes, (Figure 1c), it shows fine structure in the white region which seems to be particle domains surrounded by white thread. After considering the difference in ductile properties between the epoxy resin and the polyetherimide, it is concluded that the white thread phase corresponds to the polyetherimide domain while the dispersed particles to the epoxy domain. Because of the obvious polyetherimide phase existing in the white region, this region may be called as the PEI-rich phase and the other region called as the epoxy-rich phase.

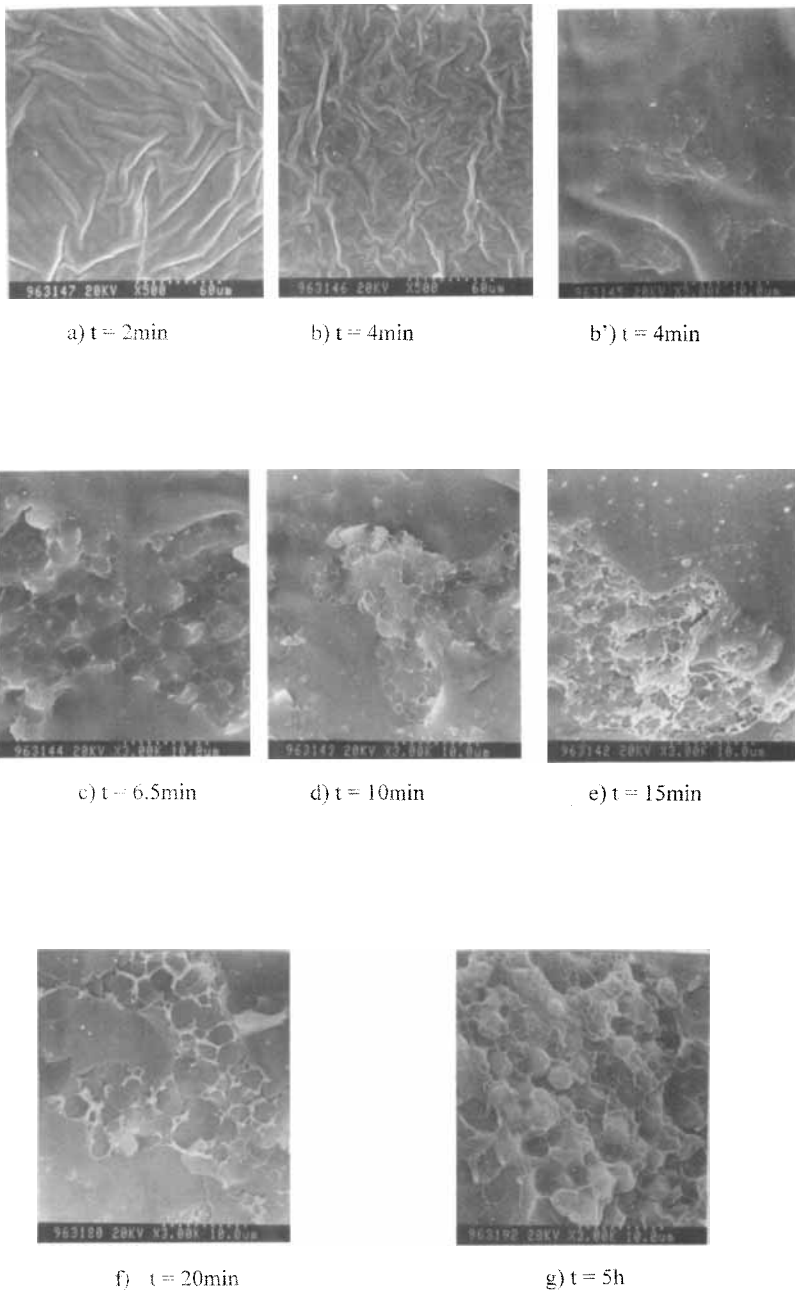


Figure 1. SEM micrographs of P-PEI (0.61) modified epoxy resin cured at 150°C for different times; a) t = 2 minutes; b) t = 4 minutes; b') t = 4 minutes; c) t = 6.5 minutes; d) t = 10 minutes; e) t = 15 minutes; f) t = 20 minutes; g) t = 5 hours.

TABLE 1. The Glass Transition Temperature of Neat Epoxy Resin and P-PEI (0.61) Modified System Cured at 150°C for Different Times

Cured time (min)	T _g of neat epoxy (°C)	T _g of modified system (°C)	
0	11	25	
2	11	14	30
3	11.5	18.5	89
4	12	20	100
10	14	61	---

As the blend cured for 10 minutes (Figure 1d), it is clear that in the PEI-rich phase the dispersed particles are obvious and the boundary between the PEI-rich phase and the epoxy-rich phase is distinct. Moreover, some white particles appeared in the dark and smooth epoxy-rich phase. That means that the phase separation also takes place in the epoxy-rich phase. In Figure 1e, the epoxy particles in the PEI-rich phase are discrete from each other with the white PEI domains around them. While the PEI particles in the epoxy-rich phase become more obvious compared with those after 10 minutes of curing. The phase separation continues under the curing conditions, but the morphological change is no longer great. In Figure 1f, the morphology is the same as that cured for 15 minutes. In the final morphology (Figure 1g), the PEI-rich phase and epoxy-rich phase are co-continuous in which there exists the other component particles.

Glass Transition Temperature

Table 1 shows the glass transition temperatures of the pure epoxy resin and the modified system at different cure times. When the glass transition temperature shifts to high temperature at about 110°C, it will overlap with the exothermic peak of the curing reaction. The glass transition temperature of pure epoxy resin changes slightly at curing temperature 150°C. In contrast, the change of glass transition temperatures of the blend is great. Before curing, the PEI is miscibility with epoxy resin and gives just one T_g which is higher than pure epoxy resin because of the existence of polyetherimide. After curing for 2 minutes, the phase separation occurs and two T_gs exhibit in the DSC curve. At that time, there is no obvious evidence of phase separation occurrence in the SEM micrograph. From this view, the DSC

method is more sensitive than SEM observation. In two T_g s, the lower one is assigned to the epoxy-rich phase and the higher ones to the PEI-rich phase. At the same cure time, the modified system gives higher T_g s than that of pure epoxy resin, that means the addition of polyetherimide increases the cure rate of modified system. The difference in the glass transition temperature between the PEI-rich phase and the epoxy-rich phase is increasing as the curing is prolonged, but less than that of pure epoxy ($T_g = -5\text{ }^\circ\text{C}$) and PEI ($T_g = 217\text{ }^\circ\text{C}$). It can be assumed that the difference in concentration of the two separated phases is small considering the $80\text{ }^\circ\text{C}$ difference in glass transition temperatures of the two separated phases after 4 minutes of curing. After 10 minutes of curing, the T_g of the PEI-rich phase is overlapped with the exothermic peak of the cure reaction and the T_g of the epoxy-rich phase is $61\text{ }^\circ\text{C}$. Based on the SEM observation, the morphology has formed after 10 minutes of curing and shows no great change compared with the morphology after 5 hours of curing. But the compositions in two separated phases is still changing as the curing reaction is prolonged. The TRLS results confirm this conclusion.

Time Resolved Light Scattering Results

Due to the overlap of the T_g and the exothermic peak of the cure reaction, it is impossible to observe the variation of the compositions in the separated phases. Time-resolved light scattering was used to trace the change of scattering light profile of blend after 10 minutes of curing. Figure 2 shows the change of light scattering profile of the blend cured at $150\text{ }^\circ\text{C}$. It indicates the light intensity decreases with the time to zero and increases again. In our previous paper [2], it has been proven that the disappearance of light profile is not the process of phase dissolution and second phase formation but the change of the phase refraction indexes. Based on the light scattering theory [12], the intensity of light scattering $I(q,t)$ can be expressed as below:

$$I(q, t) \propto \langle \eta^2 \rangle \cdot q_m(t)^{-3} \cdot S\left(\frac{q(t)}{q_m(t)}\right) \quad (1)$$

in which, $S(q(t)/q_m(t))$ is a structure function, which corresponds to the character of the phase structure; q_m is the position of the scattering vector relating to the maximum lighting intensity in the spectrum. whose equivalent is proportional to the size of phase structure; $\langle \eta^2 \rangle$ means the mean-squared fluctuations, it can be expressed as:

$$\langle \eta^2 \rangle \propto \Phi_1 \cdot \Phi_2 \cdot (n_1 - n_2)^2 \quad (2)$$

in which, ϕ_i and n_i are the volume fraction and the refraction index of component i .

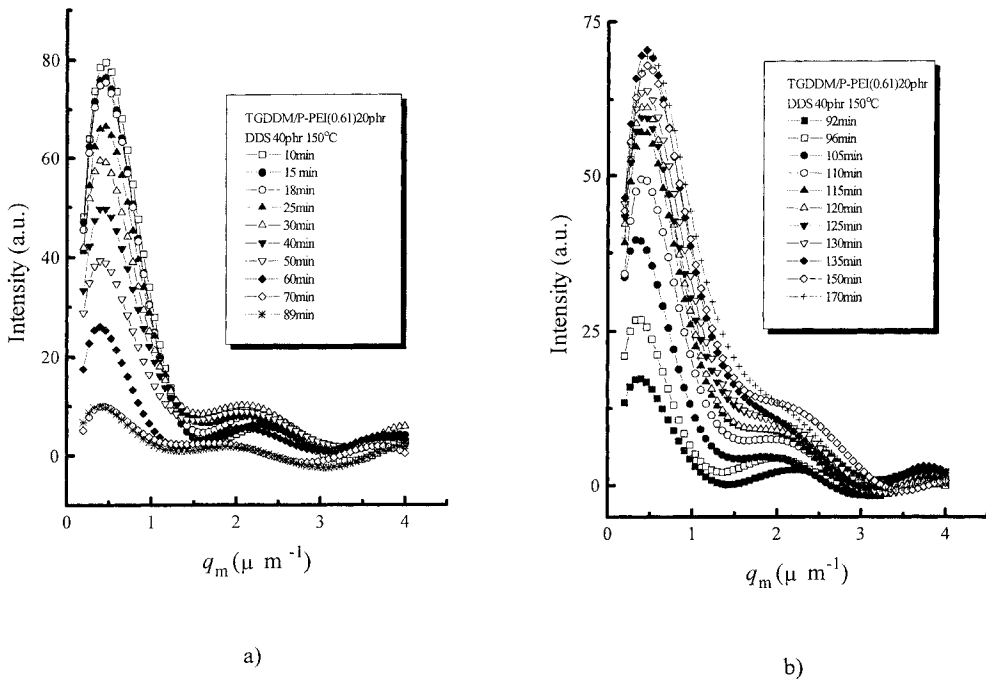


Figure 2. The change of the scattering light profiles of P-PEI (0.61) modified epoxy resin cured at 150°C.

If q_m maintains the same position just as what has been observed in our experiment through the whole procedure, the structure function $S(q(t)/q_m(t))$ and the vector q_m will not cause the change of $I(q_m, t)$. So the changing of light intensity $I(q_m, t)$ is proportional to the variety of $\langle \eta^2 \rangle$, which can also be expressed as the concentration fluctuations of two phases. After 170 minutes of curing, the scattering light profile stops fluctuating. This indicates that the diffusion of epoxy or PEI molecules to the epoxy-rich or PEI-rich phase have not stopped for a relatively long time while in this period of time the morphology remains still.

CONCLUSION

From the above results, one possible description of the phase formation is that the phase separation takes place in the initial time of curing, then the large scale of co-continuous phases appear not from the growing of small particles, but directly from the blend. The morphology is constructed in the first 10 minutes of curing and

keeps little change along the curing process. However, the diffusion of the PEI and epoxy molecules from phase to phase maintain a long time till the final stage.

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REFERENCES

- [1] J. Cui, W. J. Chen, Z. Z. Zhang, and S. J. Li, *Macromol. Chem. Phys.*, **198**, 1865 (1997).
- [2] Y. F. Yu, J. Cui, W. J. Chen, and S. J. Li, *J. Macromol. Sci. Chem.*, in press.
- [3] J. Cui, W. J. Chen, Y. F. Yu, and S. J. Li, *Macromol. Chem. Phys.*, M97/109.
- [4] C. B. Bucknall and A. H. Gilbert, *Polymer*, **30**, 213 (1989).
- [5] A. H. Gilbert and C. B. Bucknall, *Makromol. Chem., Macromol. Symp.*, **45**, 289 (1991).
- [6] J. B. Cho, J. W. Hwang, K. Cho, J. H. An, and C. E. Park, *Polymer*, **34(23)**, 4832 (1993).
- [7] K. Yamanaka and T. Inoue, *Polymer*, **30**, 662 (1989).
- [8] C. C. Su and E. M. Woo, *Polymer*, **36(15)**, 2883 (1995).
- [9] S. J. Li, B. L. Hsu, F. W. Harris, and S. Z. D.Cheng, *The Fourth International Symposium on Toughened Plastic Science and Engineering*, ACS, San Diego, USA (1994).
- [10] W. J. Chen, Z. Shen, X. Huang, and J. Huang, *Macromol. Rapid Communication*, **18**, 197 (1997).
- [11] J. Cui, Y. F. Yu, and S. J. Li, *Macromol. Chem. Phys.*, submitted.
- [12] T. Hashimoto, M. Itakura, and H. Hasegawa, *J. Chem. Phys.*, **85**, 6118 (1986).

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