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Y. F. Yu[a]; J. Cui[a]; W. J. Chen[a]; S. J. Li[a]
[a] Department of Macromolecular Science and the Laboratory of Macromolecular Engineering of Polymers, Fudan University, Shanghai, China

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STUDIES ON THE PHASE SEPARATION OF POLYETHERIMIDE MODIFIED TETRAFUNCTIONAL EPOXY RESIN. II. EFFECTS OF THE MOLECULAR WEIGHT

Y. F. Yu, J. Cui, W. J. Chen, and S. J. Li*
Department of Macromolecular Science
and the Laboratory of Macromolecular
Engineering of Polymers
Fudan University
Shanghai 200433, China

ABSTRACT

The effects of molecular weight on the phase separation of phenyl-terminated polyetherimide (P-PEI) modified tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) diaminodiphenylsulfone (DDS) systems were investigated by using Differential Scanning Calorimetry (DSC), Time-resolved Light Scattering (TRLS) and Scanning Electron Microscope (SEM). The P-PEI modified systems showed faster cure rate than the neat epoxy resin. An increase of the molecular weight of P-PEI raised the cure rate of the modified systems and changed the morphology from polyetherimide-rich domain in the low molecular weight P-PEI modified system to polyetherimide-epoxy co-continuous phase structure in the high molecular weight ones. The phase separation of high molecular weight P-PEI modified systems may proceed as a two stage process and result in the epoxy-rich spherical domains dispersed in the P-PEI-rich matrix.

INTRODUCTION

Epoxy resins are widely used in many industrial fields due to their excellent mechanical, thermal and electrical properties. The epoxy resins toughened with reactive rubbers often have significant sacrifice of some properties at elevated temperature [1]. Recently, thermoplastics, such as polysulfone (PSF), polyether-sulfone (PES), polyether ether ketone (PEEK) and polyetherimide (PEI) [2, 3, 4], were used to improve the mechanical and other properties of epoxy resins.

Yamanaka *et al.* [3] have studied the phase separation process of PES toughened epoxy resins which precedes according spinodal decomposition, and deduced that the phase separation processes of epoxy resin toughened by thermoplastics all may be spinodal decomposition induced by the increase of the molecular weight of epoxy resin during curing reaction. The ideal properties of modified epoxy resins may be controlled by the morphology of co-continuous phase structure as a result of fixing the spinodal decomposition at an earlier or later stage [5].

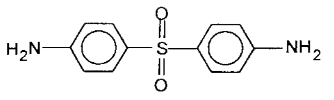
Su *et al.* [4] have studied the cure kinetics of the TGDDM epoxy systems modified with polyetherimide (G. E. Ultem-1010). It was found that the amount of polyetherimide influenced the curing rates and affected the morphology of the epoxy blends. Dong Chen *et al.* [6] studied the influence of rubber molecular weight on the phase separation process of modified epoxy resins and found that increasing the rubber molecular weight caused a decrease in the conversion and corresponding viscosity at the cloud point because of the increase of the interaction parameter x.

The preliminary study on toughening epoxy resin with a novel polyetherimide [7], which was synthesized in our laboratory following the direction of the good miscibility with epoxy resin, showed the phase structure fixed at the proper stage of spinodal decomposition to yield a co-continuous two-phase structure which favored excellent toughness. Also, the curing rate, gelation time and vitrification time greatly influenced the fixation of the phase-separation [8].

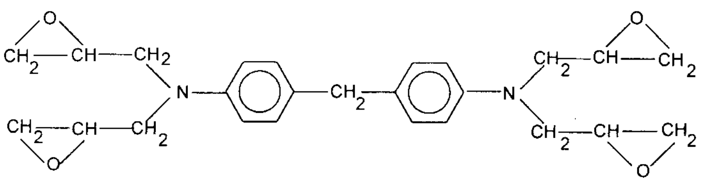
To better understand the interrelationship between the thermodynamics and the morphology of epoxy blends, we studied the influence of the molecular weight of polyetherimide on the phase structure of P-PEI/TGDDM/DDS blends. The process of phase separation in P-PEI modified epoxy resin systems was investigated by means of DSC and TRLS. In addition, the morphology of these modified systems were observed by using SEM. Based on the results, the effect of molecular weight of P-PEI on the phase structure was discussed.

EXPERIMENTAL

The epoxy resin tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) with an epoxy equivalent weight of 149gmol^{-1} was supplied by Shanghai Institute of Synthesis Resins. The resin blends with the polyetherimide were cured with an aromatic amine hardener, diaminodiphenylsulfone (DDS) (Shanghai Third Reagent Factory), which was used without further purification. The chemical structures of polyetherimide, TGDDM and DDS are shown as follows:



DDS



TGDDM

The polyetherimide was synthesized by one step from bisphenol-A dianhydride (BISA-DA) and 4, 4'-(1,4-phenylene-bis-(1-methyl-ethylidene)) bisaniline (BISP) in m-cresol at 200°C for 6 hours. Phenyl-terminated polyetherimide polymers of different molecular weight were obtained by varying the stoichimetric ratio of BISA-DA dianhydride and BISP diamine, then end-capped with phthalic anhydride [7, 9]. The inherent viscosity of P-PEI polymers were characterized at 0.5g/dl concentration in 1-methyl-2-pyrrolidinoene solvent at 30 °C. The polymer is designated as P-PEI (x), where P represents phenyl-terminated and x as the inherent viscosity (dl/g). The different kinds of P-PEI used were shown in Table 1.

Epoxy blends containing 20 phr (per hundred TGDDM resin) of P-PEI were prepared by dissolving the P-PEI in TGDDM at 150°C. The mixture was cooled to 130°C until a homogenous, clear solution was obtained and a stoichimetric amount of cure agent was added while the mixture was stirred. After the cure agent was dissolved, the blend was cooled rapidly to room temperature to avoid further curing reaction.

A Setaram Differential Scanning Calorimetry (DSC 92) instrument was used for the isothermal cure experiments and data analysis. The total area under the exothem curve, which was based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure, $\Delta H_{iso}(Jg^{-1})$. The residual reaction heat, ΔH_r (Jg^{-1}), was determined by scanning the sample after isothermal

TABLE 1. Characteristics of Polyetherimide

	P-PEI-1	P-PEI-2	P-PEI-3	P-PEI-4
Inherent Viscosity (g/dl)	0.39	0.58	0.61	0.67
T_g (°C)	210	215	217	218

curing at a rate of 10°C min^{-1} from 40 to 300°C. The total heat of cure (ΔH_t) was represented by the sum of both isothermal heat (ΔH_{iso}) and residual heat (ΔH_r) of the reaction. The isothermal conversion at time *t* was defined as α (t) = ΔH_{iso} (t)/ ΔH_t. [10,11].

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 [12]. The change of the light scattering profiles was recorded at appropriate time intervals during isothermal curing. The blend of epoxy 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 cured resins was observed under a Scanning Electron Microscope (SEM) (HITACHI S-520). The samples were fractured in liquid nitrogen and some were etched with 1,2-dichloroethane before observation.

RESULTS AND DISCUSSION

Curing Rate

The blends with a composition of TGDDM/P-PEI(20phr)/DDS(40phr) were cured at 150°C under the detecting of DSC. The curing rates of the blends and the neat resin were shown in Figure 1. The curing rate curve was obtained from the differentiation of the curve of conversion *via* time. All rate curves of the four systems show autocatalystic curing mechanism as reported in the literature [4]. The blends with P-PEI give faster curing rates than that of the neat epoxy, though at the beginning of the curing reaction there are few differences between the blends and the neat epoxy system. The blend with P-PEI (0.67) exhibits the fastest rate while the one with P-PEI (0.39) shows the slowest rate among the three kinds of blends cured at 150°C. That means the curing rates of the P-PEI modified systems are enhanced by the increase of P-PEI molecular weights. Compared with the unmodified epoxy

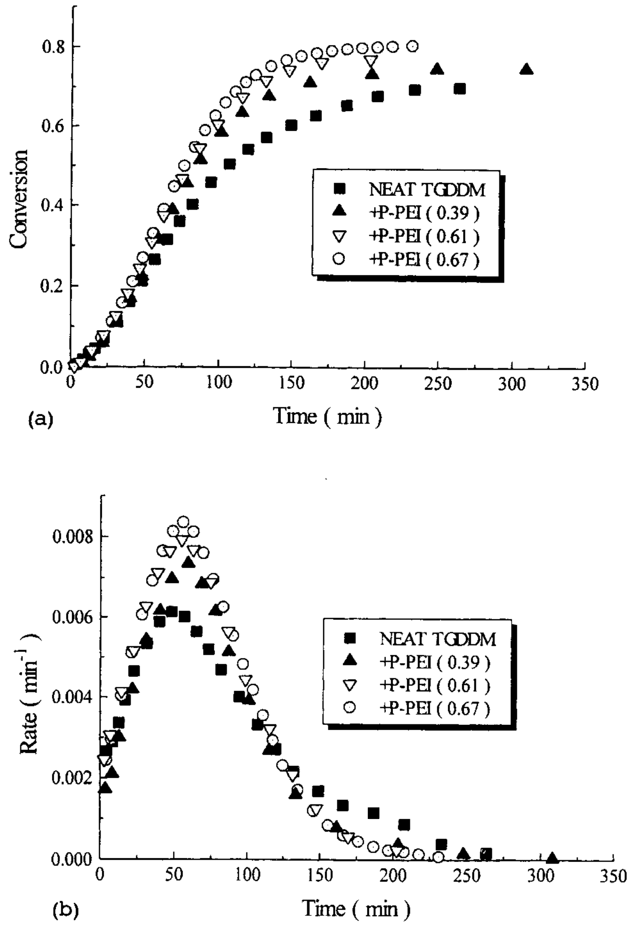


Figure 1. Curing kinetic comparison between P-PEI (0.39), P-PEI (0.61), P-PEI (0.67)/TGDDM/DDS blends and neat TGDDM curing at 150°C. (a) conversion *verse* time; (b) rate *verse* time.

resin system, the P-PEI modified systems progressed the curing reaction to further stages. This phenomenon may be caused by the relative higher concentration of curing agent DDS in the epoxy-rich phase due to the occurrence of phase separation in the epoxy/ DDS/P-PEI blend [4]. Since P-PEI has worse miscibility with DDS, as a result, the phase separation would make the P-PEI-rich phase able to have a relatively less amount of DDS, while the DDS content in epoxy-rich phase is higher than 40 phr.

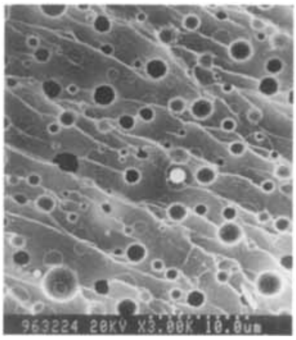


Figure 2. SEM of P-PEI (0.39) modified epoxy resin cured at 150°C for 5 hours.

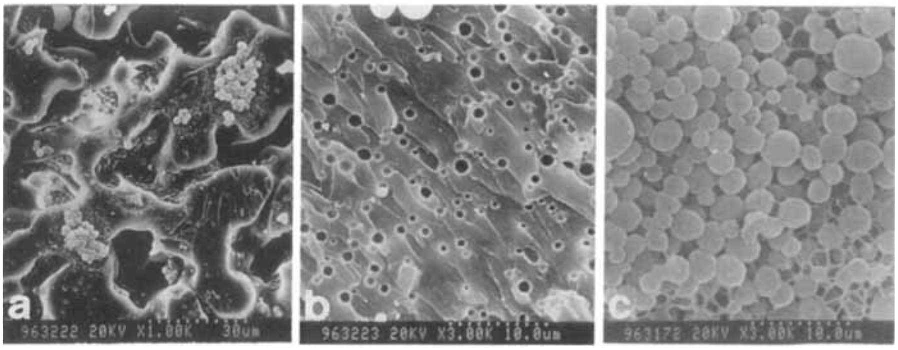


Figure 3. SEM of P-PEI (0.58) modified epoxy resin cured at 150°C for 5 hours. a) 'sandwich' morphology; b) continuous epoxy region, etched in CH_2Cl_2; c) continuous PEI region, etched in CH_2Cl_2.

Morphology

The fracture surface of the P-PEI (0.39) modified system cured at 150°C for 5 hours shows a continuous epoxy matrix with regularly dispersed P-PEI domains (Figure 2). The same picture is also observed by Bucknall [13], and Hourston [14]. The SEM micrographs of the other blends (Figures 3, 4 and 5) all show the 'sandwich' morphology, in which there are regions of phase inversion and continuous epoxy structure. The continuous epoxy phases of P-PEI (0.58, 0.61, 0.67) modified systems (Figures 3b, 4b and 5b) are somehow similar with that of P-PEI (0.39) modified system. In the regions of phase inversion, the epoxy

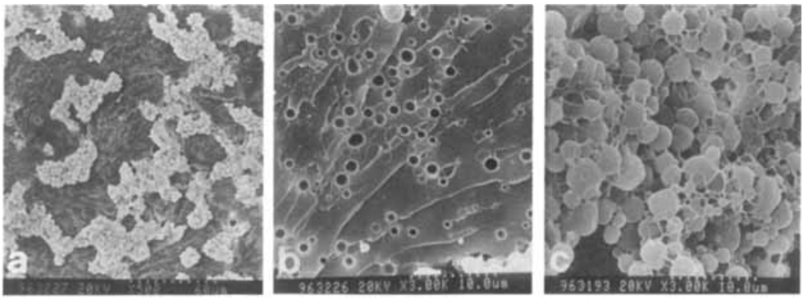


Figure 4. SEM of P-PEI (0.61) modified epoxy resin cured at 150°C for 5 hours; a) 'sandwich' morphology; b) continuous epoxy region, etched in CH_2Cl_2; c) continuous PEI region, etched in CH_2Cl_2.

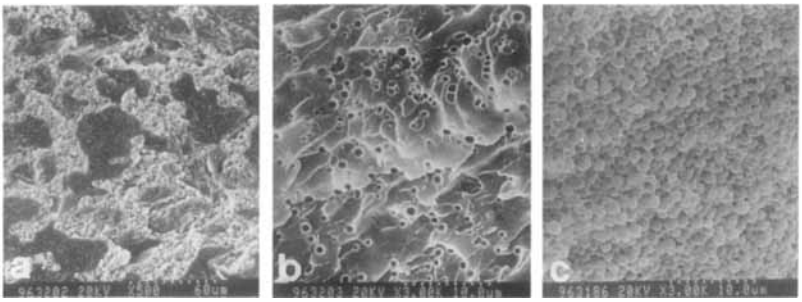


Figure 5. SEM of P-PEI (0.67) modified epoxy resin cured at 150°C for 5 hours; a) 'sandwich' morphology; b) continuous epoxy region, etched in CH_2Cl_2; c) continuous PEI region, etched in CH_2Cl_2.

domains are connected by P-PEI threads and the connected or isolated epoxy-rich spherical domains in the P-PEI-rich matrix are observed in the etched samples as shown in Figures 3c, 4c, and 5c.

Phase Separation by TRLS

The phase separation processes of the four kinds of P-PEI modified epoxy resins were observed by using TRLS, as shown in Figures 6, 7, 8 and 9. It shows the variations of the intensity of scattering light of the four kinds of P-PEI modified TGDDM-DDS systems cured at 150°C at various times. At the early stage of the curing reaction, no apparent scattering light was detected from the blends of

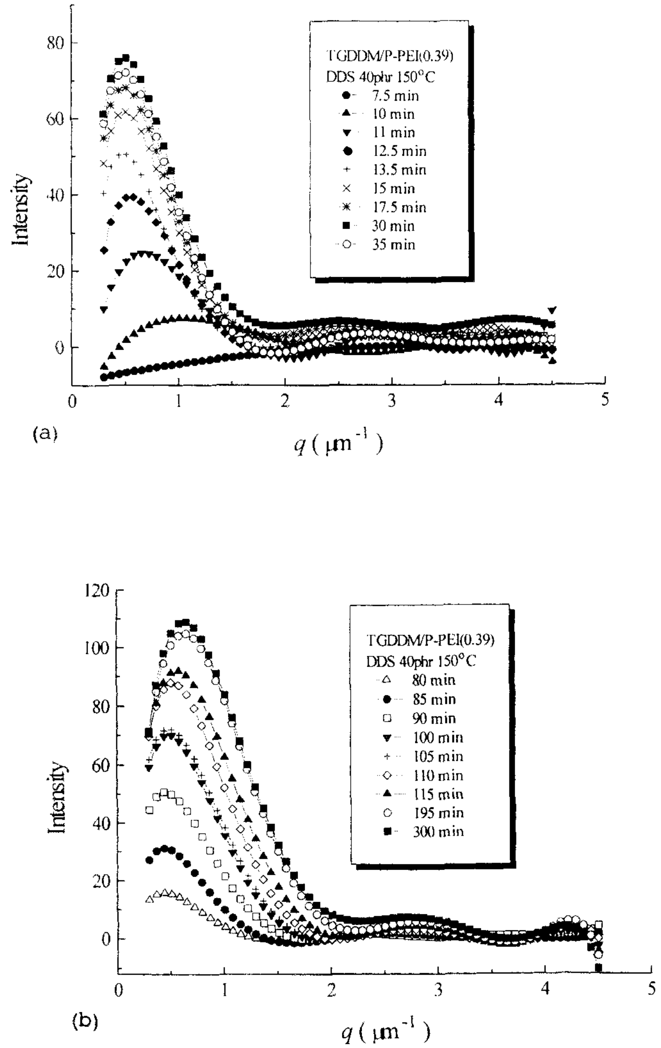


Figure 6. The change of the light scattering profiles with time of P-PEI (0.39) modified epoxy resin cured at 150°C.

TGDDM/P-PEI loaded with DDS since they were single-phase systems. As shown in Figures 6a, 7a, 8a and 9, a light scattering peak appeared after an induced period as the curing reaction proceeded. The system with P-PEI (0.39) had the longest induced period (20 minutes) while the other three systems were shorter than 10 minutes. One reasonable explanation may be that the higher molecular weight P-PEI has a larger interaction parameter x with epoxy resin, thus changing the

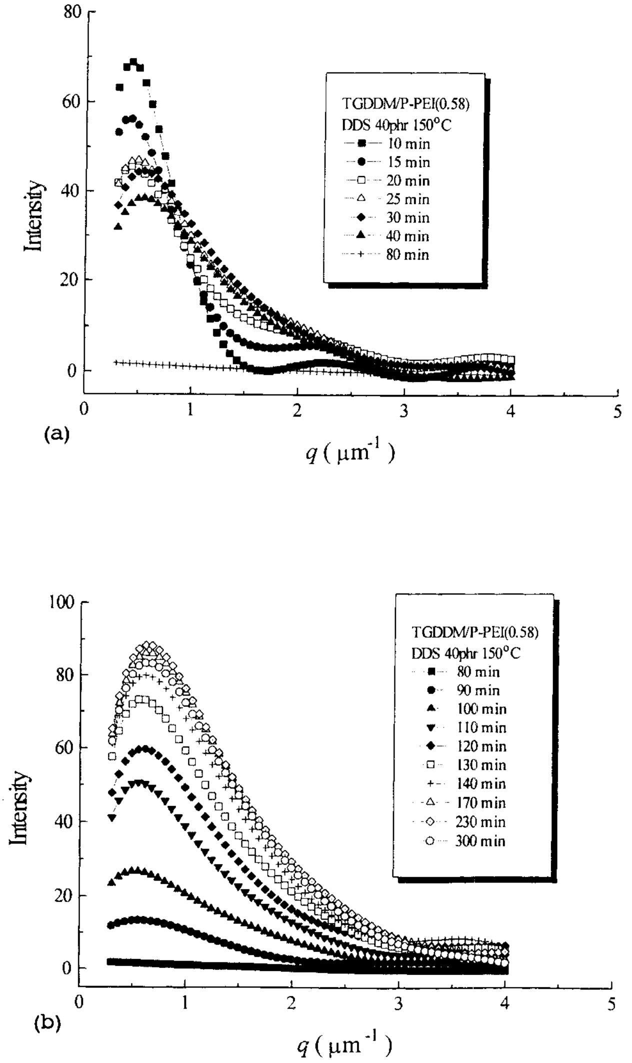
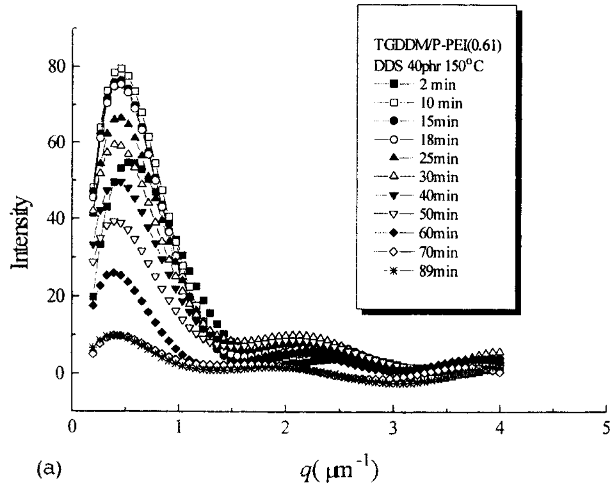


Figure 7. The change of the light scattering profiles with time of P-PEI (0.58) modified epoxy resin cured at 150°C.

miscibility of P-PEI with epoxy resin [6]. As a result, this caused the phase separation of systems with higher molecular weight P-PEI to occur at an earlier stage.

When reaching the maximum, the intensity of scattering light of all systems began to decrease with curing and finally disappeared. However, the intensity of scattering light appeared and attained another maximum at about the same position



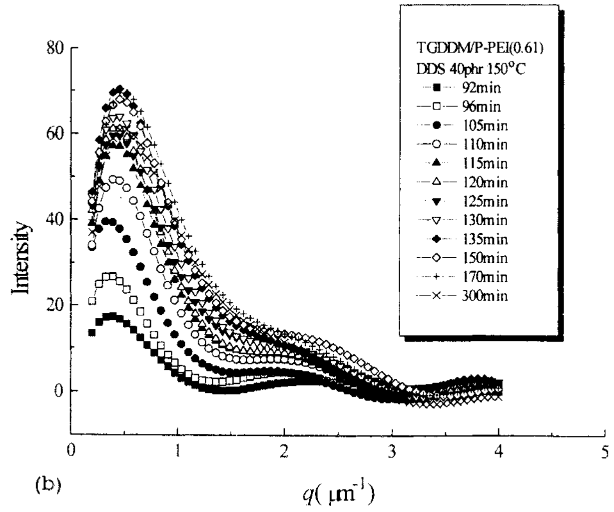


Figure 8. The change of the light scattering profiles with time of P-PEI (0.61) modified epoxy resin cured at 150C.

after a period of no detectable intensity of scattering light. The decay of the intensity of scattering light may suggest that a phase dissolution process followed the phase separation. And the reappearance of the intensity of scattering light at the later stage may be caused by a second phase separation. To inquire about whether there was a process of the phase dissolution and then another phase separation, SEM

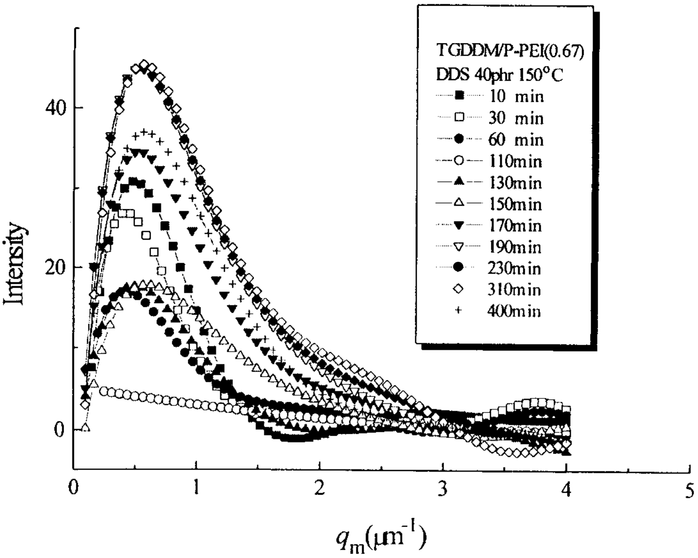


Figure 9. The change of the light scattering profiles with time of P-PEI (0.67) modified epoxy resins cured at 150°C.

micrographs of blends cured for 15 minutes (at the time of maximum intensity of scattering light) (shown in Figure 10) was used to compare with the SEM micrograph of blend cured for 5 hours (Figures 3a, 4a and 5a). Similarly, the same 'sandwich' morphologies were shown in the micrographs, i.e., there was no evidence that the process of phase dissolution followed with another phase separation. The vanishing of scattering light intensity at the curing reaction median may be caused by the change of the refractive index of epoxy-rich phase and P-PEI-rich phase which came closer to the same values when the light intensity disappeared [15].

Compared with the former light intensity peak, after the light intensity went to zero, Figures 7b, 8b and 9 showed the broader peaks of light intensity. This may suggest that another phase separation in P-PEI modified systems existed. Considering the reciprocal of the scattering vector q assigned to the periodic distance of the dispersed particles, the scattering light intensity around q = 2-3μm^{-1} may correspond to the dispersed P-PEI particles in the epoxy-rich region which was shown in the SEM results. The formation process might indicated that the phase separation took place at an early stage of polymerization (cure conversion < 3%) in the high molecular weight P-PEI modified systems. At the beginning of phase

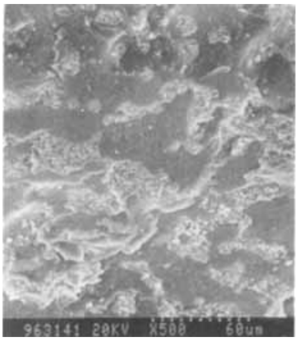


Figure 10. SEM of P-PEI (0.61) modified epoxy resin cured at 150°C for 15 minutes.

separation, the cure rate is relatively slow and the modified systems are just getting into the UCST (upper critical solution temperature) two-phase region in the phase diagram so that P-PEI precipitated with large amounts of epoxy dissolved in, getting large scale co-continuous phase structure just like dissolved in poor solvent. A low curing rate would make the quench depth shorter and yield a longer phase distance [5]. As the curing reaction proceeded, the high viscosity and large scale of P-PEI-rich phase retarded the further diffusion of both P-PEI and epoxy to the other phase thus causing another phase separation to occur in the separated phases.

Figure 11 shows the systematic change in the TRLS profile with curing time. The scattering peak position vector q_m of P-PEI (0.58) and (0.67) modified systems increase with time. This may be caused by the second phase separation of samples with high MW P-PEI which made the large co-continuous regime smaller with time. To P-PEI (0.39) modified system, the scattering peak vector q_m first goes down, then up. The reason is that the system with P-PEI (0.39) might have first undergone a phase separation process described in other papers [5] in which the phase distance grows with time and the later stage phenomenon may be caused by the crosslinking shrinkage.

Table 2 shows the value of the peak scattering vector q_m of the modified systems cured at 150°C for 5 hours. Here, the peak scattering vector q_m is the value of scattering vector at the maximum intensity of scattering profile for ultimate cured resin at 150°C, whose reciprocal is proportional to the size of phase structure. From Table 2, it can be seen that P-PEI (0.58) modified system has the largest q_m value while P-PEI (0.67) has the smallest value in the three systems having co-continuous

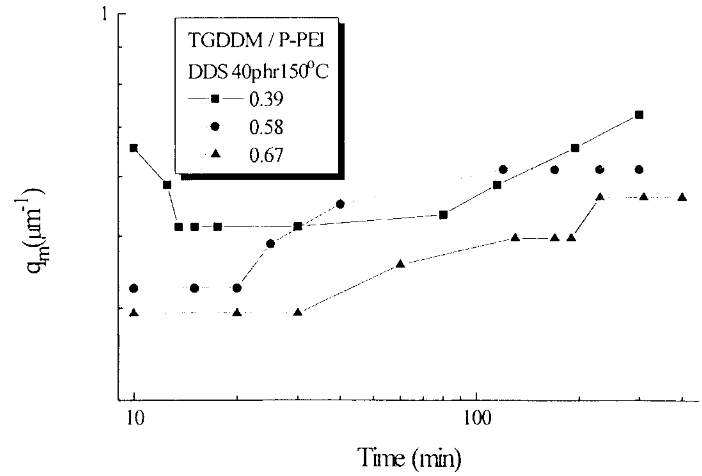


Figure 11. The TRLS light scattering peak position change with time of P-PEI (0.39), P-PEI (0.58) and P-PEI (0.67) modified systems.

TABLE 2. The Peak Scattering Vector q_m of the Different Molecular Weight Polyetherimide Modified TGDDM-DDS Systems Curing at 150°C

Inherent Viscosity of P-PEI (g/dl)	$q_m/(\mu m^{-1})$
0.39	0.66 (400min)
0.58	0.61 (300min)
0.61	0.58 (300min)
0.67	0.56 (300min)

morphology. In other words decreasing the molecular weight of P-PEI enhances the values of q_m in the modified epoxy systems. At the same temperature of 150°C, higher molecular weight P-PEI modified systems tend to have faster curing rates, than when the terminate of the phase separation is earlier. However, at the later stage of curing the viscosity of epoxy-rich phase also increases which hinders further phase separation. So the morphology is determined chiefly at the early stage. The highest MW P-PEI modified system has the smallest q_m value, or the largest size of matrix phase structure since the initial stage of phase separation decides the morphology. For the epoxy-rich spheres in the P-PEI-rich matrix, higher molecular weight P-PEI-rich phase tends to be more viscous which suppresses the phase separation [5] at an earlier stage thus giving the sample relatively smaller spheres.

CONCLUSIONS

The curing rate of the blends with different molecular weight polyetherimide were found to be higher than that of the neat epoxy resin, although they all have the same autocatalytic reaction mechanism.

The vanishing of scattering light intensity during the phase separation may be caused by the change of the refractive index of the epoxy-rich and P-PEI-rich phases which approached about the same values when the light intensity disappeared.

Different molecular weight P-PEI modified systems may not have the same phase separation process. The high molecular weight P-PEI modified systems show the co-continuous phase structure, while the lower molecular weight P-PEI system displays the dispersed P-PEI particles morphology.

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