

Studies on the phase separation of polyetherimide modified tetrafunctional epoxy resin

IV Effects of the chemical structure of polyetherimide

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ABSTRACT

To discuss the influential effect of thermodynamics and kineticon morphology of epoxy blends deeply, in this work, the four kinds of novel polyetherimide with different diamine has been used to investigate the phase structure of PEI(20phr)/ TGDDM/DDS(40phr) blends by means of DSC, SEM and TRLS(time-resolved laser scattering). It is found that the miscibility of components is a great influential in the phase separation process, however, the viscosity of system is considered as a dominated factor for the extent of phase separation and the development of blend morphology.

INTRODUCTION

Motivated by the increasing demands of the aerospace industry for new high-performance composite materials, much attention has recently been given to the toughening of thermosets by

blending with high performance aromatic thermoplastic polymers. In the case of epoxy resin, poly(ether sulfone)(1-3), poly(ether ether ketone)(4-5) and poly(etherimide)(6-8) have been used as toughening agent owing to their solubility or miscibility with the uncured starting resin. The studies have shown that these thermoplastics enhance the toughness without severely sacrificing the properties of epoxy resin. It is also known that these modified epoxy resins are two-phase systems in which the phase separations proceed via spinodal decomposition induced by the increase of the molecular weight of epoxy network during curing reaction(9). The morphology of these systems which decide the properties of modified epoxy resins is the results of the fixation of the phase-separated structure(10). However, the reality of the formation of phase structure is little reported[11].specially, the interrelationship between thermodynamics and kinetic.

In our previous work, the novel synthesized polyetherimide(PEI) has been used to modified epoxy resin tetraglycidyl-4,4'-diaminodiphenylmethane(TGDDM) / diaminodiphenylsulfone (DDS). Which shown the phase structure fixed at the proper stage of spinodal decomposition yielded a co-continuous two-phase and phase inversion structure which favored to the good toughness. To understand the thermodynamics and the morphology of epoxy blends, we studied the influence of the curing rate (12) and the molecular weight of PEI (13) on the phase structure of PEI/TGDDM blends. The scanning electron micrograph (SEM) was also 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(14).

To discuss the influential effect of thermodynamics and kinetic on morphology of epoxy blends deeply, in this work, the four kinds of novel polyetherimide with different diamine has been used to investigate the phase structure of PEI(20phr)/ TGDDM/DDS(40phr) blends by means of DSC, SEM and TRLS(time-resolved laser scattering).

Experimental part

The epoxy resin- tetraglycidyl-4,4'-diaminodiphenyl methane(TGDDM) and Bisphenol-A dianhydride(BISA-DA) used was supplied by Shanghai Institute of Synthesis Resin, m-phenylene diamine(MDA) and 4,4'-diaminodiphenylsulfone(DDS) (Shanghai Third Regent Factory) were used without further purification. 2,2-bis(4-(4-aminophenoxy)phenyl) (BAPP) was supplied by CHRISKEV CO. and 4,4'-(1,4-phenylene-bis-(1-methyl-ethylidene)) bisaniline (BISP) was

synthesized in our laboratory. The polyetherimides were synthesized from Bisphenol-A dianhydride(BISA-DA) and diamines in our laboratory and described in reference[15]. For the better discussion, all polyetherimides were synthesized in the same stoichiometric ratio of BISA-DA and diamine .The four polyetherimides with different diamine are designated as PID, PIM, PIB and PIP corresponding to different diamine DDS, MDA, BAPP and BISP respectively. The inherent viscosity was characterized at 0.5 g/dL concentration in 1-methyl-2-pyrrolidinoene solvent at 30°C . The Characteristics of polyetherimides used in this work are listed in Tab. 1.

The same stoichiometric ratio has been selected for the blends of PEI and TGDDM. The epoxy blend containing 20 phr of PEI was prepared by dissolving the PEI in TGDDM at 150°C. Until a homogenous, clear solution was obtained, the mixture was cooled to 130°C and stoichiometric amount (40 phr) of cure agent 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[15]. The change of the light scattering profiles was recorded at appropriate time intervals during isothermal curing. The blend of epoxy resin with 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.

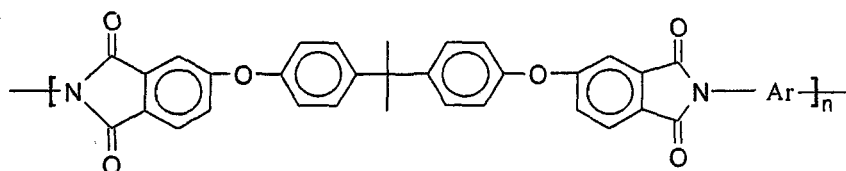
The morphology of the blend cured for 5h. at 150 °C. was observed under Scanning Electron Microscope (SEM) (HITACHI S-520). The samples were fractured in liquid nitrogen.

The glass transition temperatures of PEIs were characterized with Setaram Differential Scanning Calorimetry (DSC) instrument from -20°C to 300°C at 20°C/min heating rate. To study the miscibility of these blends, an epoxy blend containing 20 phr of PEI was prepared by dissolving the PEI in TGDDM at 150 °C. After a homogenous, clear solution being 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 rapidly cooled to room temperature in order to maintain the curing reaction at lower extent. The glass transition temperatures of the blends were conducted from -10--200 °C at 10 °C /min with Setaram Differential Scanning Calorimetry (DSC) instrument.

Table 1 Characteristics of PEI samples with different diamine

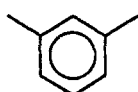
PEI	PID	PIM	PIP	PIB
Diamine	DDS	MDA	BISP	BAPP
Viscosity g/dl	0.52	0.57	1.0	1.3
Tg (°C)	242	223	220	200

PEIs were prepared in the same stoichiometric ratio of BISA-DA and diamines

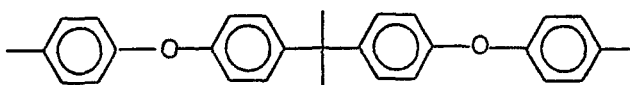


PEI

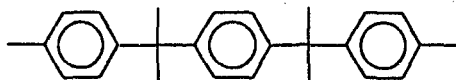
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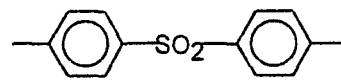
(PIM)



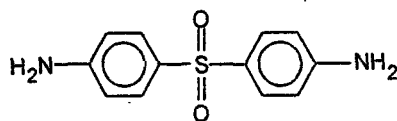
(PIP)



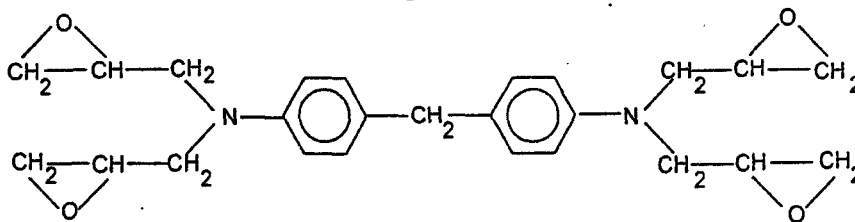
(PIB)



(PID)



DDS



TGDDM

Results and discussion

Morphology

Figure 1 shows the SEM morphologies of the fracture surface of the four blends cured at 150°C for 5 hours. The blend of TGDDM/PID appears just like a piece of silk with creases on it and did not show the presence of segregated microdomains (Fig. 1a), the blend of TGDDM/PIM shows a continuous epoxy matrix with regularly dispersed PIM domains (Fig. 1b). The SEM micrographs of the PIP modified system shows the “sandwich” morphology with fine dispersion particles (Fig. 1c). However, in the case of TGDDM/PIB, the phase inversion occurs, in which the epoxy domains are connected by PIB threads and the connected or isolated epoxy-rich spherical domains in the PIB-rich matrix are observed in the etched sample as shown in Fig. 1d. The SEM result indicates that the chemical structure of PEI used all affected significantly the morphologies of these systems.

Glass Transition Temperature

To understand the miscibility of these blends, the glass transition temperature of the four blends of TGDDM/20phrPEI was compared in DSC curve. On the basis of the results of the glass transition temperature of the modified systems and the knowledge of thermodynamics and kinetics, different phase separation processes are discussed based on. Table 2 shows the Glass Transition Temperature of the pure epoxy resin and the modified systems. The PID is miscible with epoxy resin and gives just one T_g which is higher than pure epoxy resin (11°C) because of the existence of PID. For the other three systems, after curing for 1 minute, the phase separation occurs and two T_g s exhibit in the DSC curve. In two T_g s, the lower one is assigned to the epoxy-rich phase and the higher one to the PEI-rich phase. The blend with PIM has the great ΔT_g in these systems because of the poor miscibility, moreover, the modified systems with PIP or PIB display the better miscibility.

Table 2 The Glass Transition Temperature of the blends cured at 150 °C for 1 min. and Induced period of phase separation of the blends

PEI	PID	PIM	PIP	PIB
Tg/ °C (TGDDM)	---	20	16	20
Tg/ °C (PEI)	26	86	75	65
Induced period (min) (TRSL)	---	10	15	25
Morphology (SEM)	no	dispersed particle	co-continuous	Phase inversion

T_g was observed at 10°C/min. from -10--200°C by DSC scanning

The induced period was recorded at real time at 150° isothermal curing by TRSL.

Morphology of the fracture surface of cured blends (150°C.) was observed by SEM.

Phase separation by TRLS

The phase separation processes of the four kinds of PEI modified epoxy resins were observed by using TRLS, no apparent scattering light was detected from the blend of TGDDM/PID since it was single phase system. However, for the other three blends, as shown in Figure 2—4 in which, a light scattering peak appeared after an induced period as the curing reaction proceeded, the system with PIB had the longest induced period (25 min.) owing to the lower driving force (the least ΔT_g) and higher viscosity, while the system with PIM had the shortest induced period (10 min.) owing to the great driving force (the great ΔT_g) and low viscosity.

Discussion

The SEM micrograph of TGDDM/PID system shows no morphology, it is consistent with the result of DSC scanning which has only one T_g at 25.7 °C. due to good miscibility. The blend with PIM has the great ΔT_g and the shortest induced period in these system because of the poor miscibility, moreover, the lower viscosity of the blend causes the spinodal decomposition to go further and lead to a particle dispersion morphology. For other two systems , the better miscibility and the higher viscosity would make the phase separation to be fixed at a proper stage. For the blend of TGDDM/PIP, the lower viscosity of the system leads forming a bigger region structure---co-continue, for the blend of TGDDM/PIB, the higher viscosity of the system would prevent the diffusion of the PIB and epoxy molecules from phase to phase and leads to form phase inversion.

From the above discussion, it is found that the miscibility of components is a great influential in the phase separation process, however, the viscosity of system is considered as a dominated factor (the diffusion controlled process) for the extent of phase separation and the development of blend morphology .

Acknowledgements

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