Phase separation time/temperature dependence of thermoplastics-modified thermosetting systems

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Abstract The cure-induced phase separation processes of various thermoplastics (TP)-modified thermosetting systems which show upper critical solution temperature (UCST) or lower critical solution temperature (LCST) were studied with emphasis on the temperature dependency of the phase separation time and its potential application in the cure time-temperature processing window. We found that the phase separation time/temperature relationship follows the simple Arrhenius equation. The cure-induced phase separation activation energy \( E_a(ps) \) generated from the linear fitting of the Arrhenius equation is irrelevant to the detection means of phase separation time. We also found that \( E_a(ps) \) is insensitive to TP content, TP molecular weight and curing rate, but it changes with the cure reaction kinetics and the chemical environment of the systems. With the established phase separation time-temperature dependence relation, we can easily establish the whole cure time-temperature transformation (TTT) diagram with morphology information which is a useful map for the TP/TS composites processing industry.

Keywords polymerization induced phase separation, thermosetting, thermoplastic, time and temperature dependence, Arrhenius equation, TTT diagram

1 Introduction

After the concept of cure-induced phase separation (CIPS) was proposed by Inoue et al. [1,2] in the 1980s, many experimental and theoretical investigations were carried out to toughen highly crosslinked thermosets (TS) with engineering thermoplastics (TP). It is now assumed to be a promising alternative to rubber toughening particularly when high values of the elastic modulus and glass transition temperature (\( T_g \)) are required [3–6]. The mechanical properties of the toughened materials are closely related to their final morphologies, so most of the studies have focused on phase separation mechanisms [1,2,7] and morphology control [8–12]. To explain various morphologies generated during cure, thermodynamic analysis of the Flory-Huggins-Staverman (F-H-S) theory was employed. It describes the spinodal and bimodal decomposition lines [3,13–17], but it does not relate the structural parameters and the time dependency. The solubility parameters and group contribution approaches constitute the first level of the relation for miscibility but not for the reaction-induced phase separation yet. The morphology evolution may be analyzed qualitatively using the time-dependent Ginzberg-Landau equation (TDGL) of phase separation dynamics [18] though it provides no clues about the temperature dependence of phase separation time.

As we know, all the processing of thermoplastics-modified thermosetting composites are carried out in a wide time/temperature range as presented by the TTT (time-temperature-transformation) diagram [19] and the cure time-temperature routine has a great impact on the morphology generated during cure and on the final material properties [20]. It is important to study systematically on phase separation time-temperature dependence during curing considering the variations of the material parameters in a broad time/temperature range [21]. The curing process involves several transformation. For example, the viscous clear liquid is transformed to a phase-separated opaque dope solution then to three dimensional chemical gels and further, to a vitrified solid. Phase separation occurs due to the decrease in the mixing entropy which arises from the size increase of the thermosetting oligomers. Upon gelation, the thermosetting systems lose fluidity permanently so all processing operations must be


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completed before gel point. Vitrification is solidification that is defined to occur when \( T_g \) reaches cure temperature. To get a material with the desired properties, it is necessary to exploit these transformations to design the cure time-temperature processing routine. The time-temperature dependence of gel and vitrification is well illustrated by the kinetic approach for systems with unambiguous cure kinetics [19]. As for the phase separation time-temperature dependence, few studies have been carried out on it [21].

The CIPS process can be observed in situ by different techniques, e.g. rheology [22–24], small angle light scattering (SALS) and turbidity [7]. Rheology observes certain abrupt mechanical changes upon phase separation while SALS and turbidity trace the change of the optical mismatch between TP- and TS-rich domains during phase separation. SALS is most widely used to characterize the evolution of domain size quantitatively in TP and TS blends [6,7,25]. SALS is limited by the degree of optical mismatch between blend components and it cannot be used to trace the early stages of the phase separation process [21,26].

In this work, we observed the early stage of CIPS in some TP/TS systems with a modified optical microscope system [27] and compared the microscope method with the rheology and SALS approaches in the whole CIPS process. We focused on the common features of phase separation time/temperature dependence including the effects of TP molecular weight, TP content, cure rate, cure agent content and cure reaction mechanism. The whole cure time-temperature window of the thermoplastic-modified thermosetting systems with the phase separation are also discussed so as to show the potential application of the phase separation time-temperature dependence in the composites processing industry.

2 Experimental

2.1 Materials

The epoxy monomer was based on commercial grade DGEBA (diglycidyl ether of bisphenol A) with an average epoxide equivalent of 185 (Wuxi Synthetic Resin Co, Jiangsu, China). The cyclic anhydride cure agent was methyl tetrahydrophthalic anhydride (MTHPA; HY 918, Ciba-Geigy); the anhydride initiator was benzylidimethyamine (BDMA, Sigma, USA). The aromatic cure agent 4,4′-methyleneedianiline (DDM) and 4,4′-diaminodiphenyl sulfone (DDS) were provided by Shanghai Reagent Co (Shanghai, China). 4,4′-Bismaleimidodiphenyl methane (BMI) was provided by Beijing aeronautical manufacturing technology research institute and the chain extension agent \( \text{O, O}′\)-diallylbisphenol A (DBA) was provided by Sichuan Jiangyou Insulating Material Co. The thermoplastic hydroxyl-terminated polyethersulfones (PES) with \([\eta] = 0.36, 0.43\) and 0.53 dL/g, respectively, were supplied by Jilin University (China). Phenolphthalein poly (ether ketone) (PEK-C, \([\eta] = 0.43\) dL/g) was developed in Xuzhou VAT Chemical Co Ltd. Polyetherimides (PEI, Ultem 1000) were provided by General Electric Co.

2.2 Sample preparation

The PEI-modified epoxy mixtures were prepared in a two-step process. A 10 wt-% solution of PEI methylene dichloride was mixed with the epoxy monomer at room temperature. Most of solvent in the mixture was vaporized in a circulation oven at room temperature and the residual solvent was removed in a hot vacuum oven for 24 h at 80°C. Subsequently, the cure agent was added at 135°C for DDS, 90°C for DDM and 60°C for MTHPA (with different initiator BDMA contents), respectively. For PEK-C and PES modified epoxy systems, TP was directly dissolved in the epoxy monomers at 140°C, and the cure agent was introduced in the same way as in the PEI systems. In the TGDDM/DGEBA/DDS/PEK-C blends, the mass ratio of TGDDM to DGEBA is 3 : 2.

For the preparation of the BMI/DBA/PEK-C and BMI/DBA/PES blends, TP was dissolved in DGEBA at 135°C, and then BMI was added after mixtures had cooled to 120°C. The mixture with a BMI to DGEBA molar ratio of 1:0.87 was stirred continuously until a transparent blend was obtained.

The loading level of TP to thermosetting precursors (mixture of epoxy monomer and hardener) is counted by phr (part per hundred resin). The loading level of the cure agent remains stoichiometrically balanced without denotation.

2.3 Measurements

2.3.1 TOM

To observe the initial stage of phase separation, a lab-made computerized transmission optical microscope (TOM) system equipped with an inverse optical design, long focusing objective lens and controllable oven was designed to allow long term observation and data collection with a high resolution of 0.2 μm in a wide working temperature range of room temperature to about 250°C. The system can assign the onset of phase separation for a system with a low refractive index difference and a domain size as small as 1 μm. This is not succeeded by TOM and SALS [27].

The samples for TOM observation were prepared by pressing the melt between two pieces of cover glass with a thickness of about 0.2 mm. The moment when the morphological structure appeared was defined as the phase separation time \( t_{ps} \). The value of \( t_{ps} \) at any particular temperature is the average of five tests with observation errors.