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Phase Behavior, Cure Behavior, and Morphology of Poly(Phenylene Ether)/Triallylisocyanurate Blends

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Abstract: The low molar mass PPE/TAIC blends were shown to have the upper critical solution temperature (UCST) type phase behavior, and cloud point curves intersect the glass transition-composition lines at a PPE content of about 50%. Phase behavior and cure behavior were investigated by different techniques: light transmission measurements, fourier-transform infrared spectrometer, and different scanning calorimeter. The cured morphology of the PPE/TAIC blends was studied by atomic force microscope. With increasing PPE content for PPE/TAIC blends, the diameter of the dispersed PPE particles has a significant increase, and the thermal stability of the blends is also increased. The cured PPE/TAIC systems exhibit good chemical resistance and thermal stability.

Key words: poly(phenylene ether); triallylisocyanurate; phase behavior; morphology

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Thermoset (TS)/thermoplastic (TP) blends are materials resulting from the mixing of a TP polymer and TS precursors and the subsequent reaction of the precursors. Usually the initial mixture is homogeneous, but the molar mass increase of the TS precursors involves a decrease in the conformational entropy of mixing and a liquid-liquid phase separation occurs. One of the advantages of using the reaction-induced phase separation is the broad variety of morphologies that can be generated. One important factor controlling the phase separation process and the generated morphology is the initial composition of the blend. Besides the initial blend composition, the intrinsic miscibility of the TS precursors and TP polymers involved and the competition between reaction kinetics and phase separation process. Poly(phenylene ether) is widely used in the manufacture of advanced composites^[1-3]. This is due to major advances in composite mechanical properties that have resulted from the use of tough, high glass transition temperature and low dielectric constant thermoplastics. The high T_g , however, requires processing to be carried out in the 300 - 350 temperature range. Due to the oxidative and thermal sensitivity of PPE, processing in this temperature range results in severe degradation, and therefore PPE could be classified as intractable. The deg-

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radation problem can be solved by blending with polystyrene to reduce the processing temperature. By blending, however, heat resistance is sacrificed. TAIC is a low viscosity liquid at room temperature and can be cured by peroxide, for example Dicumyl peroxide (DCP), to provide a thermoset of high heat resistance. PPE/TAIC systems are often applied in copper clad laminate matrix, but reports about their basic properties are few. This paper reports on the phase behavior, cure behavior, and morphology of PPE/TAIC blends.

1 Experimental

1.1 Reagents

Poly(phenylene ether) (PPE) of very low molar mass used throughout this work was obtained from General Electric Company (PPO857). Triallylisocyanurate (TAIC) was supplied by Liuyang Chemical Co. ($M_n = 250$). The curing agent was Dicumyl peroxide (DCP).

1.2 Blend Preparation

The TAIC and PPE were dissolved at 20% of total polymer in trichloroethylene. The solution was cast onto a cover glass (for microscopy). The cast film was further dried under vacuum for 12 h. The phase behavior of the PPE/TAIC blends was studied using a light microscope with a temperature programmable sample stage. The film was heated between two glass slides in the stage until a homogeneous solution was obtained. The onset of phase separation upon cooling ($2 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$) was observed under the light microscope. Based on this observation, the phase diagram of the PPE/TAIC blends was deduced. For blends containing more than 60% PPE, the glass transition temperature was determined by using differential scanning calorimeter (DSC) with a scan rate of $10 \text{ }^\circ\text{C} / \text{min}$.

Cured blend specimens were prepared as follows. The PPE and TAIC were mixed on a hot mold set at $160 \text{ }^\circ\text{C}$. The homogeneous mixture was then allowed to cool down to $100 \text{ }^\circ\text{C}$, and DCP (2%) was added. After mixing for 2 min, the compound was poured into a preheated mold and cured under ambient conditions for 2 h at $180 \text{ }^\circ\text{C}$. After curing, the sample was allowed to cool slowly to room temperature. The cured specimens were used for atom force microscope (AFM) observation, thermogravimetric analysis and the solvent extraction tests.

1.3 Apparatus

1.3.1 Fourier-transform Infrared Spectrometer

The Fourier-transform infrared (FTIR) spectrometer of PPE/TAIC (40% PPE) blends was investigated using a WQR-310 FTIR spectrometer.

1.3.2 Atom Force Microscope

The surfaces of PPE/TAIC blends were observed with a CSPM-3000 atom force microscope (AFM).

1.3.3 Differential Scanning Calorimeter

The curing reaction of PPE/TAIC (40% PPE) blends was made on differential scanning calorimeter (DSC) NETZSCH-STA449C with three different scan rates ($5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, $15 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ and $20 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$). NETZSCH-STA449C was also employed to investigate the thermal stability of PPE/TAIC blends with a scan rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

2 Results and Discussion

2.1 Phase Diagram

The cloud points were determined by light transmission, and the vitrification (T_g) curve was calculated

ed by Fox relationship. The cloud point curves exhibit an upper critical solution temperature (UCST) behavior, commonly observed for polymer-solvent system. Fig 1 sends several messages for PPE/TAIC system.

First, relative low temperatures, between 90 and 110 are required to obtain homogeneous solutions. The cloud point temperatures reported in the literature^[4] for high molar mass PPE/TAIC blends are in the range of 150. As expected, the decrease in the PPE molar mass enhances the miscibility of the system, resulting in a considerable shift of the cloud point curve to lower temperatures. The processing temperature of PPE was greatly reduced, avoiding degradation or scorch problems of PPE. For example, PPE/TAIC (20%) mixtures are homogeneous solution at 110, which is well below the cure temperature (about 180 for DCP).

Second, in all blends investigated, the phase separation was completely reversible such that raising the temperature above the measured UCST caused rehomogenization of the mixture. This verifies the existence of the thermodynamic phase boundary. Furthermore, the measurements were reproducible even after multiple heating and cooling cycles, suggesting minimal degradation during testing, and little reaction of the PPE and TAIC in the absence of initiator.

Third, the intersection of the cloud point and vitrification curves is called Berghmans point^[5] and corresponds to a PPE percentage of approximately 50%. This value is again lower than that reported^[4] for high molar mass PPE/TAIC blends due to the shift of the cloud point curve to lower temperatures and the decrease of the thermoplastic T_g . According to this intersection point, the phase diagram can be divided into two regions: solutions containing less than 50% PPE will show phase separation upon cooling, and the obtained materials are heterogeneous with two phases (TAIC-rich and PPE-rich). However, complete phase separation process will be arrested as soon as the PPE-rich phase vitrifies (at a PPE content of 50%). As a result of this phenomenon, all of the phase separated solutions will exhibit a T_g of about 30, schematically represented in Fig 1 by the dashed horizontal line. That is to say, the heterogeneous materials are with a concentrated phase of constant composition, and consequently with a constant T_g , equal to that at the Berghmans point. Solutions with a PPE content exceeding 50% will vitrify upon cooling before any phase separation can occur, and are homogeneous over the entire temperature range, which T_g s depend on the composition.

Fourth, the structure formation during cure should be via the reaction-induced spinodal decomposition, as in the case of PPE/epoxy systems^[6,7]. According to the classic Flory-Huggins theory for polymer mixtures^[8], the mixture is initially in the single-phase regime at the cure temperature; however, the system will be transformed into a two-phase regime as the molecular weight of TAIC increases with cure. So, the spinodal decomposition is expected to take place during cure.

2.2 FTIR Spectrometer

Fig 2 shows infrared spectra of PPE/TAIC system before curing reaction (a) and cured at 180 for 2 h (b). It is seen that the absorption bands at 1700 cm^{-1} and 933 cm^{-1} are present in these spectra. The first of these is attributed to the carbonyl band stretching of the isocyanurate ring and the other is due to C—H vibrations around the vinyl double bonds. The vinyl double bonds are the great reduction in intensity of the 933 cm^{-1} , but not disappearance, of the vinyl bonds as compared to the ring band after curing. The result indicates that curing reaction is incomplete even after 2 h of curing at 180, which may be the cross-linking reaction involving gelation and the vitrification by the T_g elevation caused by the increase in molecular weight of TAIC with curing.

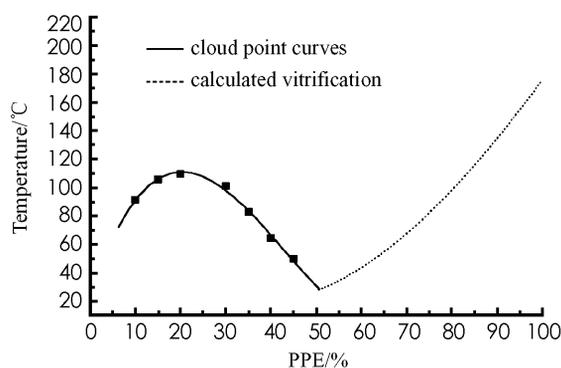
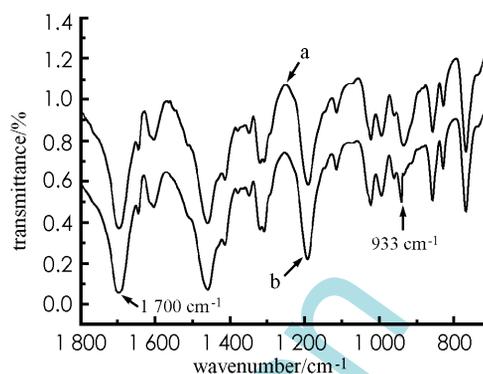


Fig. 1 Phase Diagram of PPE/ TAIC System



a) Before Curing Reaction; b) 2 h at 180 °C

Fig. 2 The FTIR Spectra of PPE/ TAIC System

2.3 Morphology of PPE/ TAIC Blends

Fig. 3 shows the AFM of different PPE content in the cured PPE/ TAIC blends. The PPE phase is dispersed phase, even when PPE is more in composition (60 %) for cured PPE/ TAIC blends^[4]. Increasing the content of PPE in a cured blend with TAIC from 30 %, to 40 %, to 50 %, corresponding to micrographs 3a, 3b and 3c, the average size of the dispersed PPE phase morphology increases from 5.8 nm, to 28.3 nm, to 94.1 nm. With increasing PPE content, a significant increase in the diameter of the dispersed PPE particles is observed. This effect is related to the volume fraction of PPE and the kinetic hindrance of the process of the spinodal decomposition. The sites of phase separating PPE may overlap and coalesce into larger domains with PPE volume fraction increasing, and moreover, an increase in the viscosity of the solution with PPE content, significantly retards the process of the spinodal decomposition, which result in a more coarse morphology. As already discussed, one can expect the spinodal decomposition driven by the cure reaction. The results in Fig. 3a, 3b and 3c imply that the cured materials have the two-phase morphology fixed at the early stage of spinodal decomposition. That is to say, the rate of spinodal decomposition is delayed and the decomposed structure is fixed by the network formation in TAIC phase. Spinodal decomposition is delayed by the incorporation of small amount of graft copolymer^[9,10]. The formation of graft copolymer in PPE/ TAIC system is conceivable because the methyl group of PPE is easily attacked by radical from TAIC^[4]. The graft reaction means that the PPE chains are bound to TAIC network. The bound PPE chain will be difficult to extract with a good solvent for PPE. PPE/ TAIC(40 %) blends cured at 180 °C for 2 h are dipped in methane chloride at 25 °C for 24 h, and then are dried in vacuum oven at 70 °C for 12 h. The results show no loss of weight after drying. Solvent extraction tests may support the incorporation of graft copolymer and also suggest an excellent chemical resistance of cured blends.

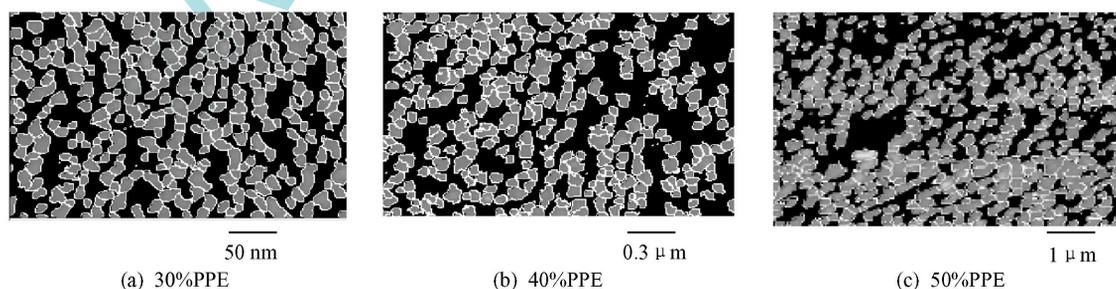


Fig. 3 AFM Micrographs of Different PPE Content in the Cured PPE/ TAIC Blends

2.4 Curing Reaction and Thermal Degradation of the Blends

Fig 4 shows the dynamic DSC scans of PPE/ TAIC (40 %) system loaded with 1 % DCP at three dif-

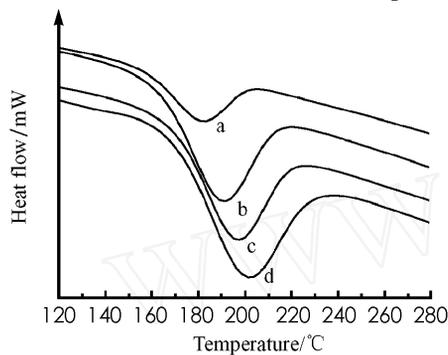
ferent heating rates ($5 \text{ } \cdot \text{min}^{-1}$, $10 \text{ } \cdot \text{min}^{-1}$, $15 \text{ } \cdot \text{min}^{-1}$ and $20 \text{ } \cdot \text{min}^{-1}$), with corresponding peak temperature 182.1 , 190.9 , 197.1 and 202.3 , respectively.

The peak temperature data obtained from DSC as a function of heating rate were processed further to obtain the activation energy for curing reaction employing the well-known Kissinger relation^[11,12].

$$\ln(\beta / T_p^2) = -\frac{E_a}{R T_p} + C \quad (1)$$

Where β is heating rate, T_p is peak temperature, E_a is the activation energy for curing reaction, R is the gas constant, C is integral constant.

We can obtain a linear relationship for $\ln(\beta / T_p^2)$ versus $1/T_p$ as shown in Fig. 5, Activation energy for curing reaction E_a obtained from the slope of Fig. 5 is 115.2 kJ/mol .



a $5 \text{ } \cdot \text{min}^{-1}$; b $10 \text{ } \cdot \text{min}^{-1}$; c $15 \text{ } \cdot \text{min}^{-1}$; d $20 \text{ } \cdot \text{min}^{-1}$

Fig. 4 The Dynamic DSC Scans of PPE/TAIC (40%) System at Different Heating Rates

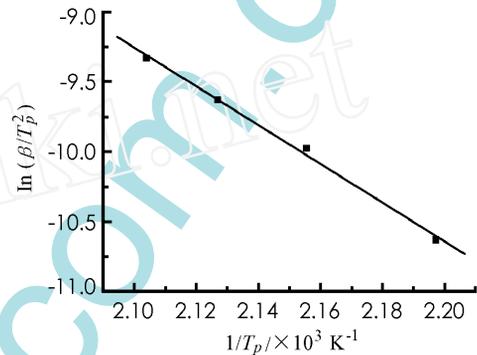


Fig. 5 Kissinger Plot of $\ln(\beta / T_p^2)$ versus $1/T_p$

Fig. 6 shows the TGA curves for pure PPE resin and PPE/TAIC blend heated at $10 \text{ } \cdot \text{min}^{-1}$ in nitrogen. The neat PPE resin starts to degrade at about 290 . The initiation temperature of thermal degradation decreases with decreasing PPE concentration. DTG peak temperature shows a decrease from 459 (neat PPE resin), 455 (50% PPE), 451 (40% PPE) to 444 in a blend containing 30% PPE. The result means that the thermal stability is decreased upon addition of TAIC. The final residual char yield of pure PPE resin is higher than that for PPE with added TAIC because the thermal stability of PPE is higher than that of TAIC.

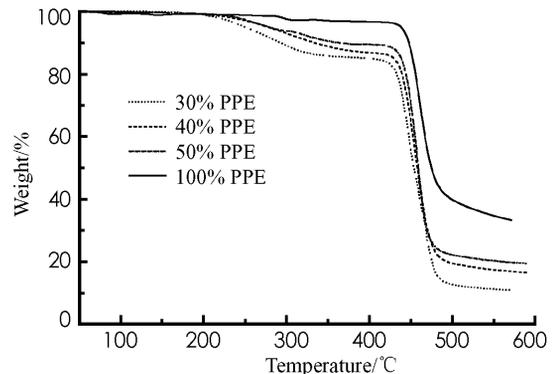


Fig. 6 TGA Curves for PPE/TAIC Systems with Various PPE Contents

3 Conclusions

Blend of low molar mass PPE and TAIC were studied, exhibiting a typical upper critical solution temperature(UCST) behavior. The low molar mass of PPE enhances the miscibility, leading to critical temperatures far below those reported for PPE/TAIC blends. With increasing PPE content for PPE/TAIC blends, the diameter of the dispersed PPE particles has a significant increase, and the thermal stability of the blends is also increased. The cured PPE/TAIC systems exhibit good chemical resistance and thermal stability.

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PPE/ TAIC 混合物的相行为、固化行为和相态

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摘要: 低分子量 PPE/ TAIC 混合物具有最高上临界温度行为, 玻璃化转变温度 (T_g) 线和浊点曲线在 PPE 的含量约为 50 wt % 时相交. 通过带有控温装置的显微镜、红外和 DSC 来研究 PPE/ TAIC 混合物的相行为和固化行为. 采用原子力显微镜研究 PPE/ TAIC 混合物固化材料的相态. 研究表明, 随着 PPE/ TAIC 混合物中 PPE 含量的增加, 分散相 PPE 颗粒的大小明显地增加, 另外混合物的热稳定性也随之增强. 固化后的 PPE/ TAIC 体系具有良好的耐化学药品性和耐热性.

关键词: 聚苯醚; 三烯丙基异氰酸酯; 相行为; 相态

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