

Compatibilized the thermosetting blend of epoxy and redistributed low molecular weight poly(phenylene oxide) with triallylisocyanurate

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ABSTRACT: Vinyl-containing low molecular weight PPO (R-PPO) was prepared by redistribution reaction between commercially available PPO and maleic anhydride (MAH) and used to modify epoxy resin (EP). TAIC was furthermore used as the compatibilizer of EP/R-PPO system in this study. The curing reaction kinetics, compatibility of the components, morphology, dielectric properties and impact toughness of EP/R-PPO/TAIC systems were investigated. The experimental results showed that the cured EP/R-PPO (80/20) system had two phase morphology, the R-PPO particles of about 1 μm were evenly dispersed in continuous epoxy phase. After addition of TAIC, the EP/R-PPO/TAIC systems were transferred to single phase. The glass transition temperature of cured EP/R-PPO/TAIC (80/20/10) system was 150.2 °C. With the increase of TAIC content, the dielectric constant (D_k) and dissipation factor (D_f) of cured EP/R-PPO/TAIC systems were both reduced. The dielectric constant and dissipation factor at 1MHz of cured EP/R-PPO/TAIC (80/20/10) system was 2.72 and 0.006, respectively. Compared with those of cured EP/R-PPO (80/20) system ($D_k = 2.82$ and $D_f = 0.0078$ at 1MHz), they decreased by 3.6% and 23.1%, respectively. With the increase of TAIC content, the impact strength of cured EP/R-PPO (80/20) system increased and reached to a maximum value (2.41 kJ/m²) when TAIC content was 10 phr, which was improved by 23% compared with that of cured EP/R-PPO (80/20) system (1.96 kJ/m²). © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43293.

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INTRODUCTION

Conventional printed circuit boards (PCBs) made from glass fiber reinforced epoxy (EP) resins have been widely used in the field of electronic materials because of their availability, low cost, good process ability, reasonable thermal, and mechanical properties. However, epoxy resins have usually an undesirably high dielectric constant and loss (dielectric constant and dissipation factor at 1 MHz was 3.30 and 0.02, respectively), and low dimensional stability at high temperature. With the current trend toward high frequency and high speed devices, PCBs with low dielectric characteristics are required so as to increase signal transmission speed and minimize signal transmission loss.^{1–3} The epoxy resin-based PCBs have been unable to meet the performance requirements of developing modern high frequency and high speed devices. One of the most commonly investigated methods to improve the dielectric properties of epoxy resin is to blend it with other high performance materials. The blends of epoxy resin with several polymers such as poly(phenylene oxide) (PPO),^{4–7} cyanate ester (CE),^{8,9} and polyimide (PI)^{10,11} have been studied.

PPO has a low dielectric constant and loss, as well as excellent mechanical properties, high dimensional stability and low moisture uptake. However, as a thermoplastic polymer, PPO has a number of drawbacks, such as poor film-forming ability and low solvent resistance to halogenated hydrocarbon or aromatic hydrocarbon, etc. These drawbacks determine that PPO is impossible to be used directly as PCB matrix. Blending PPO with EP resin could not only improve the dielectric properties, toughness, and thermal stability of EP resin, but also overcome the drawbacks of PPO resin as was mentioned above.^{6,12,13} The EP/PPO blend was considered as a qualified matrix for high frequency and high speed electronic substrates.

However, owing to their different chemical structure and physical property, PPO, and EP resin have poor compatibility, especially for the PPO of high molecular weight. EP/PPO systems exhibit an upper critical solution temperature (UCST) behavior. Phase separation would occur while temperature is lower than UCST.^{6,14} In order to obtain high performance thermosetting EP/PPO system, it is extremely essential to improve the compatibility between EP and PPO resin. Some efficient methods

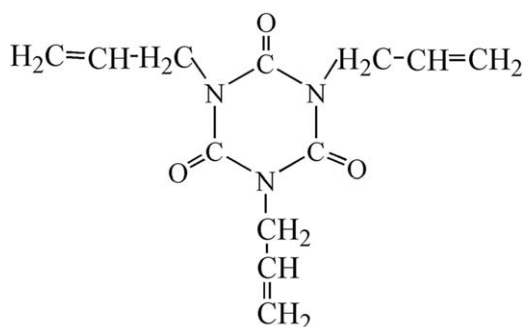


Figure 1. The schematics of molecular structure of TAIC.

include reducing the molecular weight of PPO^{15–17} or adding reactive monomers as compatibilizer to EP/PPO system. Triallylisocyanurate (TAIC) has good compatibility with EP and also contains three allyl groups which could react with various molecules or self-polymerize to form a network. So, TAIC has been used to modify EP/PPO system.^{18–20}

Redistribution is an efficient method to obtain low molecular weight PPO with the desired end groups. In this research work, in order to improve the compatibility of EP and PPO resin, vinyl-containing low molecular weight PPO (R-PPO) was prepared by redistribution reaction between commercially available PPO and maleic anhydride (MAH) initiated by benzoyl peroxide (BPO).² Moreover, considering that TAIC can react with the vinyl groups of R-PPO, so it was used as compatibilizer to improve the compatibility of EP with R-PPO resin further. Curing reaction kinetics, compatibility, morphology, dielectric properties and impact strength of EP/R-PPO system compatibilized with TAIC were further studied in this article.

EXPERIMENTAL

Materials

Poly(phenylene oxide) ($M_n = 16785$ g/mol, $M_w/M_n = 1.5$) was supplied by Blue Star Chemical New Material of China. A commercial bisphenol A epoxy resin (E-51) with an epoxy value of 0.48~0.54 eq/100 g was obtained from Nantong Stars Synthetic Material of China. The maleic anhydride (MAH), benzoyl peroxide (BPO) and dicumyl peroxide (DCP) were obtained from Chengdu Kelong Chemical Reagent Factory of China. 2-ethyl-4-methylimidazole (2, 4-EMI), as the curing agent, was obtained from Chenguang Chemical Reagent of China. Triallylisocyanurate (TAIC) was supplied by Hunan Minhe Chemical of China. The chemical structure of TAIC was illustrated in Figure 1.

Redistribution of PPO

After 80 g PPO was dissolved in 200 mL toluene in four-necked bottle with stirring at 90 °C, 24 g MAH was added into the solution, then 171 mL solution of BPO in toluene (concentration: 14 g/100 mL) was added dropwise. Followed the above procedure, maintaining the reaction for another 12 h at 90 °C under nitrogen atmosphere, then the mixture was cooled to room temperature and added to 200 mL methanol to precipitate the product. The precipitate was collected by filtration, washed several times with saturated aqueous solution of NaHCO_3 so as to remove the excess BPO. Finally the product was dried at 110 °C in vacuum oven. The reaction mechanism was shown in Figure 2. The M_n value of

the redistributed PPO (R-PPO) was 4930 g/mol and $M_w/M_n = 1.8$, which were measured with GPC.

Preparation of EP/R-PPO/TAIC Blends

Totally, 40 g epoxy and 10 g R-PPO were added into a three-necked bottle, stirred, and slowly heated to 180 °C and remained for 1 h. After cooled down to 120 °C, formulated TAIC was added and continued stirring for 30 min, then DCP (2 wt % of the total weight of R-PPO and TAIC) was added and stirring for 10 min. Afterwards, the mixture was cooled to 80 °C and 2, 4-EMI (2.5 wt % of epoxy resin) was added and continued to stir at 300 rpm for 5 min. The mixture was poured into a PTFE mold and successively cured at 150 °C for 2 h, 180 °C for 2 h under atmospheric pressure. For preparing EP/R-PPO system, the mixing procedure was as follows: 40 g epoxy and 10 g R-PPO in three-necked bottle were stirred and slowly heated to 180 °C and remained for 1 h. After cooled down to 80 °C, 2, 4-EMI (2.5 wt % of epoxy) was added and continued to stir at 300 rpm for 5 min. The mixture was poured into a PTFE mold and successively cured for 1 h at 100 °C, 2 h at 130 °C, and 2 h at 150 °C under atmospheric pressure.

Measurements and Characterization

Fourier Transform Infrared Spectroscopy. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-500 FTIR spectrometer (Nicolet Co., USA). The uncured samples were coated on KBr crystal surface to form thin films. The cured samples were compressed to pellet together with KBr powder.

Differential Scanning Calorimetry Analysis. Non-isothermal curing reaction of the EP/PPO/TAIC blends was performed on a Netzsch 204 Phoenix differential scanning calorimeter (DSC) (Netzsch Group, Germany). The samples of about 8 mg were heated under N_2 atmosphere from 50 to 250 °C at a heating rate of 10 °C/min.

Gel Permeation Chromatography Analysis. Gel permeation chromatography (GPC) analyses were performed using an

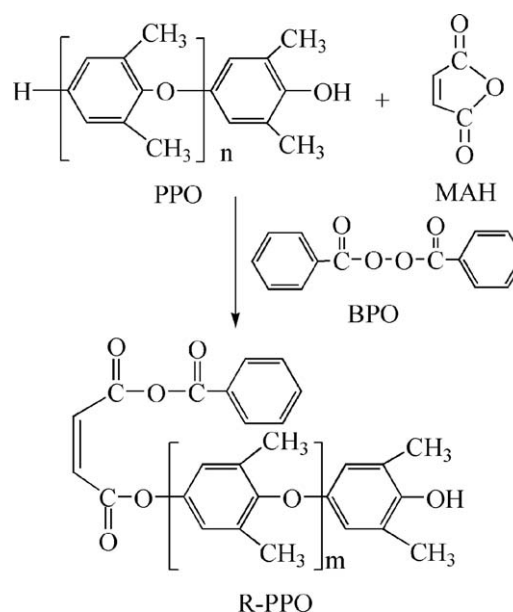


Figure 2. Schematic diagram of redistributed PPO with MAH.

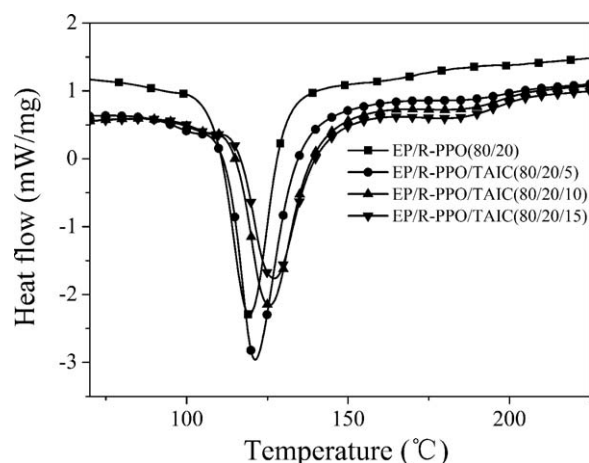


Figure 3. DSC curves of EP/R-PPO/TAIC systems cured at heating rate of 10 °C/min.

HLC-8320 GPC instrument (TOSOH Co., Japan) at 40 °C with two TSK gel columns (super HZM-M/Super HZ3000). The mobile phase was tetrahydrofuran, and its flow rate was 0.6 mL/min.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) was performed on a Q800 dynamic mechanical analyzer (TA Instruments, USA). The cured specimens were cut into strips of 40 × 10 × 4 mm. The dynamic mechanical behavior was measured from 50 to 250 °C at a heating rate of 3 °C/min in three-point bending mode. The frequency was fixed at 1 Hz.

Scanning Electron Microscopy Observation

Morphology of the samples was observed with a Quanta 250 scanning electron microscope (FEI Instrument, USA). The samples were frozen in liquid nitrogen and fractured. To clearly observe the phase morphology, some of the fractured surfaces were etched with trichloro ethylene at 25 °C for 24 h in order to remove R-PPO phase. The fractured surfaces were sputter-coated with gold in argon by a SC7620 sputter coater (Quorum Technologies, Britain). The resultant thickness of sputtering layer was 275 Å.

Dielectric Properties Measurement

Dielectric constant and dissipation factor were measured at 1 MHz under ambient condition using a SBJDCS-B dielectric constant and dielectric loss tester (Yangzhou Subo Electric, China) according to Chinese standard GB/T1408-2006. The sample diameter was 26 mm, and the thickness was 3 mm. For each data, five specimens were measured.

Table I. The Reaction Enthalpy (ΔH) of EP in EP/R-PPO (80/20)/TAIC Systems

TAIC content (phr)	EP reaction enthalpy (J/g)
0	262.0
5	258.2
10	253.5
15	218.1

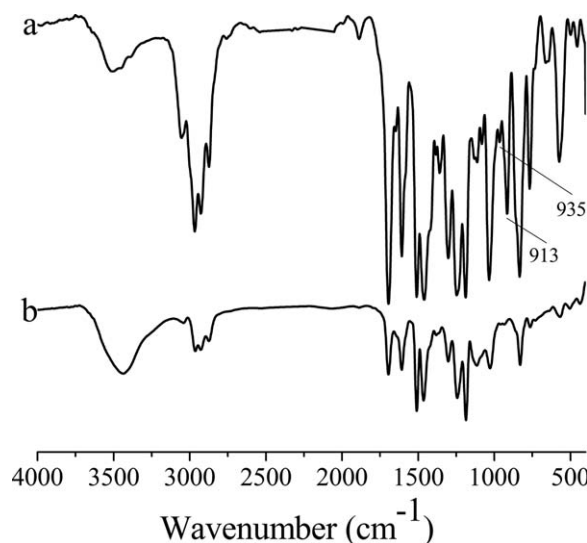


Figure 4. FTIR spectra of EP/R-PPO/TAIC (80/20/10) system: (a) before curing, (b) after curing.

Notched Impact Strength Measurement

Notched impact tests were conducted with XJU-5.5 cantilever beam impact tester (Chengde Jinjian Testing Instrument, China) according to ISO180:2000. The sample size was 80 × 10 × 4 mm. For each data, five specimens were measured.

RESULTS AND DISCUSSION

Effect of TAIC Amount on the Curing Characteristics of EP/R-PPO/TAIC System

Nonisothermal curing reaction of EP/PPO/TAIC systems containing different amount of TAIC were studied with DSC (Figure 3). The corresponding characteristic data were listed in Table I. The DSC heating curves exhibited two exothermic peaks. One sharp peak nearby 125 °C corresponded to epoxy curing reaction, the other wide peak nearby 185 °C was attributed to the reaction of TAIC. With the increase of TAIC addition, the exothermic peak area of TAIC reaction increased, while the peak area of epoxy curing decreased and the peak shifted to higher temperature. For EP/R-PPO (80/20) system, reaction enthalpy of EP was 262.0 J/g. Compared with it, the EP reaction enthalpy of EP/R-PPO/TAIC (80/20/15) system decreased to 218.1 J/g. The calculation of reaction enthalpy of the system was based on the total weight of epoxy, R-PPO and TAIC in the system, so the decrease of EP reaction enthalpy of EP/R-PPO/TAIC (80/20/15) system should be a result of dilution effect caused by the addition of TAIC. Moreover, this was also a result of steric hindrance and diffusional limitation imposed by the TAIC, which restricted the reaction of epoxy. Furthermore, the curing peak of epoxy in EP/R-PPO/TAIC system shifted to higher temperature meant that the reaction rate of the epoxy was hindered by the presence of TAIC.

The FTIR spectra of EP/R-PPO/TAIC (80/20/10) system before and after curing were shown in Figure 4. Before curing, the absorption peak situated at 913 cm⁻¹ was very obvious [Figure 4(a)], which was attributed to the epoxy group. Besides this, the absorption peak at 935 cm⁻¹ belonged to the C—H bending

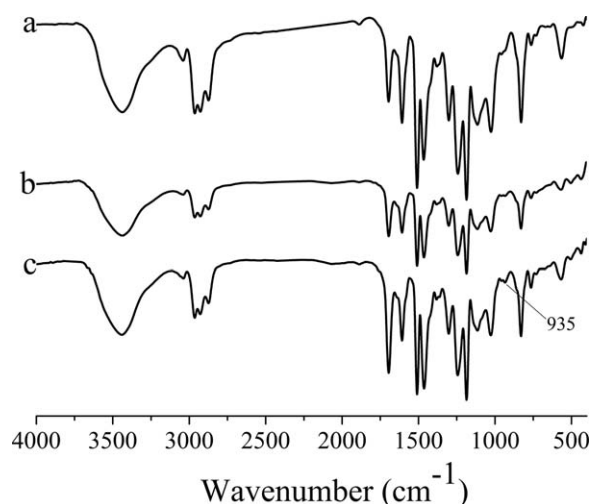


Figure 5. FTIR spectra of cured EP/R-PPO (80/20)/TAIC systems with various TAIC content: (a) 5 phr, (b) 10 phr, (c) 15 phr.

vibration of vinyl group ($-\text{CH}=\text{CH}_2$) of TAIC [Figure 4(a)]. After curing, the peak located at 913 cm^{-1} disappeared [Figure 4(b)], indicating that the epoxy resins were completely involved in curing reaction. The peak situated at 935 cm^{-1} weakened to a small peak [Figure 4(b)], indicating that most of TAIC was converted.

The FTIR spectra of cured EP/R-PPO (80/20)/TAIC systems with different content of TAIC were also recorded (Figure 5). For the cured EP/R-PPO (80/20)/TAIC systems containing 5 phr TAIC, the absorption peak of vinyl group located at 935 cm^{-1} disappeared [Figure 5(a)], indicating that TAIC in the system was completely consumed. However, for cured EP/R-PPO/TAIC (80/20/10) and EP/R-PPO/TAIC (80/20/15) system, the absorption peak at 935 cm^{-1} did not completely disappear, indicating that the TAIC in system was not completely converted. This result may be caused by two factors: first, during the curing process of TAIC and epoxy, the increasing viscosity lowered the diffusion rate of TAIC, and thus lowered the conversion of TAIC. Second, with the forming of TAIC network, the steric effect hindered the reaction of TAIC with the network.

Dynamic Mechanical Analysis of EP/R-PPO/TAIC Blend

Dynamic mechanical analysis (DMA) is commonly used to determine the glass transition temperature (T_g) of thermosetting resins. The loss tangent ($\tan \delta$) curves of cured EP/R-PPO/TAIC systems were shown in Figure 6, and the T_g values were listed in Table II. The DMA curve of cured EP/R-PPO (80/20) system exhibited two $\tan \delta$ peaks, one peak located at 140°C was corresponding to the T_g of EP-rich phase, the other peak located at 200.6°C was attributed to the glass transition of PPO-rich phase. This indicated that the cured EP/R-PPO (80/20) system still had two phase. After addition of TAIC into the system, both the $\tan \delta$ peaks were gradually close to each other and translated to single one, indicating the compatibility of epoxy with R-PPO was improved by TAIC and the cured systems turned into single phase morphology.

As shown in Table II, with the increase of TAIC content, the T_g of cured EP/R-PPO/TAIC (80/20/10) system was increased to

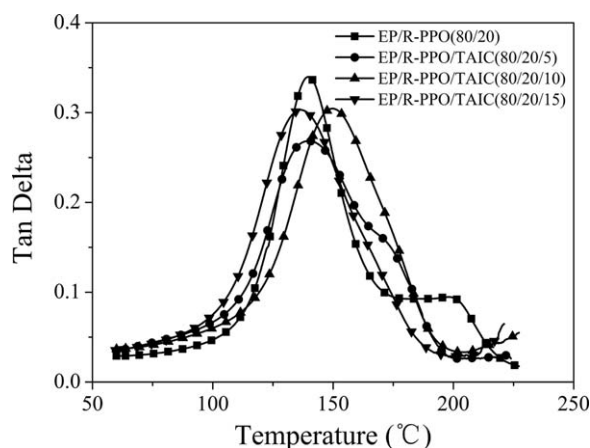


Figure 6. DMA curves of cured EP/R-PPO/TAIC systems with various TAIC content.

150.2°C from 141.7°C of the cured EP/R-PPO/TAIC (80/20/5) system. Further increasing TAIC content, the T_g of cured EP/R-PPO/TAIC (80/20/15) system was decreased to 138.2°C . When TAIC was added, the compatibility of EP and R-PPO was improved. Therefore, the T_g of cured EP and R-PPO would be close to each other, and the T_g of cured EP was increased. However, during the curing process of TAIC and EP, the increasing content of TAIC may reduce the crosslinking density of EP and thus resulted in the lower T_g .

SEM Observation

The morphology of cured EP/R-PPO (80/20)/TAIC systems were observed with SEM and shown in Figure 7. For the EP/R-PPO (80/20) system, the fractured surface after frozen in liquid nitrogen was flat [Figure 7(a)]. After etched with trichloro ethylene, there appeared some fine holes of about $1\ \mu\text{m}$ on the fractured surface [Figure 7(b)], indicating that the R-PPO particles were evenly dispersed in EP matrix. The EP/R-PPO (80/20) system had two phase morphology. This conclusion corresponded with above DMA results. For the EP/R-PPO (80/20)/TAIC systems containing 5 phr TAIC, the fractured surfaces before and after etching showed no clear difference, no holes were left on the etched surfaces [Figure 7(c,d)]. Although the EP/R-PPO/TAIC (80/20/5) system had two T_g peak (Figure 6), the T_g peak at 171.0°C was weak, the phase separation was not clear. For the EP/R-PPO (80/20)/TAIC systems containing 10 phr TAIC, the fractured surfaces before and after etching also showed no clear difference, no holes were left on the etched surfaces [Figure 7(e,f)], indicating the different components in

Table II. T_g of Cured EP/R-PPO (80/20)/TAIC Systems with Various TAIC Content

TAIC content (phr)	T_g ($^\circ\text{C}$)	
	EP phase	R-PPO phase
0	140.0	200.6
5	141.7	171.0 (weak)
10	-	150.2
15	-	138.2

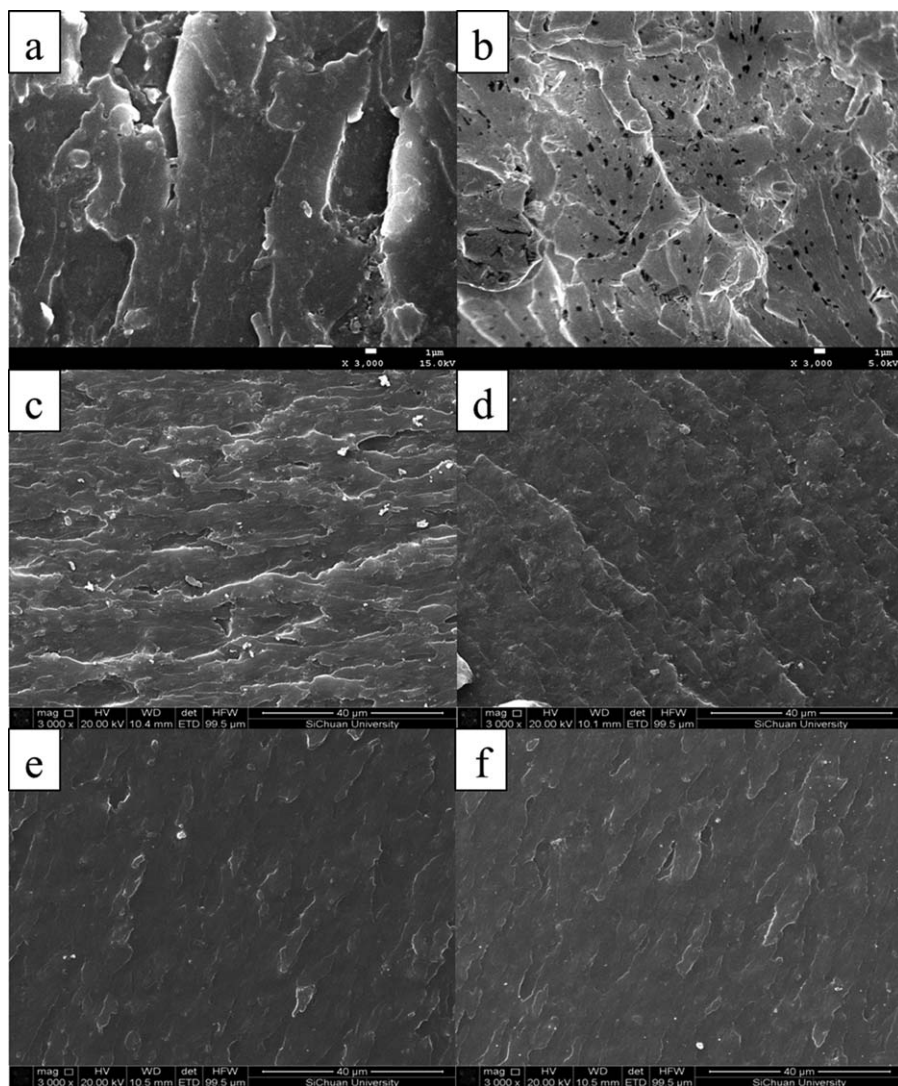


Figure 7. SEM photographs of EP/R-PPO (80/20)/TAIC systems with various TAIC content ($\times 3000$): (a) 0 phr TAIC, (b) 0 phr TAIC (etched), (c) 5 phr TAIC, (d) 5 phr TAIC (etched), (e) 10 phr TAIC, (f) 10 phr TAIC (etched).

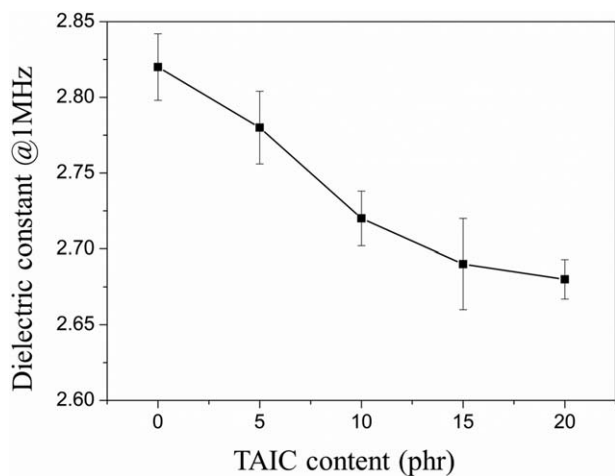


Figure 8. Dielectric constant at 1MHz of cured EP/R-PPO (80/20)/TAIC systems vs TAIC content.

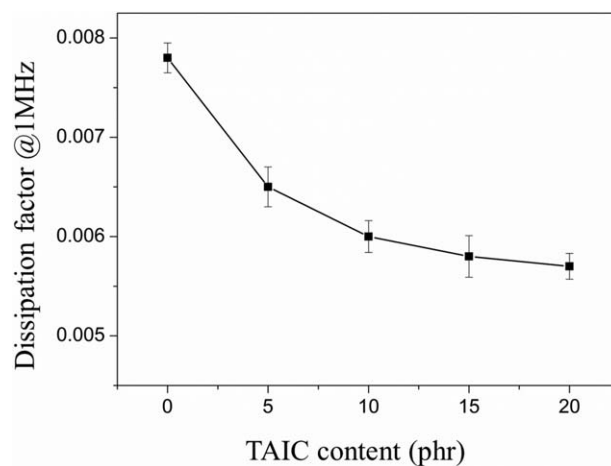


Figure 9. Dissipation factor at 1MHz of cured EP/R-PPO (80/20)/TAIC systems vs TAIC content.

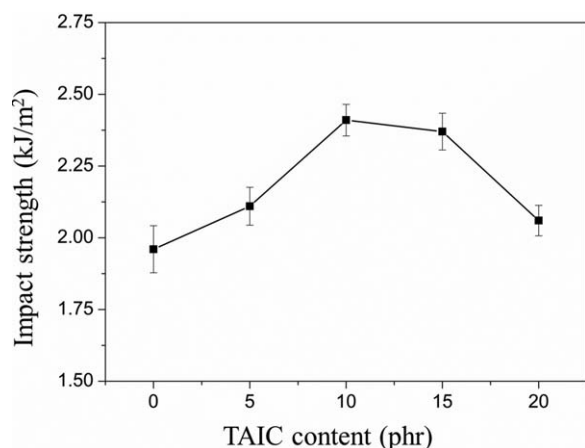


Figure 10. Impact strength of cured EP/R-PPO (80/20)/TAIC systems vs. TAIC content.

the EP/R-PPO/TAIC (80/20/5) systems had excellent compatibility, there was no phase separation occurred in these systems. The SEM observations also corresponded with above DMA results. The improved compatibility could be ascribed to the following reason: TAIC had excellent compatibility with epoxy resin. R-PPO was grafted onto the TAIC network through free radical reaction. The network of TAIC grafted with R-PPO entangled with epoxy network, and the compatibility of R-PPO with cured epoxy was thus improved.

Dielectric Constant and Loss

With the increase of TAIC content, the dielectric constant and dissipation factor at 1 MHz of cured EP/R-PPO (80/20) systems were both decreased (Figures 8 and 9). The dielectric constant and dissipation factor at 1 MHz of cured EP/R-PPO/TAIC(80/20/10) system were 2.72 and 0.006 respectively, were obviously lower than those of cured EP/R-PPO (80/20) system, which were 2.82 and 0.0078, respectively.

Notch Impact Strength

The impact strength of cured EP/R-PPO (80/20) system was 1.96 kJ/m². With the increase of TAIC content, the impact strength of cured EP/R-PPO (80/20)/TAIC system increased and reached to a maximum value (2.41 kJ/m²) when TAIC content was 10 phr, then it decreased (Figure 10). TAIC and EP have excellent compatibility. Furthermore, R-PPO was grafted onto the TAIC network through free radical reaction. The role of the graft copolymer could reduce the interfacial tension and improved the compatibility of the EP/R-PPO system, so a uniform and stable morphology was established.^{21,22} The impact strength of EP/R-PPO system was thus improved with the addition of TAIC. However, when TAIC content was excessive, TAIC monomer or oligomers existed in the matrix resin. In this way, the defects of matrix resin were created, which caused the decline of the impact strength.

CONCLUSIONS

Vinyl-containing low molecular weight PPO (R-PPO) was prepared by redistribution reaction. The EP/R-PPO (80/20) system exhibited two phase morphology, the R-PPO particles of about 1 μm were evenly dispersed in continuous epoxy phase. After addition of TAIC, the EP/R-PPO/TAIC systems were transferred to

single phase. The glass transition temperature of cured EP/R-PPO/TAIC (80/20/10) system was 150.2 °C. With the increment of TAIC content, the dielectric constant and loss of cured EP/R-PPO (80/20)/TAIC systems were both reduced. The dielectric constant and dissipation factor at 1 MHz of cured EP/R-PPO/TAIC(80/20/10) system were 2.72 and 0.006, respectively. Compared with those of cured EP/R-PPO (80/20) system ($D_k = 2.82$ and $D_f = 0.0078$ at 1 MHz), the dielectric constant and dissipation factor of cured EP/R-PPO/TAIC (80/20/10) system were decreased by 3.6% and 23.1%, respectively. With the increase of TAIC content, the impact strength of cured EP/R-PPO (80/20)/TAIC system increased and reached to a maximum value (2.41 kJ/m²) when TAIC content was 10 phr. Compared with that of cured EP/R-PPO (80/20) system (1.96 kJ/m²), the impact strength of cured EP/R-PPO/TAIC (80/20/10) system was improved by 23%.

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