Modification of Epoxy Resin by Cyanate Ester Resin and Liquid Butadiene-Acrylonitrile Rubbers

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In this paper, the results showed that the addition of an appropriate amount of reactive rubbers (e.g., carboxyl randomized butadiene-acrylonitrile rubber (CRBN) and hydroxyl terminated butadiene-acrylonitrile rubber (HTBN)) to epoxy resin/cyanate ester resin (EP/CE) (70/30) improved both the mechanical properties and thermal stability of the resulting blends. CRBN and HTBN have different reactive activity and dispersion state in EP/CE/rubbers. No drop in the thermal stability of the EP/CE network with addition of these two rubber component is related to the low rubber concentrate and the reactions between the rubbers and EP or CE.

Keywords Blends; Thermal properties; Toughness

INTRODUCTION

Epoxy resins (EP) are used in a variety of applications since their properties, such as thermal stability, mechanical response, low density and electrical resistance, can be varied considerably. However, these materials are rather brittle and, for this reason, their toughening has been extensively studied in the last decades. Modification of epoxy resin has been carried out to improve the impact strength of cured epoxy by incorporating thermoplastic polymers, rubbers, and nanoparticles. One of the most successful methods involves the addition of a suitable rubber to the uncured EP and then controlling the polymerization reactions in order to induce phase separation[1–6]. The great majority of the studies involve its chemical modification with a reactive elastomer, particularly nitrile rubbers[7–9].

During the polymerization, the rubber phase separates because it becomes less miscible with the matrix, forming tiny particles of rubber that are dispersed in the EP matrix. However, the addition of rubber usually brings to the decrease of other properties, especially the thermal stability properties and the modulus of the resulting composites. Recently, there has emerged a new approach for improving the thermal stability and modulus of EP matrix through the formation of interpenetrating networks with other thermo-set resins[10–12].

Among them, cyanate esters (CE) are expected to be the best materials to improve thermomechanical properties[10–12]. CE has superior thermomechanical properties such as high cross-linking ability, high glass transition temperature, high thermal stability, lower water absorption than EP. Each of them can be utilized as latent catalysts to the other component. Though the cured CE network itself is also brittle, the addition of CE monomer can improve the thermal stability and modulus of EP matrix.

In the present investigation, an attempt has been made to improve the thermal stability of epoxy resin by forming a network of epoxy-cyanate ester, and using nitrile rubber as chemical modifiers for improving the toughness of the network. It is expected that there will be a synergism improvement in toughness and thermal properties to the EP matrix. The modification method will greatly extend the utility of EP resins. The nitrile rubbers used in this work are carboxyl randomized butadiene-acrylonitrile rubber (CRBN) and hydroxyl terminated butadiene-acrylonitrile rubber (HTBN).

EXPERIMENTAL

Materials

Bisphenol A type epoxy resin (E-51) was purchased from Wuxi Huili Resin Factory (Jiangsu, China). A phenolic-based CE resin (melting point: 76°C) was supplied by Jinan Special Structure Institute of China Aero-Industry (Jinan, China). The CRBN and HTBN were provided by Lanzhou Chemical Industry Company (Lanzhou, China). The molecular weights of CRBN and HTBN were between 3000—5000 with the acrylonitrile content of both being 22–25% by weight. The data of the molecular weight and acrylonitrile content of the rubbers was kindly provided by Lanzhou Chemical Industry Company (Lanzhou, China). Mold release agent (JR105
silicone grease) was supplied by Jinrong Grease Company (Fuyang, China).

**Preparation of the Composites**

EP/CE mixtures with mass ratio 70/30 were thoroughly blended at 90°C for 30 min with constant stirring. Then, certain amount of CRBN or HTBN (rubber content: 0, 3, 5, 8, 10, 15% by weight) was added to the EP/CE mixtures at 90°C with stirring. After completely mixing, mixture was quickly poured into a preheated steel mold coated with right amounts of the mold release agent (just put a cover over the steel mold). After degasification under vacuum (about 1000 Pa) for 30 min at 110°C, the mold was kept via the following cure procedure: 130°C/1 hr + 150°C/1 hr + 170°C/1 hr + 190°C/1 hr + 210°C/1 hr + 230°C/1 hr + 250°C/1 hr to form the specimens. Neat EP specimens were prepared with the process: an appropriate amount of DDM (curing agent, 10 wt%) was added to EP at 90°C, stirred for several minutes, and quickly poured into a preheated steel mold coated with the release agent. After degasification under vacuum (about 1000 Pa) at 90°C for about half an hour, the sample was allowed to cure at 90°C for 2 hr and then at 150°C for 5 hr.

**Characterization of the Composites**

The unnotched impact strength was measured with a Charpy impact tester (XJC-5, Chengde Testing Machine Co. Ltd., China). The tests were according to the Chinese national standard methods for impact resistance of resin casting body (GB/T 2571-1995) at 23 ± 2°C. The size of the samples for impact testing is about: 80 mm × 10 mm × 5 mm.

The reactions were tracked by infrared spectrometry with Fourier transform infrared spectrum (FTIR-Nicolet 740). The pre-polymer of EP-CE was blended with appropriate amount of KBr to form a sheet. The sheet was scanned firstly by FTIR for its initial curve, and then interval and scanned once again by FTIR for its part-cured curve.

Differential scanning calorimetric (DSC, PekinElmer DSC-7) measurements were made at a scan rate of 10°C/min with 4-6 mg samples in a nitrogen atmosphere. The morphology of the fracture surfaces of composites after impact tests were examined by scanning electron microscopy (SEM) with a JEM-6360 SEM (JEOL Ltd., Japan). The specimens were coated with gold to improve SEM imaging. Before a transmission electron microscopy (TEM) observation, the composite samples were cut by a ultramicrotome (Power Tome-PC, RMC Products by Boeckeler Instruments, USA) to obtain the ultra thin films of the samples. Then, the ultra thin sample films were first stained with osmium tetraoxide (OsO4) and then observed with a JEM-1200EX TEM (JEOL Ltd., Japan). The detail of the staining treatment is as follows: the ultra thin films were fumigated by a dilute OsO4 solution for about half an hour in a stink cupboard.

Thermo gravimetric analysis was performed using a NETZSCH STA 449C (NETZSCH Company, German) thermal analyzer. The samples were heated from 30°C to 800°C at a heating rate of 20°C/min under nitrogen atmosphere.

**RESULTS AND DISCUSSION**

**Mechanical Properties and Phase Behavior of the Blends**

Figure 1 shows the influence of rubber content on the impact strength of the EP/CE (70/30) blend. For comparing, the impact strength of EP cured with DDM (8.1 KJ/m²) is also shown in Figure 1. With addition of CE, the blend of EP/CE (70/30) has lower toughness (7.7 KJ/m²) than EP cured with DDM. This means the addition of CE has little modification effect on the toughness of EP. As shown in Figure 1, the impact strength of EP/CE/CRBN increases as the CRBN content increase. As for EP/CE/HTBN blends, the impact strength increases firstly with the addition of HTBN (up to 8 wt%), and then decreases slightly with further addition of HTBN. The value of impact strength (14.0 KJ/m²) shows a maximum for the EP/CE/CRBN (70/30/15) blend. Which is much higher than EP/CE (70/30) or EP cured with DDM. These results refer that there is an effective improvement in the toughness of EP/CE network with addition of these two rubbers.

SEM observations of the fracture surface are indicative of the compatibility and the fracture mode of the materials. The fracture surface of rubber-modified EP/CE networks has been analyzed by SEM (Figure 2). It can be seen that...
the fracture surface of both EP/CE/CRBN and EP/CE/HTBN blend systems are much rougher than EP/CE, indicating better toughness in the modified EP/CE matrix. However, the fracture mode of these two blend systems is different. The fracture surface micrographs of EP/CE modified with CRBN shows many cavities (about 1 μm), indicating a heterogeneous system. And the number of the cavities increases as the CRBN content increases. The fracture surface micrographs of EP/CE modified with HTBN do not show any cavities, but consisting of more crevices and all directions crack propagation.

Usually, during the curing reaction of thermosetting resin/rubber systems, the rubber phase will separate and form tiny particles dispersed in the thermosetting resin network. Most of the cavities result from some CRBN particles pulled out during the fracture process. The other possible reason is attributed to the fact that a slight weight loss of the rubbers during the curing cycle. The gas molecules (the decomposition products of low molecular weight part of rubber) were trapped by the crosslinking network of EP/CE and formed the pores after the curing process[13–15]. The induced pores might be another toughening mechanism that ever proposed by several investigators[16,17]. This maybe the main reason for that the toughness of EP/CE/CRBN is higher than EP/CE/HTBN as the rubber content higher than 8%. The no cavity structure of EP/CE/HTBN blends might be attributed to their good compatibility and the phase size is too small to be detected by SEM.

TEM was used to further confirm the phase size of the composites. The ultra thin sample films were stained with OsO₄. It is well known that the double bonds of alkenes can be easily oxidized by OsO₄. Since the CE monomers (containing –OCN groups) and EP monomers have already reacted entirely forming stable triazine ring networks and oxazolidinone during the cure process, the matrix is difficult to be stained by OsO₄. Only the C=C bonds within the rubber backbone were stained and obvious color differences would appear between the rubber-rich phase (often dark zone) and the matrix in the TEM photos.

As shown in Figure 3, for EP/CE/CRBN blends, CRBN aggregated to form regular spherical and its phase size is about 1 μm. In addition, there are some white content in the dispersed CRBN spherical. This is assign to the pores containing in the samples that caused by the decomposition of CRBN. As for EP/CE/HTBN blends, HTBN phase do not aggregate to form regular spherical. The HTBN phase dispersed homogeneously with its size in nanolevel (about 10 nm). HTBN had better compatibility with EP/CE network than CRBN though the –COOH groups of CRBN usually have higher activity than terminated –OH groups of HTBN. This difference in phase behavior might be attributed to the kinetics of phase separation.
In summary, the modification mechanism of HTBN and CRBN for EP/CE matrix is different. The presence of a dispersed, secondary rubber phase is the main toughening mechanism in EP/CE/CRBN blend system. In addition, the existence of cavities induced by low molecular weight part of rubber during curing is another toughening mechanism. The flexibilizing effect caused by the presence of dissolved rubber inside EP/CE matrix is the main toughening mechanism in EP/CE/HTBN blend system.

Curing Products of the Blends

FTIR has been employed to study the curing reactions of the blends at 170°C. The possible reaction pathways are given in Scheme 1. Figure 4 shows the isothermal curing behavior at 170°C of EP/CE (70/30) blend. In the early stage (the first 10 min), we see (1) disappearing absorptions of cyanate group (2272 cm\(^{-1}\) and 2232 cm\(^{-1}\)) and decreasing absorptions of epoxide group (915 cm\(^{-1}\)), (2) emerging and increasing absorptions of oxazoline (1680 cm\(^{-1}\) and 1295 cm\(^{-1}\)), (3) increasing absorptions at 1370 cm\(^{-1}\), but no obvious absorption at 1565 cm\(^{-1}\), meaning the presence of triazine is rare.

The intensities of the absorption peaks of the oxazoline structure, triazine ring reach maximum level as compared with the internal standard (–CH\(_3\), 1505 cm\(^{-1}\)) during the isothermal cure at 170°C for the first 10 min. In the early stage, the main reaction is pathway 1. The late stage of the isothermal curing process: (1) decreasing of the absorption of oxazoline (1680 cm\(^{-1}\) and 1295 cm\(^{-1}\)) and disappeared as cured for 60 min, (2) decreasing of the absorption of triazine (1370 cm\(^{-1}\)) and, (3) increasing absorptions at 1370 cm\(^{-1}\), but no obvious absorption at 1565 cm\(^{-1}\), meaning the presence of triazine is rare.

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The reactions in the late stage are pathway 3, 4, 5, 6. Meanwhile, the excess EP goes on ring-open polymerization to form polyesters network (pathway 7). In this EP-rich blend system, the main curing products are polyester network, oxazolidinone and isocyanurate, whereas the triazine ring network is rare for the lack of CE.

In the recent works\(^{[14,19,20]}\), it has been confirmed that the reactive rubbers would react with both CE and EP monomers during the curing process. The molecular structure and the FTIR spectra of the rubbers are shown in Figure 5. It is believed that the reactive rubbers would react with both CE and EP monomers during the curing process. However, the absorption of the functional groups of the rubbers is overlapped with the functional groups of EP and CE. Thus, the reactions between the rubber and EP or CE are difficult to determine by FTIR in such blend system.

Figure 6 shows the DSC results of the curing reaction of the blends. Considering the results of FTIR, the first weak curing peak in the system is much related to the products of cross-linked oxazoline and polytriazine networks. And the second strong curing peak in the blend system is much related to the products of polyether network, oxazolidinone, isocyanurate. The first curing peak temperature of both two blend systems shifts to higher temperature with addition of rubbers. It is mainly due to the steric effect at...
the beginning of curing reaction of the system. The added rubber molecules decrease the collision probability of EP and CE molecules. As for the second curing peak temperature, it shows a different shift with addition of different type of rubbers. For EP/CE/CRBN blends, the peak temperature decreased from 232.3°C to 220.8°C. And for EP/CE/HTBN blends, the peak temperature increased from 232.3°C to 239°C.

The reason of this phenomenon is attributed to differences in the reactivity and dispersion state of these two rubbers. The decrease in the peak temperature in EP/CE/CRBN blends is mainly caused by the higher reactivity of –COOH groups in CRBN. The increase in the peak temperature in EP/CE/HTBN blends is mainly due to the steric effect during the curing reaction of the system. The well dispersed HTBN during the cure process (as seen from TEM photos) will decrease the collision probability of EP or CE molecules. In addition, according to the DSC results, the curing exothermic heat ($\Delta H$) of EP/CE decreases obviously with addition of the rubbers. This might be attributed to the reactions between the rubbers and EP via carboxyl (–COOH) groups and hydroxyl (–OH) groups. It leads to a decrease of EP forming polyether network, and an increase of the co-cured products of EP, CE and rubbers.

Thermal Stability of the Blends

The thermal stability of the blends was determined by thermal gravimetric analyzer (TG) and shown in the Figures 7 and 8. It is well known that EP is difficult to cure without any curing agent. Polyamine is often used as the cross-linking agent of EP. For comparing, EP cured with DDM is also given. $T_{10}$ (temperature of 10% weight loss) is the main criterion to indicate the thermal stability of polymers: the higher the value of $T_{10}$, the higher the thermal stability. $T_{10}$ improved from 352°C for EP cured with DDM to 402°C for the EP/CE (70/30). The EP/CE (70/30) blends have a much higher stability than EP cured with
DDM. The main reason of this phenomenon should be attributed to the following two factors. On the one hand, the polyether networks formed in the EP = CE blends had a higher cross-linking density and compactness of each cross-linking unit than that of EP cured with DDM. The other hand is that the co-cured products of EP and CE (oxazolidinone, isocyanurate, and even some triazine ring network) have higher thermal stability than the curing products of EP cured with DDM.

Meanwhile, it is found that the addition of reactive rubbers do not have negative effects on the thermal stability of EP = CE (70/30). $T_{10}$ of EP/CE/HTBN (404°C) is even higher than neat EP/CE (70/30). This is attributed to the reactions between the rubbers and the curing resins. The rubbers acted as a bridge to connect the EP and CE molecules. Thus, the flexibility and the rigidity of the system have been improved synergistically.

**Conclusions**

The addition of an appropriate amount of reactive rubbers and CE to EP improved the mechanical properties and thermal stability of the resulting blends. CRBN and HTBN have different reactive activity and dispersion state in EP = rubbers. The presence of a dispersed, secondary rubber phase is the main toughening mechanism in EP/CE/CRBN blend system. In addition, the existence of cavities induced by low molecular weight part of rubber during curing is another toughening mechanism. The flexibilizing effect caused by the presence of dissolved rubber inside EP/CE matrix is the main toughening mechanism in EP/CE/HTBN blend system. The co-cured products of EP and CE have a higher stability than EP cured with polyamine. No drop in the thermal stability of the EP/CE network with addition of these two rubber components should be related to the low rubber concentration and the reactions between the rubbers and EP or CE.

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