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Effect of bentonite on the structure and mechanical properties of CE/CTBN system

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Abstract Cyanate ester (CE) resins are among the most important engineering thermosetting polymers and have received attention because of their outstanding physical properties. However, their main drawback is brittleness. Toughening by rubbers is a notable way to improve the toughness but unfortunately it decreases the modulus and thermostability. The CE/carboxyl terminal butadiene-acrylonitrile (CTBN)/bentonite (BT, a kind of clay) composites were prepared by two-step melt blending of CE, CTBN and amino-modified bentonite. The nanostructure and mechanical properties of the CE/CTBN/BT composites were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM) and dynamic mechanical analysis (DMA). Both of the intercalated and exfoliated structures of BT existed in CE/CTBN/BT composites while rubber particles also could be observed in CE/CTBN/BT composites by TEM. When an appropriate amount (about 0.5 wt.%) of BT added into CE/CTBN (100/10 by weight) system, both of the modulus and impact strength increased. A 30% increase of the modulus was obtained without greatly sacrificing the impact strength of the composite when the BT content was 1 wt.%.

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Introduction

Cyanate ester (CE) resins are currently important materials for the encapsulation of electronic devices, high-temperature adhesive and structural aerospace composites. CE monomers undergo polycyclotrimerization to form trifunctional triazine rings, which exhibit excellent dielectrical, thermal and adhesive properties [1]. However, like most of the thermosetting resins, the brittleness of CE limits its application as structural material. It is necessary to develop suitable modification methods to improve its toughness without reducing the intrinsic physical properties [2].

In fact, a number of studies have been carried out on the toughening of this thermoset. Among them, using the reactive elastomers such as liquid nitrile rubber has been proven to be one of the most successful techniques. So many researchers have investigated the toughening effect of functionalized butadiene-acrylonitrile rubbers [3–8]. With various types of functional groups that investigated, carboxylic acid end group is proven to be the most effective. In our previous work, the impact strength of CE/CTBN system was improved significantly by the addition of CTBN, especially when the CTBN loading was 10 wt.% in CE/CTBN blend. The value of impact strength was twice higher than that of pure CE when the CTBN loading was 10 wt.% [8]. Unfortunately addition of CTBN reduced the modulus and thermostability of CE resins due to the low modulus and thermostability of CTBN. Because the high modulus and thermostability are as important as toughness to engineering plastics, other routes should be developed to overcome the drawback of rubber modification.

Interests in the addition of nano-scale fillers, such as layered silicates, into polymers as an approach to enhance performance have substantially increased recently [9–16]. Many researches have found that the presence of layered silicates can improve the modulus, thermal stability, gas barrier properties of thermosetting resins [17–19].

In a previous study [20], the addition of an organic modified bentonite into CE improved modulus and thermostability of the composite obviously. It also had a positive effect on its impact strength. We also found that cyanate monomers could easily diffuse into the galleries of organic modified bentonite due to their high polarity. The polarity of the –OCN group is thought to promote diffusion into the clay galleries. When heated, the cyanate monomers that intercalated into the galleries began to polymerize, and with the formation of the triazine network via cyclotrimerization, the galleries gradually expanded. For the existence of the $–NH_4^+$ group (which is a good curing agent for cyanate monomer) in galleries, intragallery polymerization begins prior to extragallery polymerization. The maximum layer expansion is obtained when the polymerization rate in intragallery regions is equal to that in the extragallery regions, allowing for exfoliation before gelation. An unbalance between these rates guarantees the formation of an exfoliated structure.

Noting that the addition of CTBN improved the impact strength of composite and the addition of BT improved the modulus of composite, we added both of CTBN and BT into CE, in order to improve the modulus and impact strength of the composite simultaneously. Besides, the main toughening mechanism for CE/CTBN systems is thought to be the enhancement of shear yielding at the crack tip through a change in stress state in the region around a rubber particle [21, 22]. While for organo-clay modified CE systems, clay particles in CE matrix can induce the crevices. Therefore, it is expected to get synergistic toughening effect by adding both CE and CTBN into CE matrix.

Experimental

A phenolic-based cyanate ester resin (CE) (melting point: 79 °C) was supplied by Jinan Special Structure Institute of China Aero-Industry (Jinan, China). CTBN was provided by Lanzhou Chemical Company (Lanzhou, China) and used as received. The molecular weight of CTBN is between 2,000 and 3,000 g/mol and the acrylonitrile content is 25 wt.%. Organic modified bentonite (BT, Code: NB905) was obtained from Zhejiang Huate Group Co. Ltd., Hangzhou, China, which was ion-exchanged with octadyl trimethyl ammonium.

In this study, the composites were designated by the weight ratio of their components in this order: CE, CTBN and BT. For example, a composite containing 100 wt.% CE and 10 wt.% CTBN was abbreviated as CE/CTBN = 100/10. Similarly, a ternary blend containing 100 wt.% CE, 10 wt.% CTBN and 0.5 wt.% BT was coded as CE/CTBN/BT = 100/10/0.5.

CE was placed in a beaker maintained at 90 °C. Sequential mixing (two-steps) was used: first, BT was slowly added (0.5, 1, 1.5, 2, 2.5 and 5 wt.%) to CE resin under simultaneous stirring for 15 min; second, CTBN was added to these pre-intercalates of CE/BT to obtain the ternary mixture. After 15 min's stirring, the mixture was degassed under vacuum at 140 °C over 30 min, and cured via following procedure: 160 °C/1 h + 180 °C/1 h + 200 °C/1 h + 220 °C/1 h + 240 °C/1 h + 260 °C/1 h. After curing, the composites were exposed to the air and let the composite temperature decreased from 260 °C to room temperature.

X-ray diffraction (XRD) measurements were performed on a Rigaku D/Max-2550PC system with Eulerian 1/4 cradle and CuKα radiation (40 kV, 300 mA, $\lambda = 1.540$ Å), 2°/min. Transmission electron microscopy (TEM) was done using a JEM-1200EX electron microscope, Japan. Samples were previously stained with OsO_4 before TEM observation. Dynamic mechanical analysis (DMA) was performed using a DMA Q800 V3.13 Build 74 by TA Instruments, USA. Unless otherwise stated, the testing was carried out in dual cantilever bending mode at a vibration frequency of 1 Hz in a temperature range from 40 to 250 °C, and the heating rate was 2 °C/min. The impact test was performed according to GB/T2571-1995 (similar to ISO179-1993) on an XCJ-4 Charpy impact instrument at 23 ± 2 °C. The results of the impact test were obtained by averaging the results of five measurements.

Result and discussion

Structure of composite

In present study, nanocomposites are prepared via the diffusion of the oligomeric pre-polymer into the interlayer regions, followed by cross-linking. Due to the high polarity of the group –OCN, cyanate monomers could easily diffuse into the amino-modified bentonite clay galleries. In CE/CTBN/BT blends, if CTBN were first intercalated into clay galleries, the content of amino ($–NH_4^+$) in galleries of BT would decrease due to its reaction with the terminated carboxyl (–COOH) of CTBN, which would reduce the ability of intercalation of CE monomers into clay layers. In order to avoid the disadvantageous, sequential mixing (two-steps) is selected. In the first step, the CE monomers and BT mixture was prepared by melt blending. Because of the high polarity of cyanate monomers, CE monomers can easily diffuse into the organic modified bentonite clay galleries in this step. In other words, the pre-intercalates of the CE monomer and BT were prepared in the first step; then the CTBN was added to these pre-intercalates of CE/BT to obtain the ternary mixture.

The evolution of the morphology during this process was studied by XRD and TEM. Figure 1 shows the XRD diffraction patterns of BT and CE/CTBN//BT nanocomposites with different BT content. According to Fig. 1, the BT curve reveals that the peak is located at around 6.32°, corresponding to a basal spacing of 1.397 nm. For the CE/CTBN/BT composites, the characteristic diffraction peaks decrease obviously in intensity and move to lower angle. There is no obviously peak in the curve of CE/CTBN/BT = 100/10/0.5, which means the bentonite had been exfoliated. When the BT loadings were 1, 2 and 5 wt.%, the characteristic diffraction peaks shifted left to 2.54°, 2.68° and 2.74°, corresponding to the interlayer distances of 3.47, 3.29 and 3.22 nm, respectively. This suggests that CE monomers have intercalated into the interlayer of BT. In CE/CTBN/BT = 100/10/5 and CE/CTBN/BT = 100/10/2 composites, a second characteristic diffraction peak at lower angle (around 1.04°) was observed. It was thought as an intercalated peak induced by low molecular weight parts of CTBN. The increased spacing indicated that a small degree of mass transferred into the galleries. The fact above suggests that CTBN do have obviously effect on intercalation of BT in the composites especially for high BT loadings.

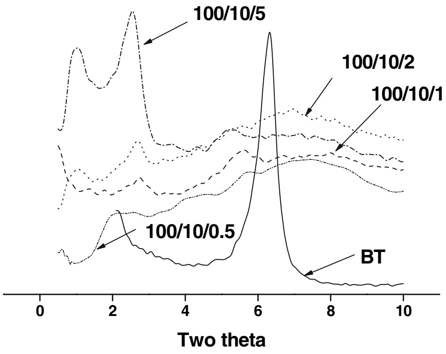

Fig. 1 X-ray diffraction patterns of BT and CE/CTBN/BT composites

Figure 2 shows the TEM micrographs of CE/CTBN/BT nanocomposites. It can be observed that exfoliated layers and small clay aggregates (in different thickness and length) dispersed inhomogeneously in CE matrix in Fig. 2a and b. Both of the exfoliated and intercalated structures can be seen. Obviously, most clay layers were not separate but existed in several stacked layers. This suggested that the van der Waals force and Coulombic force between the BT intergalleries were so strong that the silicate layers could not separate from each other easily. Even if the CE monomers intercalated and cured in intergalleries, the strong polarity of layers endowed by $-NH_4^+$ hold them tightly. Whether the layers were in exfoliated state or aggregated state was determined by the two forces above and the force between CE monomers and BT. Therefore, as analyzed above, it is reasonable to conclude that CE monomers intercalate into stacks of several BT layers easily, while individual BT layer appears rarely under these conditions.

When the sample is cured, layer separation can be observed which indicated that a certain degree of mass was transferred into the galleries. The $-NH_4^+$ group catalyzed the curing process in galleries prior to that in extragallery area, which attracted further diffusion of the pre-polymer into the galleries and accelerated extensive layer separation. The maximum layer

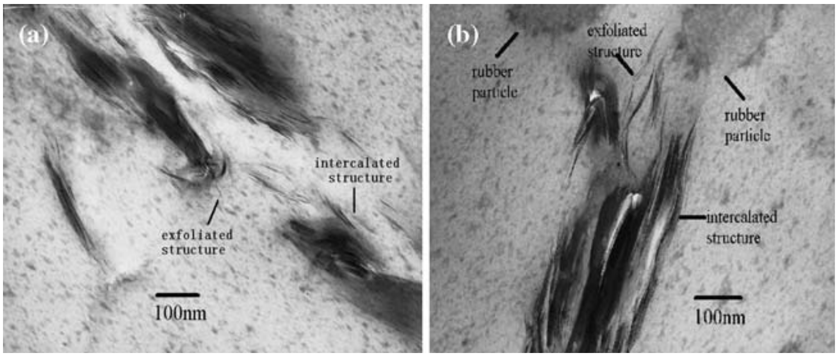

Fig. 2 TEM micrographs of CE/CTBN/BT nanocomposites

expansion was obtained when the intragallery polymerization rates equaled the extragallery polymerization rate, allowing exfoliation before gelation. A balance between these rates must be maintained in order to ensure the formation of a homogeneous, three-dimensional network. However, it should be noted that highly electronegative –OCN groups endowed CE with strong polarity. At the same time, large quantities of polar –OCN groups and silica-oxygen layers existing on the surface of BT layers made the surface of layer to be a polar surface. In this case, the dipole–dipole interaction between CE oligomers and silicate layers may act as a driving force for CE oligomers to intercalating into silicate layers. Moreover, during the melt blending process, the elevated processing temperature and shear stress may facilitate the intercalation. Therefore, it is interesting to note that disordered and partially intercalated CE/BT nanocomposites can be formed during melt blending of CE and hydrophilic BT, which cannot be realized in other weak polar polymer/BT system. Correspondingly, it can be concluded that dipolar interactions between the relatively polar polymer chains and the surface of BT layers are the main driving force for the intercalation of CE.

Rubber particles also can be seen by TEM in Fig. 2b in CE/CTBN/BT system. CTBN-modified composite samples were characterized after staining by OsO_4. The rubber-rich phases appeared dark in the picture because CE was already polycondensated through their –OCN, and only the unreacted C=C bonds of CTBN were stained by OsO_4. The CTBN-rich phases appeared black globular as shown in the picture. This result verified that CE/CTBN/BT composite was not a single-phase material. Figure 2b reveals the intercalated and exfoliated layers structures coexist in nanocomposite as well as rubber particles. The rubber particles toughening mechanism is thought to be the enhancement of shear yielding at the crack tip through a change in stress state in the region around a rubber particle [21, 22]; while the nano-particles toughening mechanism is thought that clay particles in CE matrix could induce the crevices, terminate the crack yielding by shear force [23, 24]. Therefore, it is inferred that the two different toughening mechanisms may work together in CE/CTBN/BT composite.

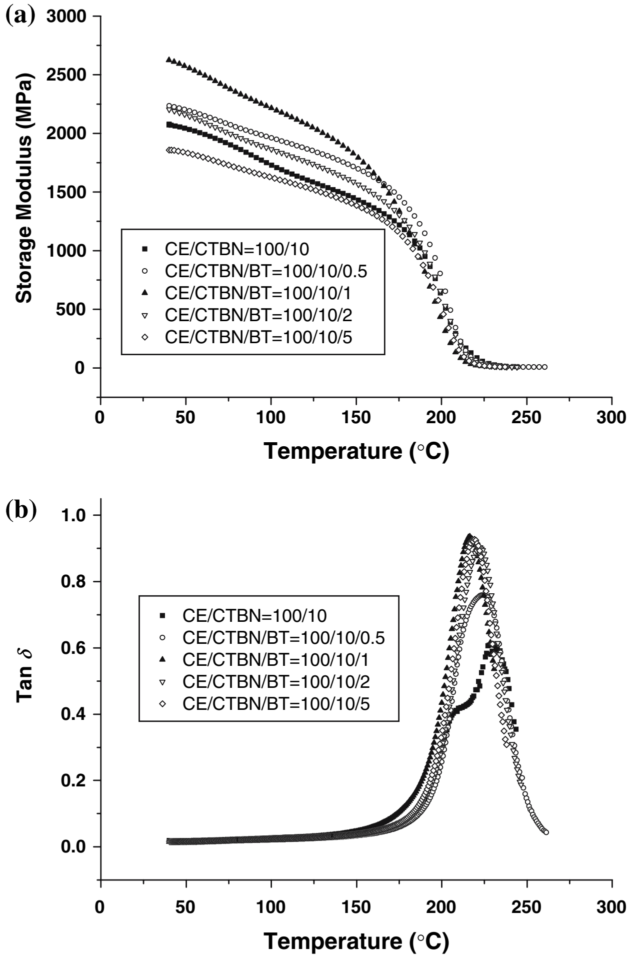

Fig. 3 Temperature dependences of storage modulus (**a**) and Tanδ (**b**) for CE/CTBN/BT composites

Mechanical properties of the composites

Figure 3 shows the dependence of storage modulus (G') and loss tangent (Tanδ) on temperature of CE/CTBN/BT blends. According to Fig. 3a, the initial modulus of CE/CTBN/BT composite was obviously higher than that of the CE/CTBN blend except the 100/10/5 composite. When the BT content was below 2 wt.%, the initial storage modulus increased with the increase of BT content. In 100/10/1 composite, a 30% increase in the initial storage modulus was obtained. But when the BT content was increased further, the modulus of the composite deteriorated. The changing of initial storage modulus of CE/CTBN/BT composite showed the same trend of CE/BT composite in our previous work [20]. Comparing with former work, the initial storage modulus of CE/CTBN/BT composite is only a little lower than that of CE/BT composite because of the low modulus of CTBN. When the BT content was below 2 wt.%, the increase in modulus may be caused by the accordingly increase in the number of exfoliated BT sheets at a low BT content. The decrease in modulus may be caused by the aggregation of BT in the samples when the BT content was above 2 wt.%. This result was in good agreement with the XRD results and what was observed in the dispersion of BT in CE matrix (Fig. 2).

In Fig. 3b, the peak point of loss tangent (Tanδ) is considered as the glass transition temperature (T_g). Figure 3b indicated that all composites studied show a relaxation peak, which was analogous to the glass transition temperature. T_g of CE/CTBN/BT (0.5, 1, 2 and 5 wt.% BT) was 224.3, 216.8, 222.4 and 218.6 °C, respectively, while CE/CTBN blend had two transitions at 208 and 230.4 °C. It is proposed that the intercalation and exfoliation of the clay in the CE resin effectively changed the temperature of glass transition from a topological perspective by decreasing the number of crosslinks. In terms of the explanation put forth, the crosslink density is inversely proportional to the degree of exfoliation and direct ratio to the degree of intercalation. The T_g changed with various clay content, indicating a change in the cross-link density. However, excessive BT loadings will produce more clay aggregates that would depress the T_g, such as 218.6 °C for 100/10/5 composite.

The Tan peak was slightly broadened which may result from the motion of polymers at the clay–polymer matrix interface. By increasing the loading of layered clay, the glass transition temperature of soft segments shifted to high temperature. As we known, high modulus of a glassy material results from the fact that the chain conformations are frozen into an amorphous rigid network. The higher the glassy temperature (T_g) is, the more lightly the modulus decrease in the temperature zone tested. The T_g of 100/10/1 composite is the lowest among these composites, it can be seen that a marked drop in storage module's curves for 100/10/1 composite and crossed with other composites.

The results of the impact strength are showed in Fig. 4. In the range of 0.5–5 wt.% BT loadings, the values of impact strength showed a maximum at 0.5 wt.% BT loading in CE/CTBN/BT composite. Combining with XRD result, it is seen above that exfoliated clay particles helped improve the impact properties of CE mixtures, while clay particles in intercalated state in CE/CTBN/BT composites might deteriorate it. The state of dispersion of clay particles in CE/CTBN/BT composites, therefore, dictated the mechanical properties. When the BT loading was 0.5 wt.%, the impact strength of CE/CTBN/BT composite is a little better than that of CE/CTBN system. This fact indicated that addition of appropriate amount of BT in CE/CTBN system could improve the impact property of CE/CTBN system. In view of the great improvement in impact strength of CE/CTBN blend we had studied before [8], this slight improvement was also a remarkable achievement. From Fig. 4, it is also seen that the addition of BT did not obviously deteriorate the value of impact strength of CE/CTBN composites. On the contrary, in 100/10/5 composite, the value of impact strength had been appreciably improved.

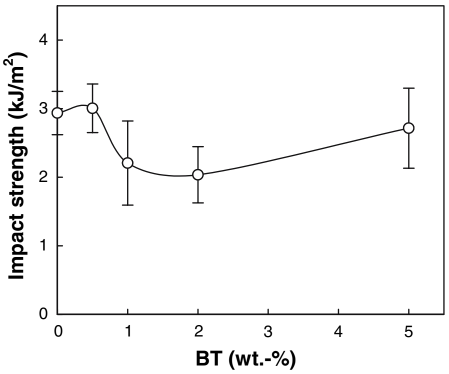

Fig. 4 Influence of BT content on the impact strength of CE/CTBN/BT (100/10/*x*) composites

Conclusions

Partially intercalated and partially exfoliated structures of bentonite coexisted in CE/CTBN/BT composites while rubber particles also can be observed in CE/CTBN/BT composites. The addition of appropriate amount of BT in CE/CTBN system could obviously increase the modulus of the composites. Addition of 0.5 wt.% BT into CE/CTBN (100/10) systems cannot only improve the modulus, but also improve the impact property of the composites.

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