Study on the Structure and Properties of Cyanate Ester/Bentonite Nanocomposites

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ABSTRACT: Cyanate ester (CE)/bentonite (BT) nanocomposites were prepared by melt blending of CE with NH_4^+-BT. The nanostructure of CE/BT nanocomposites was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). It was found that partially intercalated and partially exfoliated structures coexisted in CE/BT nanocomposites containing 2.5 wt % BT with respect to that of bulk CE. Below 2.5 wt % BT content, a totally exfoliated and disordered structure was formed in the nanocomposites. The exfoliated BT enhanced the toughness of CE/BT nanocomposites. The impact strength showed a maximum of $7.1 kJ/m^2$ at 1 wt % BT, compared to $3.8 kJ/m^2$ of pure CE. Furthermore, results of thermogravimetric analysis (TGA) suggest that CE/BT nanocomposites have higher thermal stability. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 632–637, 2005

Key words: cyanate ester; clay; nanocomposites; toughness; thermostability

INTRODUCTION

Cyanate esters are currently important thermosetting materials for the encapsulation of electronic devices, high-temperature adhesives, and structural aerospace materials since they have excellent mechanical, thermal, and adhesive properties.[1] These properties are accompanied by low dielectric (2.5–3.1) dimensional stability at curing temperatures (T_g: 250–290°C) and low moisture absorption (0.6–2.5%). Unfortunately, like most highly crosslinked thermosets, cyanate esters tend to be brittle and to have reduced impact resistance. Although a cured cyanate resin has a relatively higher toughness than other commonly used resins such as bimaleimide (BMI) or epoxy resin (EP), it is still necessary to improve toughness without the sacrifice of other intrinsic characteristics of the cyanate ester resin.

To improve the toughness of cured cyanate resin, approaches such as the incorporation of flexible segments in cyanate monomers, the utilization of rubber toughening technologies, and the preparation of semi-interpenetrating networks have proven useful.[2,3] However, toughening usually occurs at the expense of other characteristics of the cyanate ester resin. Interest in the addition of nano-scale fillers, such as layered silicates and clays, to polymers as an approach to enhance performance has substantially increased recently.[4] Bentonite (BT) is a kind of naturally abundant clay. It has been applied in numerous industrial fields due to its good performance–cost ratio. The outstanding feature of BT is that the silicate layers can be expanded and even delaminated by organic molecules under proper conditions.[5,6] Thus, during the processing of polymer/BT nanocomposites, the nano-scale silicate layers can be dispersed in the polymer matrix and the reinforcement phase forms *in situ* on the molecular level, which is very different from conventional filled composites. Therefore, fabricating such nanocomposites is efficient and cost effective, which has drawn increasing attention in recent years.

Polymer-clay nanocomposites were first introduced in the literature as early as 1984, when Roy and Komarneni first got multiphase nanocomposites by the sol-gel way.[7] Numerous methods to prepare polymer-clay nanocomposites have been developed in the past decades.[8–10] For example, Messersmith et al. have achieved intercalated morphologies using epoxy resin.[11] This is presumably due primarily to the relatively high polarity of these systems, which promote diffusion into the clay galleries.

Because of its high polarity, monocyanate can easily diffuse into the organic modified bentonite clay galleries. The polarity of the group -OCN is thought to promote diffusion into the clay (modified by organic amine) galleries. When heated, the monocyanate that intercalated into galleries began polymerization; with the formation of the network of triazine (cyclotrimerization), the galleries were gradually expanded. For existence of the group NH_4^+ (a good curing agent to monocyanate) in galleries, intragallery polymerization

begins prior to the extragallery one. The maximum layer expansion is obtained when intragallery polymerization rates equal that in the extragallery regions, allowing exfoliation before gelation. An imbalance between these rates assures the formation of an exfoliated structure.

In this study, we suggested a new organic modified bentonite (BT) to prepare CE/BT nanocomposites. Nanocomposite formation is followed using transmission electron microscopy (TEM) and X-ray diffraction (XRD). The impact properties and thermostability of the nanocomposite are also evaluated.

EXPERIMENTAL

A phenolic-based cyanate ester resin (Jinan, China, melt point: 79°C) was supplied by Jinan Special Structure Institute of China Aero-Industry. Organically modified bentonite (BT, Code: NB905) was obtained from the Zhejiang Huate Group, Hangzhou, China, which is ion-exchanged with octadyl trimethyl ammonium. The cyanate ester resin was placed in a beaker maintained at a temperature of 90°C. A high-shear mixing blade was placed into the resin and stirred. BT was then slowly added (1, 2.5, and 5 wt %) and mixed for 15 min. The cure schedule was: heat to 120–150°C over 30 min under vacuum, then ramp to 160°C and hold for 1 h; then 180°C/1 h, 200°C/1 h, 220°C/1 h, 240°C/1 h, and 260°C/1 h.

XRD measurements were performed in a Rigaku D/Max-2550PC system with Eulerian 1/4 cradle and Cu Kα radiation (40kV, 300mA, $\lambda = 1.540$Å); 2°/min. SEM photographs were handled on a Hitachi S-570, Japan. TEM photographs were taken by a JEM-1200EX electronic microscope, Japan. The weight loss measurements were performed using a Perkin–Elmer Pyris 1 Thermogravimetric Analyzer (TGA) in nitrogen media. The heating program developed for this composite consists of heating from 20 to 800°C at a 20°C/min heating rate. The impact test was performed according to GB/T2571–1995 (similar to ISO179–1993) on an XCJ-4 Charpy impact instrument. The temperature of the testing room was 23 $\pm$ 2°C. The results of the impact test were obtained by averaging the results of five measurements.

RESULTS AND DISCUSSION

Formation of nanostructure

In the present study, nanocomposites are formed via diffusion of the oligomeric prepolymer into the interlayer regions, followed by crosslinking. The structure of BT in the composites was studied by X-ray diffraction. Figure 1 shows the X-ray diffraction patterns of NH_4^+-BT and CE/NH_4^+-BT nanocomposites with different NH_4^+-BT content. The NH_4^+-BT curve reveals
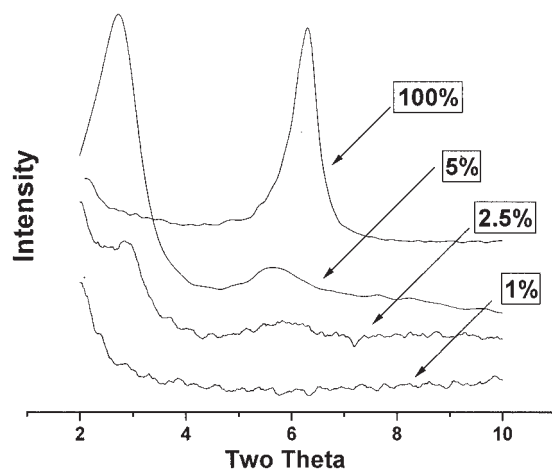

Figure 1 X-ray diffraction patterns of BT and CE/BT nanocomposites with various BT content.

that the peak is located at around 6.32°, corresponding to a basal spacing of 1.397nm. For CE/NH_4^+-BT composites having 2.5 wt % and 5 wt % BT, the basal spacing increases to 3.11nm ($2\theta = 2.84°$) and 3.22nm ($2\theta = 2.74°$), implying that CE has intercalated into the galleries. Meanwhile, when NH_4^+-BT loading was 1 wt %, the characteristic diffraction peaks of nanocomposites disappeared, corresponding to the exfoliated structure.

Figure 2 shows the TEM micrographs of CE/NH_4^+-BT (1, 2.5, and 5 wt %) nanocomposites. It is easy to observe the exfoliated and intercalated BT layers (in different thickness and length) in Figure 2a where BT content is 1 wt %, which coincides with the XRD results mentioned above. Meanwhile, the intercalated structure can be watched in Figures 2b and c. As shown in Figure 2b, the dark lines are cross sections of silicate layers and they are approximately 20nm in thickness, which corresponds to the size of 15 parallel stacked silicate layers. Obviously, most BT layers are not individual but exist in several stacked layers. The coexistence of exfoliated and intercalated structure implies that for NH_4^+-BT, the van der Waals force and Coulombic force between intergalleries are so strong that the silicate layers are not to be separated easily. Even if the monocyanate intercalated and cured in intergalleries, the strong polarity of layers endowed by NH_4^+ holds them tightly. Whether it is exfoliated individually or merely intercalated is determined by the above two forces and the force between monocyanate and NH_4^+-BT. Besides, the nano-scale NH_4^+-BT layers have high specific surface area and surface energy, which also makes them tend to aggregate together rather than to disperse homogeneously in the continuous CE matrix, especially at high BT loading. Therefore, as analyzed above, it is possible to conclude that CE oligomers intercalate into stacks of several NH_4^+-BT layers more easily than they do into individual BT layers under these processing conditions.
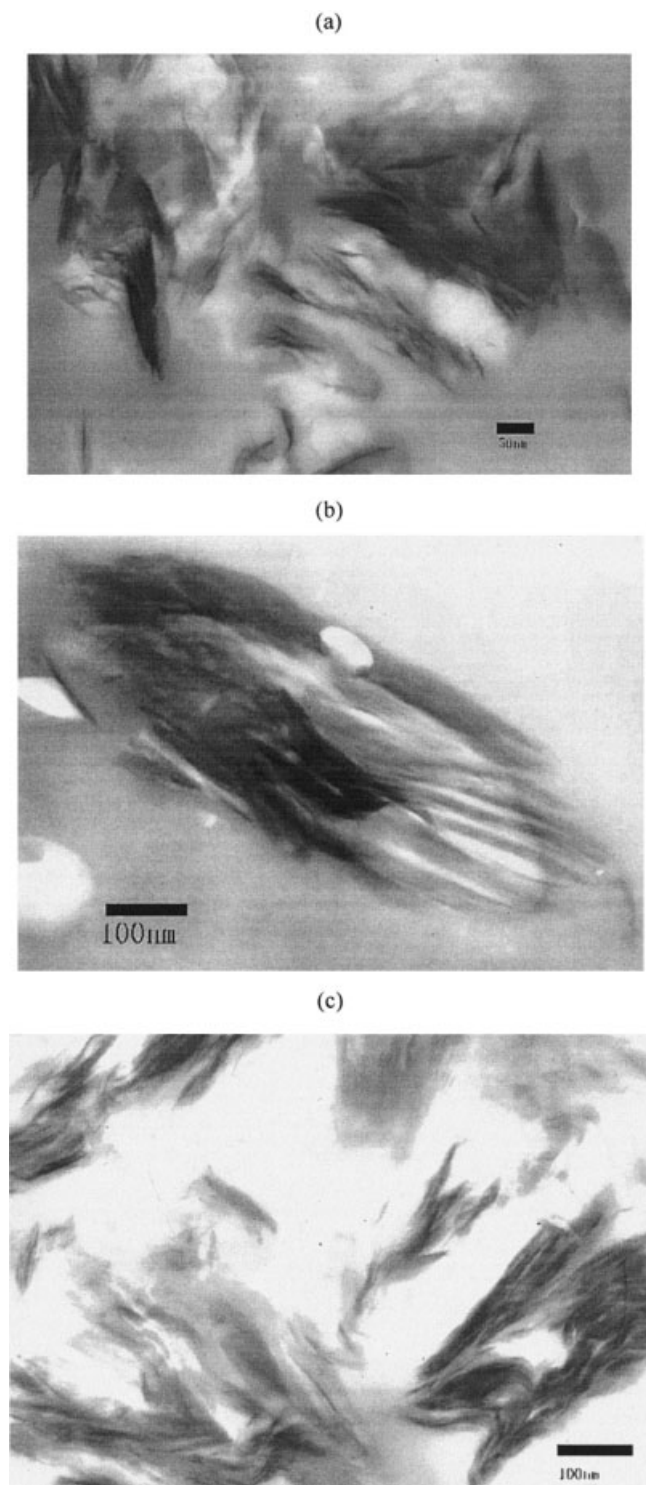
Figure 2 TEM micrographs of CE/BT nanocomposites. BT content: (a) 1 wt %, (b) 2.5 wt %, (c) 5 wt %.

It should be noted that highly electronegative –OCN groups endow the CE monomer with strong polarity. And large quantities of –OH groups on the surface of NH_4^+-BT make the layer surface polar, too. Thus, the dipole–dipole interaction between CE oligomers and silicate layers may act as a driving force for CE oli-

gomers to intercalate 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/NH_4^+-BT nanocomposites can form during melt blending of CE and hydrophilic NH_4^+-BT, which cannot be realized in a weak polar polymer/NH_4^+-BT system. Correspondingly, it can be concluded that dipolar interactions between the relatively polar polymer chains and the surface of NH_4^+-BT layers are the main driving force for intercalation of CE chains.

Besides, when the sample is cured, layer separation can be observed, indicative of a certain degree of mass transfer into the galleries. The NH_4^+ group catalyzes the curing process in galleries prior to the extragallery one, which attracts further diffusion of the prepolymer into the galleries and accelerates extensive layer separation, leading to rapid gelation. The maximum layer expansion is obtained when intragallery polymerization rates equal that in the extragallery regions, allowing exfoliation before gelation. A balance between these rates must be maintained to ensure a homogeneous, three-dimensional network is formed.

Impact properties of the composite

The results of the impact strength tests are shown in Figure 3. The dependence of impact strength of CE/BT nanocomposites on the BT content shows a single peak curve. The impact strength improved significantly with the addition of BT, showing a maximum of 7.1kJ/m² at 1 wt % BT, compared to 3.8kJ/m² of pure CE. Then, it decreased with further addition of BT. Comparing to the TEM observations, it is reasonable to say that exfoliated BT sheets helped improve
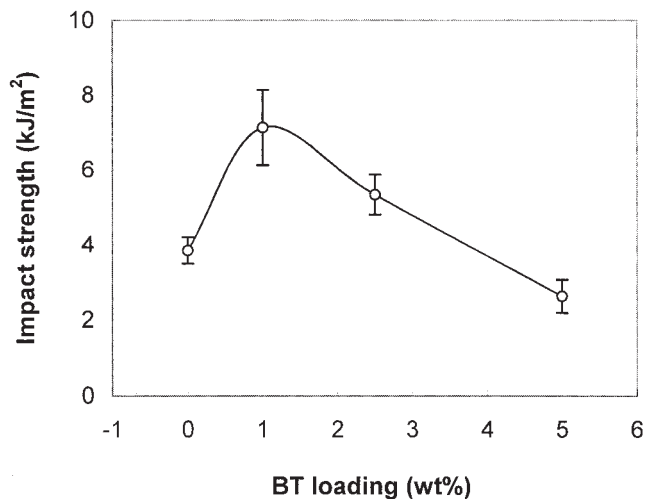

Figure 3 Influence of BT content on the impact strength of CE/BT nanocomposites.
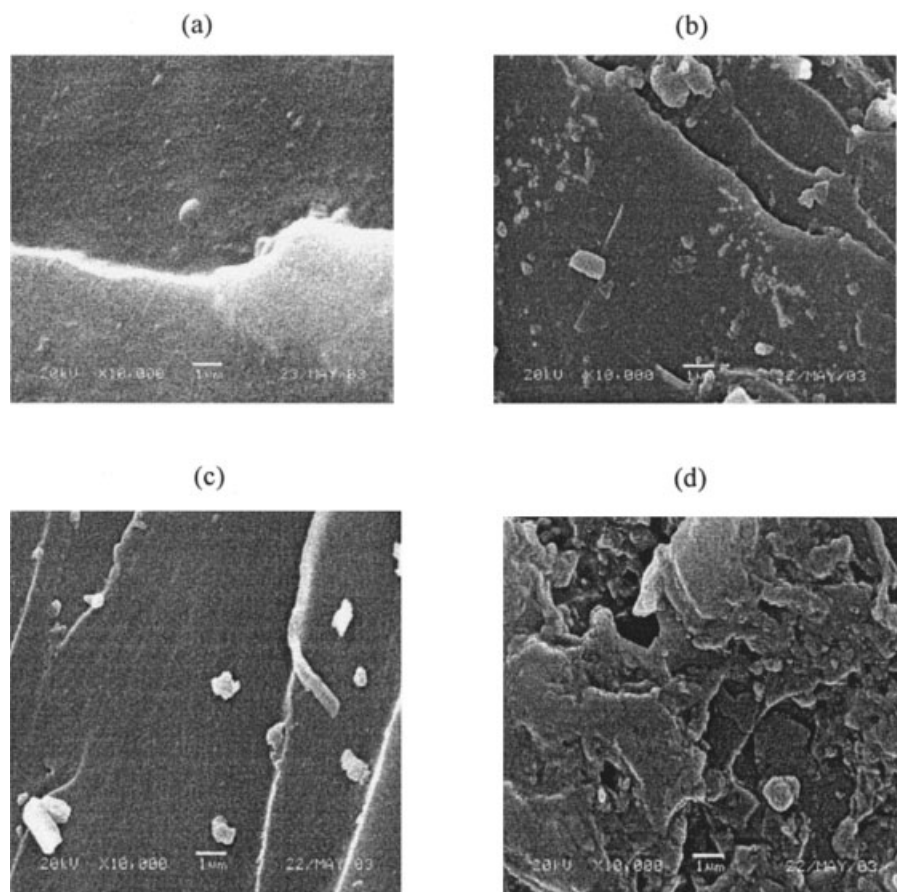
Figure 4   SEM images of fractured surface of CE and CE/BT nanocomposites. BT content: (a) 0 wt %, (b) 1 wt %, (c) 2.5 wt %, (d) 5 wt %.

the toughness of CE mixtures, while BT particles in intercalated and aggregate state may deteriorate its toughness. The dispersion state of BT particles in CE/NH_4^+-BT composites, therefore, would dictate the mechanical properties.

From SEM photographs it can be seen that BT were inhomogeneously distributed in the specimen (Fig. 4b). Although it was hard to catch the fatal crack and follow it up to final fracture since the final fracture usually burst instantaneously, it was still possible to get some information about the fracture mode from SEM observation. Pure CE basically shows a brittle fracture surface. The crevice extended through the fracture surface, as shown in Figure 4a. Some dimple pattern could be found on the fracture surface although the fracture of the specimen was brittle as a whole. Samples with 1 wt % BT concentration show a fracture surface consisting of narrow crevices and more particles (in smaller length), shown in Figure 4b. Further loading made the crevice wider (Fig. 4c) and irregular (Fig. 4d).

Evidently it can be concluded that the dispersion state of BT determined the fracture mode and hence the toughness of the composites. CE/BT (1 wt %) with exfoliated BT state has a fracture surface consisting of narrow crevices, which related to high toughness. CE/BT (2.5 wt %) with intercalated BT state has a fracture surface consisting of wide crevices, which related to moderate toughness. CE/BT (5 wt %) with aggregate BT state has an irregular fracture surface, relating to low toughness. Because of the change of BT content, the development of the cracks is changed drastically.

Thermostability of the composite

Figure 5 shows the thermogravimetric curves (TG curves) and corresponding derivative curves (DTG curves) for pristine NH_4^+-BT, pure CE, and CE/NH_4^+-BT composites. According to Figure 5a, the pristine NH_4^+-BT exhibits a significant weight loss between 250 and 430°C. Presumably this is due to the loss of organic modifier. The initial thermal decomposition temperature (onset temperature) of pure CE and CE/NH_4^+-BT nanocomposites (1 wt % and 2.5 wt %) was 404°C, 432°C, and 434°C, respectively. The onset degradation temperature of the nanocomposite was higher than CE. That means the nanocomposite has

higher thermal stability compared to pure CE. This may result from the interaction between organic and inorganic phases and copolymerization between CE and NH_4^+-BT. Similar results of higher thermal decomposition temperature of intercalated CE/organoclay nanocomposites were reported by Ganguli and Dean.[12]

There are two peak temperatures in the typical DTG thermograms of pure CE and CE/NH_4^+-BT composite in nitrogen, as shown in Figure 5b. The maximum degradation rate temperatures of pure CE and CE/NH_4^+-BT composites with 1 wt % and 2.5 wt % BT were 453°C, 459°C, and 460°C, respectively, indicating that CE/NH_4^+-BT composites began degradation at higher temperature. The second degradation rate occurred at 529°C for pristine CE and 532°C for two CE/BT composites. This result implies that CE/BT composites had better thermal stability than pristine CE.
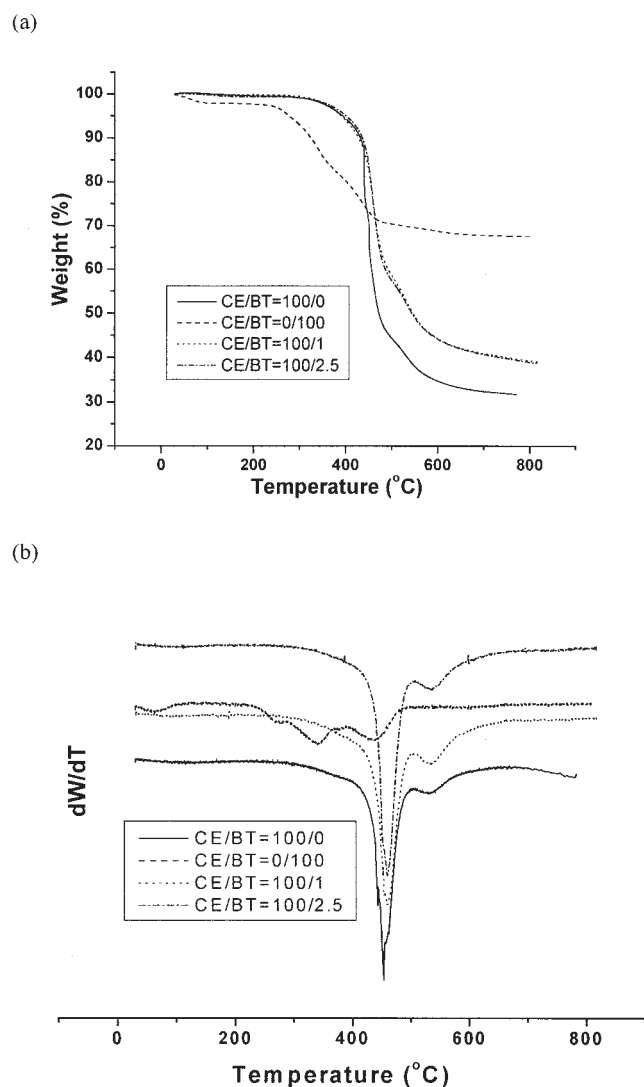
TABLE I
Characteristic Temperatures in TGA Curves of CE/BT Composites

CE/BT mass ratio	Temperature at different weight loss (°C)			
	T_5	T_{10}	T_{20}	T_{50}
100/0	394	432	441	472
0/100	277	325	402	–
100/1	391	428	454	546
100/2.5	401	437	455	544

The thermograms obtained during TGA scans were analyzed to give the percentage weight loss as a function of temperature. T_5 (temperature of 5% weight loss), T_{10} (temperature of 10% weight loss), T_{20} (temperature of 20% weight loss), and T_{50} (temperature of 50% weight loss) are the main criteria to indicate the thermal stability of the composites. The higher the

(a)

(b)

Figure 5 TG (a) and DTG (b) curves of CE and CE/BT nanocomposites with various BT content under nitrogen.
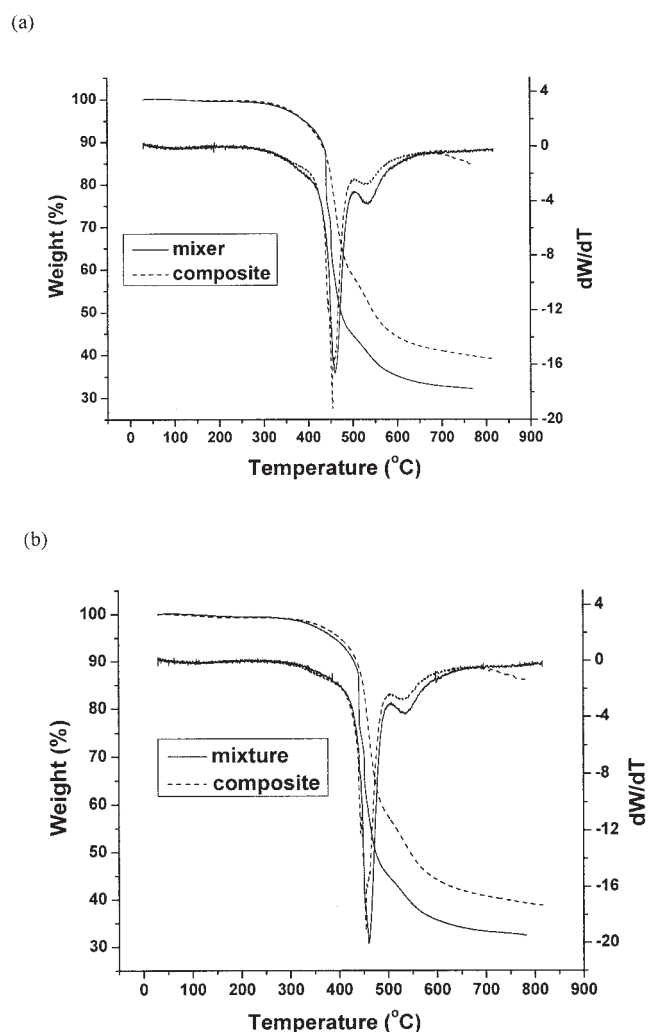
(a)

(b)

Figure 6 Comparison of TG and DTG curves for CE/BT nanocomposites and simple mixtures under nitrogen. (a) CE/BT (1 wt %), (b) CE/BT (2.5 wt %).

values of T_5, T_{10}, T_{20}, and T_{50} are, the higher is the thermal stability. The relative thermal stability of CE/BT composites was evaluated by comparing decomposition temperatures at various percentage weight losses given in Table I. It can be seen that T_5 and T_{10} of CE/BT composites are almost the same as pristine CE, while T_{20} and T_{50} of CE/BT composites are higher than pristine CE.

To carefully compare the thermal behavior of the nanocomposites (with exfoliated structure) with pure CE and BT, we mixed pure CE with BT mechanically by the makeup of corresponding nanocomposites, shown in Figure 6. It was found that the peak temperature of the DTG curve for the mixture is almost the same as that of pure CE at 453°C, attributed to the thermal decomposition of pure CE backbone chains, but the peak temperature in the case of the CE/BT nanocomposite is slightly shifted to a higher temperature by about 6°C. This result also suggests that the exfoliated nanocomposite system is more thermally stable than pure CE.

CONCLUSIONS

Partially exfoliated and partially intercalated CE/NH_4^+-BT nanocomposites were obtained via a melt blending process. The impact strength and thermostability of CE were improved simultaneously with the loading of NH_4^+-BT. The exfoliated BT had the best toughening effect, whereas the aggregate BT particles may deteriorate it.

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