

## THERMAL CHARACTERIZATION OF SURFACTANT-MODIFIED MONTMORILLONITES

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**Abstract**—The thermal stability of surfactant-modified clays plays a key role in the synthesis and processing of organoclay-based nanocomposites. Differential thermal analysis (DTA), thermogravimetric measurement and differential scanning calorimetry (DSC) were used in this study to characterize the thermal stability of hexadecyltrimethylammonium bromide-modified montmorillonites prepared at different surfactant concentrations. Analysis by DSC shows that the molecular environment of the surfactant within the montmorillonite galleries is different from that in the bulk state. The endothermic peak at 70–100°C in the DTA curves of the modified montmorillonites is attributed to both the surfactant phase transformation and the loss of free and interlayer water. With an increase of surfactant-packing density, the amount of water residing in the modified montmorillonite decreases gradually, reflecting the improvement of the hydrophobic property for the organoclay. However, the increase in the surfactant packing density within the galleries leads to a decrease in the thermal stability of the organoclays.

With an increase of initial surfactant concentration for the preparation of organoclays, the surfactant-packing density increases gradually to a ‘saturated’ state. It was found that the cationic surfactant was introduced into the montmorillonite interlayer not only by cation exchange but also by physical adsorption.

**Key Words**—DSC, DTA, Surfactant-modified Montmorillonite, Thermal Stability, TG.

### INTRODUCTION

In recent years organoclays have attracted great interest owing to their academic and industrial importance (Adebajo *et al.*, 2003; Ray and Okamoto, 2003). Organoclays have been shown to be potential candidates for use in oil-spill clean-up operations. In particular, the granular organoclays are seen to be considerably more effective than activated carbon for removal of oil from oil-water mixtures (Adebajo *et al.*, 2003). Moreover, organoclay-based nanocomposites exhibit a remarkable improvement in properties when compared with untreated polymer or conventional micro- and macro-composites. These improvements include increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymer (Ray and Okamoto, 2003). These improvements depend heavily on the structure and properties of the organoclays. Hence, understanding the microstructure and the thermal stability of the organoclays is essential for many industrial applications.

The layer silicates used most commonly (montmorillonite, hectorite and saponite) in the preparation of polymer/layer silicate nanocomposites belong to the swelling clays (smectites). Because of an isomorphic

substitution within the layers (*e.g.* Al<sup>3+</sup> replaced by Mg<sup>2+</sup> or Fe<sup>2+</sup>, or Mg<sup>2+</sup> replaced by Li<sup>+</sup> in the octahedral sheet; Si<sup>4+</sup> replaced by Al<sup>3+</sup> in the tetrahedral sheet), the clay layer is negatively charged, which is counterbalanced by cations in the galleries between layers. These cations are exchangeable and the sum of their charges is the cation exchange capacity (CEC), the value of which determines the number of organic molecules that can be intercalated into the galleries by ion exchange. Clay minerals are relatively thermally stable compared with organic molecules. These minerals will begin to lose structural hydroxyl groups at ~600°C but will maintain the layer structure up to ~900°C (He *et al.*, 2003). Clay minerals are hydrophilic and only miscible with hydrophilic polymers. Hence, modifying the clay mineral surface with cationic surfactants, to convert the normally hydrophilic silicate surface to an organophilic surface, is a strategic step for the preparation of polymer/layer silicate nanocomposites.

The structure of organoclays has been characterized extensively using techniques such as X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and <sup>13</sup>C magic angle spinning nuclear magnetic resonance (<sup>13</sup>C MAS NMR). From XRD results, various idealized models have been proposed for the arrangement of the surfactant molecules within the galleries, including lateral monolayer, lateral bilayer, paraffin monolayer, paraffin bilayer and pseudotrilinear (Lagaly, 1981; Tamura and Nakazawa, 1996; Klapayta *et al.*, 2001;

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Yui *et al.*, 2002; Zhu *et al.*, 2003). However, these idealized structural models have been shown to be unrealistic by Vaia *et al.* (1994) and Li and Ishida (2003) by using FTIR experiments. They showed that alkyl chains can vary from liquid-like (disordered) to solid-like (ordered) and the confined amine chains exist in states with varying degrees of order in conformation. Our recent  $^{13}\text{C}$  MAS NMR study of surfactant-modified montmorillonites supported these conclusions (He *et al.*, 2004b).

More recently, the thermal stability of organoclays has attracted much attention because it plays a key role in the synthesis and processing of polymer-layer silicate nanocomposites. Xie and co-workers (Xie *et al.*, 2001a,b, 2002) systematically reported the thermal stability and the decomposition products of various organic-modified montmorillonites. The main results are summarized as follows: (1) The release of organic compounds from surfactant-modified layer silicates (OLS) is staged and shows different mechanisms. (2) The chain length of exchange cations has little influence on the decomposition temperature of OLS. (3) The interlayer environment of the montmorillonite has a greater effect on the stability of the phosphonium surfactant than does ammonium-modified montmorillonite. In addition, the intercalation process of hexadecylamine into montmorillonite and the fine structure of hexadecylamine in the nanoscale confined space were studied by DSC in conjunction with XRD (Li and Ishida, 2002).

The aim of this work was to investigate the effect of surfactant-packing density within the galleries on the thermal stability of the modified montmorillonites, the behavior of the interlayer water, and the surfactant intercalation styles at different initial concentrations. These studies provide new insights into the properties of organoclays and are important in the synthesis and processing of organoclay-based nanocomposites.

## MATERIALS AND METHODS

The montmorillonite (HM) was obtained from Hebei, China. The sample was purified by sedimentation and the  $<2\ \mu\text{m}$  fraction was collected and dried at  $90^\circ\text{C}$ . The sample was ground through a 200 mesh sieve and sealed in a glass tube for use. As indicated by XRD (Zhu *et al.*, 2003), the montmorillonite collected contains minor illite and kaolinite. The CEC is 57.9 meq/100 g. The structural formula is  $[\text{Na}_{0.05}\text{Ca}_{0.18}\text{Mg}_{0.10}][\text{Al}_{1.58}\text{Fe}_{0.03}\text{Mg}_{0.39}][\text{Si}_{3.77}\text{Al}_{0.23}]\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ . The surfactant used in this study, provided by YuanJu Chem. Co., China, is hexadecyltrimethylammonium bromide (HDTMAB) with a purity of 99%.

The Na-mont was prepared as follows: 10 g of the mixture of HM (9.4 g) and  $\text{Na}_2\text{CO}_3$  (0.6 g) were added to 100 mL of deionized water and stirred at  $80^\circ\text{C}$  for 3 h. The Na-mont was collected by centrifugation and washed with deionized water until the pH of the solution

was 7. The Na-mont was dried at  $105^\circ\text{C}$ , ground and sieved through a 200 mesh sieve and then placed in a bottle and sealed.

The surfactant-modified montmorillonites were synthesized as follows: 2.5 g of Na-mont were first dispersed in  $\sim 300$  mL of deionized water and then HDTMAB was added slowly. The concentrations of HDTMAB added varied from 0.2 CEC to 5.0 CEC of the montmorillonite. The reaction mixtures were stirred for 10 h at  $80^\circ\text{C}$ . All products were washed free of bromide anions, dried at  $90^\circ\text{C}$ , ground in an agate mortar and passed through a 200 mesh sieve. The surfactant-modified montmorillonite prepared at the concentration of 0.2 CEC was labeled  $\text{HM}_{0.2\text{CEC}}$  and the others were named accordingly.

The DTA and TG measurements were performed using an LCT-2 differential thermobalance in air. Samples (of  $\sim 20$  mg) were loaded into Pt crucibles in a dry atmosphere and the sample chamber was heated at  $20^\circ\text{C}/\text{min}$  in air. Differential scanning calorimetry and temperature-modulated DSC were performed on a TA Instrument, a DSC Q100 analyzer. Cooling and temperature modulation were accomplished with a liquid nitrogen cooling accessory. Dry nitrogen gas with a flow rate of 80 mL/min was purged through the DSC cell. Each 5 mg of sample powder was loaded into a sealed alumina pan and heated to  $200^\circ\text{C}$  at a heating rate of  $3^\circ\text{C}/\text{min}$  for DSC and  $5^\circ\text{C}/\text{min}$  for temperature-modulated DSC. An empty alumina pan was used as reference and the heat flow between the sample and reference pans was recorded.

## RESULTS AND DISCUSSION

The surfactant-modified montmorillonites used in this study have been studied by XRD, FTIR and Raman (Zhu *et al.*, 2003; He *et al.*, 2004a,c). Our XRD results have shown that, with the increase of the surfactant-packing density, the arrangement of surfactant in the clay interlayer will vary from lateral-monolayer, to lateral-bilayer, then to paraffin-type monolayer and finally to paraffin-type bilayer (Zhu *et al.*, 2003).

### *Thermal characteristics of the neat surfactant and Na-montmorillonite*

Figure 1 shows the DTA and TG curves of Na-montmorillonite and HDTMAB. The DTA curve of Na-mont (Figure 1a) comprises two parts: (1) the free water (interstitial water and surface adsorbed water) and interlayer water region at  $121^\circ\text{C}$  (Greene-Kelly, 1955; Xie *et al.*, 2001a); (2) the structural water (bonded hydroxyl that undergoes dehydroxylation) region at  $\sim 685^\circ\text{C}$ .

As shown by the TG curve of neat HDTMAB (Figure 1b), the decomposition of the neat surfactant begins at  $\sim 210^\circ\text{C}$ , which corresponds to the two exothermic peaks at  $212^\circ\text{C}$  and  $325^\circ\text{C}$  on the DTA

curve. From the TG curve, the mass loss corresponding to the two exothermic peaks accounts for 94%, indicating the formation of a small amount of charcoal (~6.4%) because of the insufficient supply of oxygen for complete burning of the HDTMAB (Yariv, 2004). These residual organic compounds are completely oxidized to  $\text{CO}_2$  and  $\text{NO}_2$  at  $\sim 473^\circ\text{C}$  as indicated by DTA and TG curves (Yariv, 2004). The endothermic peak at  $115^\circ\text{C}$  on the DTA curve is attributed to the phase transition of HDTMAB.

#### Low-temperature portion of the DTA curve

The DTA curves of the surfactant-modified montmorillonites prepared at different concentrations are shown in Figure 2 in which we note that the endothermic peak at  $\sim 121^\circ\text{C}$  for Na-mont (Figure 1a) appears to shift to a lower temperature with the increase of surfactant-packing density within the montmorillonite galleries. In addition, it becomes broader when compared with the corresponding peak for the neat surfactant or Na-mont. On the basis of the DTA curves of neat HDTMAB and Na-mont, this endothermic peak may arise from two possible contributions: (1) the phase transformation of surfactant; (2) the loss of free and interlayer water of montmorillonite. To identify the contribution of this

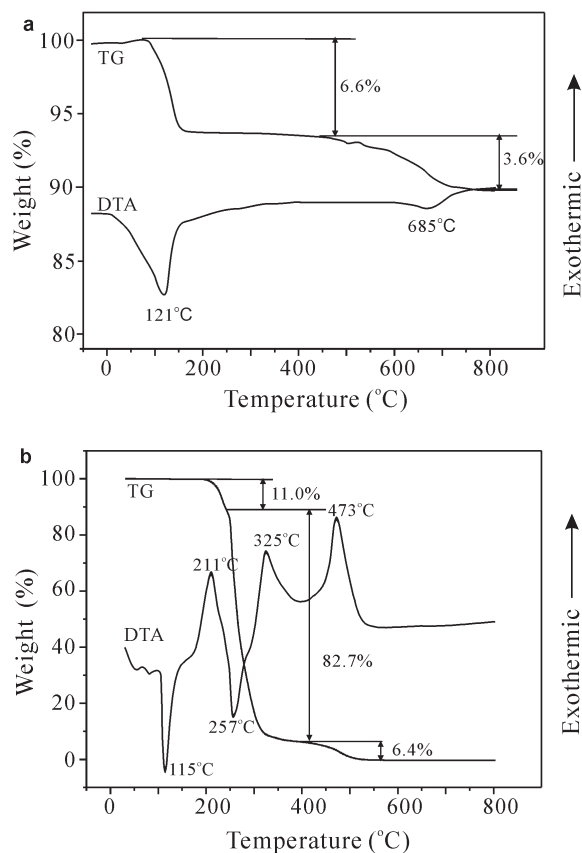


Figure 1. DTA and TG curves of (a) Na montmorillonite and (b) of neat HDTMAB.

endothermic peak, DSC analysis of the surfactant-modified montmorillonites was performed. Figure 3 shows the DSC curves of the neat HDTMAB and  $\text{HM}_{0.5\text{CEC}}$ ,  $\text{HM}_{1.9\text{CEC}}$  and  $\text{HM}_{5.0\text{CEC}}$ . These three surfactant-modified montmorillonites represent lateral-monolayer, paraffin-type monolayer and paraffin-type bilayer of surfactant in the clay interlayer, respectively, as shown in our previous study (Zhu *et al.*, 2003). The DSC curve of the neat surfactant (Figure 3a) displays only one strong and symmetric endothermic peak centered at  $115^\circ\text{C}$ , which is related to the phase transformation of the surfactant. However, not all of the DSC curves of the

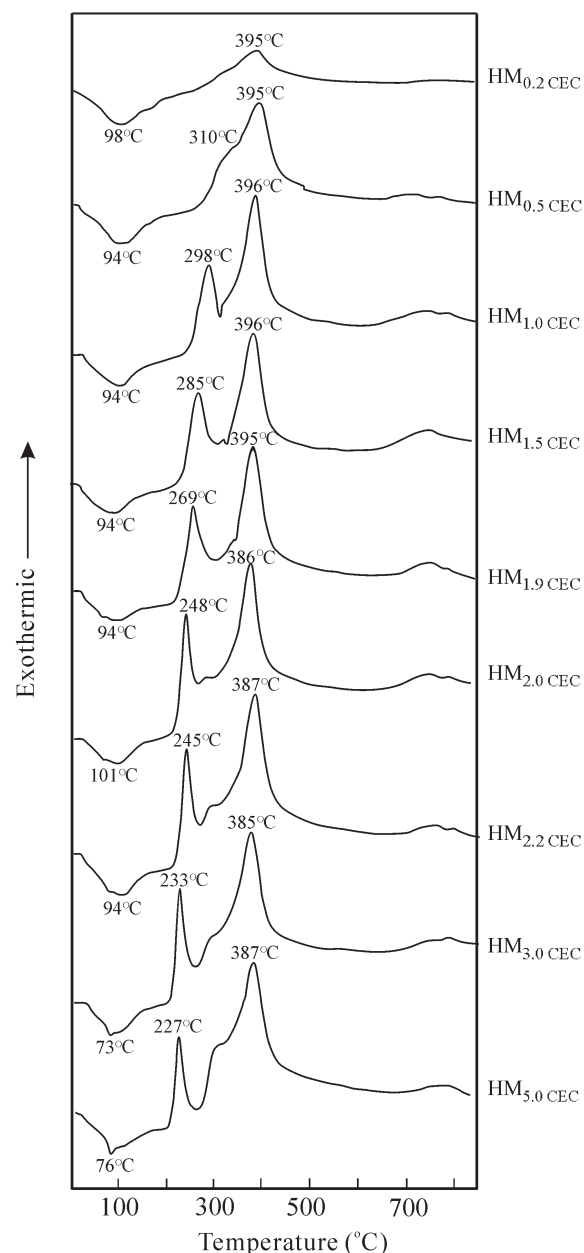


Figure 2. DTA curves of the modified montmorillonites with different surfactant-packing density.

surfactant-modified montmorillonites (Figure 3b–d) would appear to display an analogous endothermic peak. The DSC curve of  $\text{HM}_{0.5\text{CEC}}$  shows a much broader endothermic peak (Figure 3d) which splits into two resolved peaks at 64°C and 80–130°C in the DSC curve of  $\text{HM}_{5.0\text{CEC}}$  (Figure 3b). This indicates that the molecular environment of the surfactant within the galleries is very different from that in the bulk state (Li and Ishida, 2002).

It is reasonable to compare the crystal structure of the neat HDTMAB with that in the modified montmorillonites. The crystal structure of the neat HDTMAB is such that the hexadecyltrimethylammonium cations ( $\text{HDTMA}^+$ ) and bromide anions extend bidimensionally to form an ionic layer which is sandwiched between the hydrocarbon chain layers, leading to a relatively high phase-transformation temperature (Endoh and Suga, 1999). However, when the  $\text{HDTMA}^+$  cations intercalate into the montmorillonite interlayer, their local environment depends strongly on the packing density. For example, the  $\text{HDTMA}^+$  cations are well separated in low packing density, where they undergo the phase transformation more readily, whereas the

paraffin-type monolayer and paraffin-type bilayer are adopted at higher packing densities (Vaia *et al.*, 1994; Li and Ishida, 2002, 2003; Zhu *et al.*, 2003). In the latter case, the interaction among hydrocarbon chains is much stronger, leading to the phase transformation occurring at elevated temperatures. This has been shown clearly in Figure 3. With the increase of the packing density, there is an obvious shift of the first endothermic peak to higher temperature with higher symmetry. The higher-symmetry peak is, therefore, assigned to the phase transformation of  $\text{HDTMA}^+$ .

To verify this assignment further, modulated DSC was conducted. Figure 4 shows the DSC curves of  $\text{HM}_{1.9\text{CEC}}$  and  $\text{HM}_{5.0\text{CEC}}$  with three cycles of heating and cooling. As shown in Figure 4, for  $\text{HM}_{1.9\text{CEC}}$  (Figure 4a) and  $\text{HM}_{5.0\text{CEC}}$  (Figure 4b), the second, broader endothermic peak, occurring in the first heating, is absent from the second and third heatings, whereas the first, stronger peak remains, but with a shift to lower temperature and a decrease in its intensity. This confirms the attribution of the two endothermic peaks in the DSC curves, *i.e.* the peak at ~64°C relates to the phase transformation and the broader peak (80–130°C) to the loss of free and interlayer water. Here, DSC analysis demonstrates that the broad endothermic peaks (at <130°C) on the DTA curves of

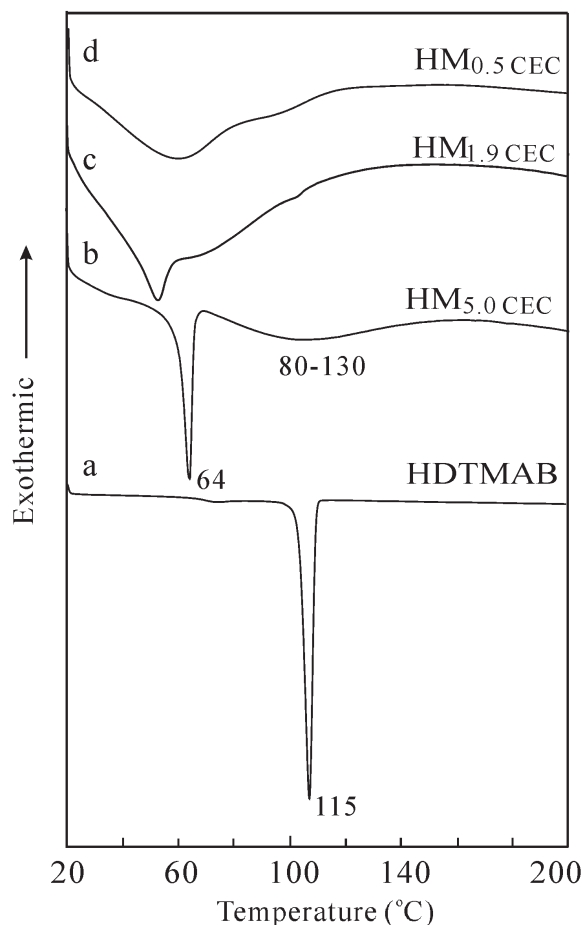


Figure 3. DSC curves of the neat surfactant and  $\text{HM}_{0.5\text{CEC}}$ ,  $\text{HM}_{1.9\text{CEC}}$ ,  $\text{HM}_{5.0\text{CEC}}$ .

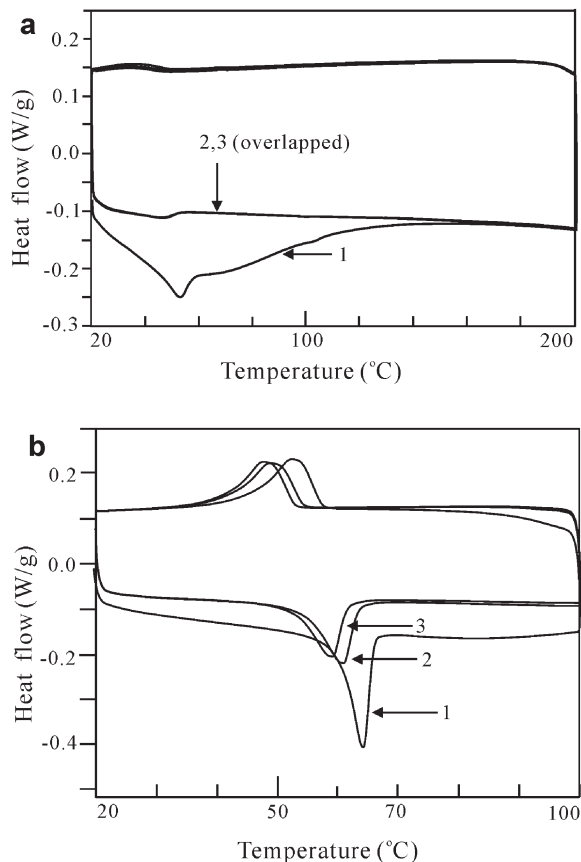


Figure 4. DSC curves of (a)  $\text{HM}_{1.9\text{CEC}}$  and (b)  $\text{HM}_{5.0\text{CEC}}$ , with three cycles of heating and cooling.



surfactant-modified montmorillonite are a function of both the surfactant phase transformation and the loss of free and interlayer water in montmorillonite. Additionally, their temperature shift depends heavily on the relative amount of surfactant and hydrated cations in the

interlayer. That is to say, the temperature of this endothermic peak in the DTA curve will shift to a lower temperature with an increase of surfactant-packing density within the galleries.

The TG curves of surfactant-modified montmorillonites (Figure 5) demonstrate that the amount of free and interlayer water in montmorillonite will decrease with the increase of surfactant-packing density within the montmorillonite galleries. This conclusion is consistent with the frequency shifts of the absorption in the ranges  $1600\text{--}1700\text{ cm}^{-1}$  and  $3100\text{--}3550\text{ cm}^{-1}$  in our previous FTIR study of these samples (He *et al.*, 2004a). The decrease in the amount of free and interlayer water results from the replacement of hydrated cations by surfactant and the improvement of the hydrophobic property of surfactant-modified montmorillonite. Normally, there are two distinct types of water present in natural montmorillonite. Type I is adsorbed water owing to the large specific surface area, which possesses great mobility and is easy to lose. Type II constitutes the hydration shell around the exchangeable cation and its presence depends on the number of hydrated cations residing in the interlayer. Our CEC measurement (Table 1) indicates that the CEC of surfactant-modified montmorillonites decreases with the intercalation of surfactant. From the integration of XRD and TG patterns, we believe that samples  $\text{HM}_{3.0\text{CEC}}$  and  $\text{HM}_{5.0\text{CEC}}$  are saturated with surfactant (see below). However, even for these samples, there is still a small CEC. This suggests that the exchangeable hydrated cations are not fully replaced in the course of intercalation (Klapyta *et al.*, 2001). This explains why the second broad and weak endothermic peak exists in the DSC curves of the modified samples with the highest surfactant-packing density, *e.g.*  $\text{HM}_{5.0\text{CEC}}$ .

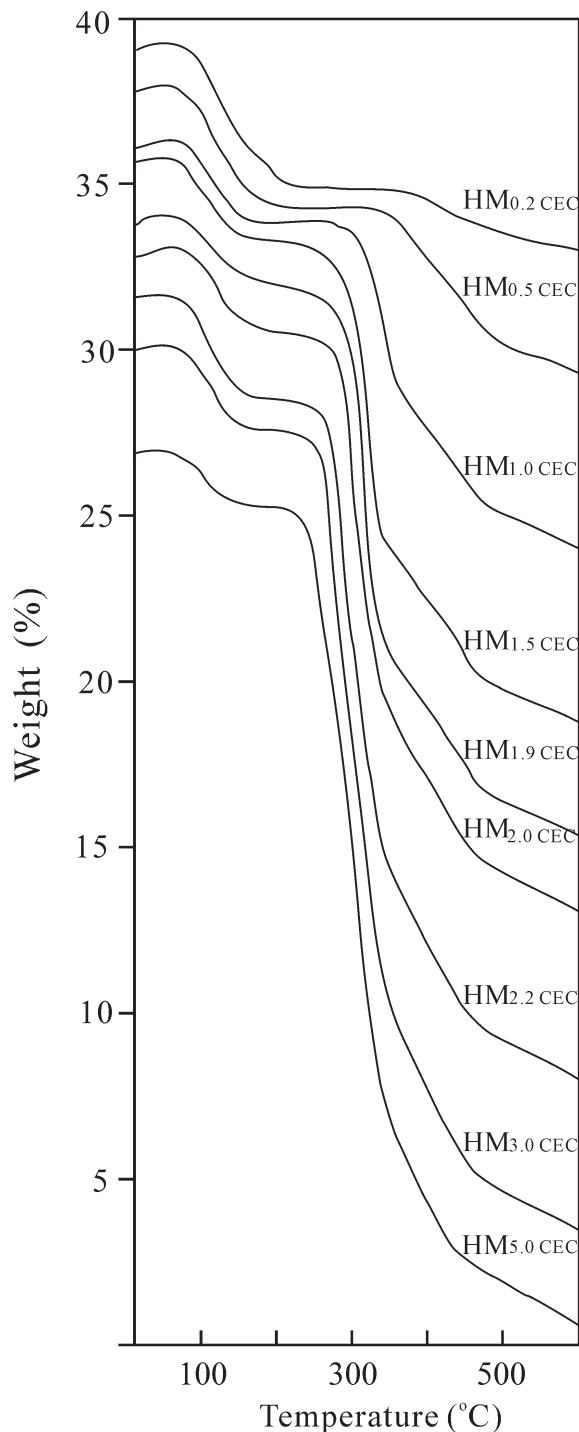


Figure 5. TG curves of the modified montmorillonites with different surfactant-packing densities.

#### Stability of surfactant-modified montmorillonite

In the temperature range  $200\text{--}500^\circ\text{C}$ , montmorillonite does not undergo any thermally induced changes as shown in Figure 1a. Therefore, the exothermic peaks in this region (Figure 2) are attributed to the decomposition of surfactant (Xie *et al.*, 2001a,b, 2002). Compared with the DTA curve of the neat surfactant (Figure 1b), the two main exothermic peaks at  $211^\circ\text{C}$  and  $325^\circ\text{C}$ , corresponding to the decomposition of the neat surfactant, do not occur at these temperatures in any of the DTA patterns of the surfactant-modified montmorillonites. For sample  $\text{HM}_{0.2\text{CEC}}$ , only one broad and asymmetric exothermic peak at  $\sim 395^\circ\text{C}$  is recorded in this temperature range. However, with the increase of surfactant-packing density, two well resolved and strong exothermic peaks at  $227\text{--}310^\circ\text{C}$  and  $387\text{--}395^\circ\text{C}$  are observed. In addition, a shoulder at  $\sim 300^\circ\text{C}$  occurs on the DTA curves of the modified samples with higher surfactant-packing density, *i.e.* see  $\text{HM}_{5.0\text{CEC}}$ . This suggests three decomposition steps for the intercalated surfactant as reported in the literature (Xie *et al.*,

Table 1. The amounts of surfactant in the modified samples determined by TG, and their measured CEC.

Samples	Initial surfactant concentration (vs. CEC)	Weight loss at 200–500°C (wt.%)	Surfactant in montmorillonite (vs. CEC)	CEC of modified montmorillonite
HM <sub>0.2</sub> CEC	0.2	2.6	0.16	0.84
HM <sub>0.5</sub> CEC	0.5	7.6	0.46	0.48
HM <sub>1.0</sub> CEC	1.0	10.5	0.64	0.21
HM <sub>1.5</sub> CEC	1.5	15.3	0.93	0.18
HM <sub>1.9</sub> CEC	1.9	17.0	1.03	0.10
HM <sub>2.0</sub> CEC	2.0	18.0	1.09	0.14
HM <sub>2.2</sub> CEC	2.2	23.2	1.41	0.12
HM <sub>3.0</sub> CEC	3.0	26.0	1.58	0.14
HM <sub>5.0</sub> CEC	5.0	26.0	1.58	0.06

The residual CEC measurement of the modified montmorillonite was performed three times and the value shown in the table is their average.

2001a,b, 2002). The TG results support the DTA results (Figure 5). As shown by the DTA curves (Figure 2), the decomposition temperature of the intercalated surfactant is dramatically increased when compared with that of the neat surfactant. In addition, a broad and weak exothermic peak appears at 700–800°C on DTA curves of the modified montmorillonites. This peak corresponds to the oxidation of residual organic carbonaceous residue (Xie *et al.*, 2001b; Yariv, 2004).

The dependence of the surfactant decomposition temperature on the surfactant-packing density within the interlayer of montmorillonite is shown in Figure 6. Note that the location of the exothermic peak at 227–310°C is more sensitive to the surfactant-packing density than the peak at 387–395°C. The temperature corresponding to the surfactant decomposition (387–395°C) decreases with the increase of surfactant-packing density within the galleries. Thus, the increase of the surfactant-packing density will decrease the

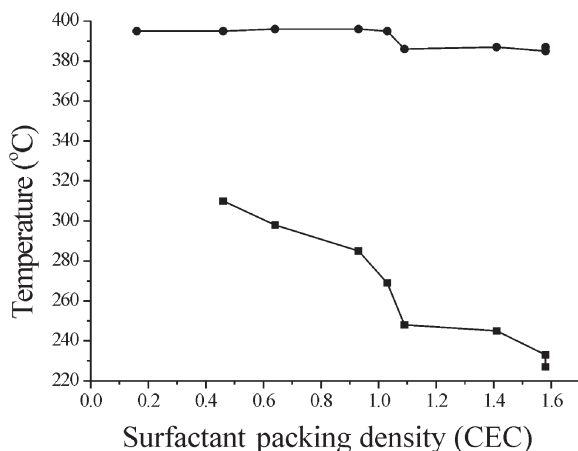


Figure 6. The change in the surfactant decomposition temperature for modified montmorillonite as a function of the surfactant-packing density within the montmorillonite interlayer. The surfactant-packing density refers to the amount of the surfactant within the montmorillonite interlayer as shown in Table 1.

thermal stability of the modified montmorillonites despite a large basal spacing and excellent organophilic property. This results from the physically adsorbed surfactants (see below).

#### The intercalation style of surfactant

There are two primary preparation methods for organoclay: ion exchange and ion-dipole intercalation. The former was used in this study. In this method, the cationic surfactant intercalates into the montmorillonite interlayer by replacing the exchangeable cations in the interlayer. Thus, the CEC value of montmorillonite determines the amount of surfactant exchanged into the clay interlayer, *i.e.* the amount of exchanged cationic surfactant could not exceed the CEC.

Based on the weight loss in the temperature range of 200–500°C, the amounts of surfactant within the modified samples were calculated and shown in Table 1, where it is seen that with an increase in the initial surfactant concentration, a greater number of surfactant molecules enter into the interlayer. Accordingly, the packing density increases gradually and the arrangement of surfactant in the clay interlayer will vary from lateral-monolayer, to lateral-bilayer, then to paraffin-type monolayer and finally to paraffin-type bilayer as indicated by our previous XRD patterns (Zhu *et al.*, 2003). However, as shown in Table 1, the amount of surfactant residing in the montmorillonite obviously exceeds the montmorillonite's CEC. Thus, in addition to the surfactant ions bonded to the exchangeable sites, a considerable amount of the surfactant is physically adsorbed to the clay surface or exists as surfactant molecules. These two types of intercalation lead to the surfactant decomposition peaks in different temperature ranges. From Figure 2, the decomposition peaks at 387–395°C are attributed to the surfactant intercalated through ion exchange, whereas peaks at 227–310°C correspond to the surfactant intercalated through physical adsorption. The greater the surfactant-packing density, the greater the amount of physical adsorption,

leading to a general shift of the decomposition peaks to lower temperatures. Nevertheless, compared with the neat surfactant, the thermal stability of the intercalated surfactant is greatly improved.

Furthermore, when the surfactant concentration reaches 3.0–5.0 CEC, the TG results show that the amount of surfactant entering into the montmorillonite interlayers remains unchanged (Figure 5, Table 1). Thus, the surfactant-modified montmorillonite is 'saturated' and this is the 'final' state of the intercalation. This assumption is supported by the XRD and FTIR results from our previous studies: (1) all samples prepared at 3.0–5.0 CEC showed identical XRD patterns (Zhu *et al.*, 2003); (2) the two intense adsorption bands at 2917 and 2849  $\text{cm}^{-1}$ , corresponding to the antisymmetric and symmetric  $\text{CH}_2$ -stretching modes of amine, respectively, remained constant in their FTIR spectra (He *et al.*, 2004a), indicating that the chains were very ordered (all-*trans* conformation) (Li and Ishida, 2003).

### CONCLUSIONS

The properties of HDTMAB-modified montmorillonites with different surfactant-packing densities were examined using DTA, TG and DSC. The DTA/TG study demonstrates that the cationic surfactant is introduced into the montmorillonite galleries through both ion exchange and physical adsorption processes and the surfactant-packing density reaches a maximum when the surfactant concentration in the preparatory solution is >3.0 CEC. An increase in surfactant-packing density within the galleries improves the hydrophobic properties of organoclay whereas the thermal stability is decreased due to the physically adsorbed surfactant. This is important in the synthesis and processing of organoclay-based nanocomposites. In addition, these studies provide important information for molecular dynamic simulation of organoclay, *e.g.* in previous studies about molecular simulation, the researchers did not take account of the effect of physically adsorbed surfactant on the properties of organoclay.

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