

Thermogravimetric analysis of organoclays intercalated with the gemini surfactants

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Abstract Sodium montmorillonite has been modified via cation exchange reaction using gemini surfactants. Montmorillonite modified by cetyltrimethyl ammonium bromide (CTAB) is used for comparison. Basal spacings and thermal stability of these organo-montmorillonite clays have been characterized using X-ray diffraction analysis and thermogravimetric analysis. The $d(001)$ spacings of montmorillonite-Gemini14, montmorillonite-Gemini16, montmorillonite-Gemini18 can reach above 35 Å compared with the 23.66 Å of the montmorillonite-CTAB at 2.2CEC. The thermogravimetric analysis show four-step degradation which corresponds to residual water desorption, dehydration, followed by decomposition of the organic modifier and the dehydroxylation of the organo-montmorillonite. In addition, DTG enables two different structural arrangements of gemini surfactant molecules intercalating the montmorillonite to be proposed that is different from montmorillonite-CTAB.

Keywords Montmorillonite · Gemini surfactants · Thermogravimetric analysis

Introduction

Smectites are widely used clays by virtue of their high cation exchange capacity, excellent ability to swell, and ease with which their surface can be chemically and physically modified [1–5]. More often than not the smectite is the montmorillonite, which has two siloxane tetrahedral

sheets sandwiching an aluminium octahedral sheet. Because of the replacement of silicon by aluminium in the tetrahedral layers or similar replacement of aluminium ions by magnesium ions, the montmorillonite layers are negatively charged [6]. Thus, cations such as sodium and calcium ions are attracted to the mineral surface or interlayer to counterbalance the negative layer charges. The hydration of inorganic cations on the exchange sites causes the clay mineral surface to be hydrophilic, therefore, the natural montmorillonite is an ineffective sorbent for organic compounds [7]. However, such a difficulty can be overcome by intercalating cationic surfactants such as quaternary ammonium salts into the interlayer space by ion exchange [8–12]. The intercalating of a cationic surfactant not only changes the surface properties from hydrophilic to hydrophobic but also greatly increases the basal spacing of the layers [13–15].

Organoclays have firstly found wide applications in pollution prevention and environmental remediation on account of their efficiency in taking up anthropogenic, non-ionic organic compounds from aqueous solutions. They have been shown to be superior to other waste treatment technologies, especially when the contaminated water contains substantial amounts of oil, grease, or humic acid [16–18].

And nowadays, the focus of attention has been on the use of organoclays as nanometer-size fillers of organic polymers [19, 20]. The clay polymer nanocomposites have huge potential industrial use because the dispersion of a small amount of organoclay in the polymer matrix can dramatically increased strength and heat resistance, biodegradability of biodegradable polymers, decreased gas permeability and flammability [21–23].

As regards organic modification of montmorillonite, most of the investigation in literature deal with ion-exchanged

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alkylammonium salts. Ammonium surfactants used in commercially available organoclays usually incorporate short aliphatic chains and benzyl and sometimes hydroxyl groups. They also contain at least one long aliphatic chain (C12–C18) to cause expansion of the distance between the layers [24, 25]. Other montmorillonite modifiers include alkyl amines [26], alkyl carbazol [27], poly(dimethylsiloxane) [28], and quinolinium [29] or pyridinium [30]. Other ammonium surfactants are more complex molecules, oligomers and reactive groups [31–33]. However little work has been done using gemini surfactants on intercalating the montmorillonite. The objective of this study is to investigate the properties of the montmorillonite modified with gemini surfactants has different alkyl chain length, and we also use montmorillonite-CTAB for comparison. Such a study is of high importance for understanding the structure, properties, and potential application of these organoclays.

Experimental

Materials

The commercial sodium montmorillonite used in the present study was supplied by Zhejiang fenghong clay company, China. The cation exchange capacity (CEC) of montmorillonite (MMT) is 90 mequiv/100 g as reported by the supplier. This Na-MMT was used as such without any further purification.

Synthesis of gemini surfactants

The intermediate bis(2-bromoethyl) ether was synthesized from diglycol and phosphorus tribromide [34]. All the surfactants labeled as Gemini12, Gemini14, Gemini16, and Gemini18 were obtained by refluxing the bis(2-bromoethyl) ether with N-n,alkyl-N,N-dimethylamine in isopropanol at 78 °C for 48 h. Solvent was removed under vacuum from the reaction mixture, and the solid thus obtained was recrystallized three times from ethyl acetate–ethanol solvent mixture (volume ratio is 2:1).

Preparation of surfactant-modified montmorillonites

The synthesis of surfactant-clay hybrids were undertaken by each of the following procedure: 5 g of dehydrated montmorillonite was first dispersed in about 300 mL of distilled water, to which the surfactant was slowly added. The concentrations of surfactants were all at 2.2CEC of montmorillonite in order to make fully exchange of sodium ions. The reaction mixtures were stirred vigorously with magnetic stirrer at 500 rpm for 6 h at 75 °C, filtered in vacuum, washed with deionised water to remove bromide

anions as confirmed by AgNO₃ test. The organically modified montmorillonites were dried in an air circulatory oven for 4 h at 90 °C, then ground and sieved through 280 mesh and kept in a sealed bottle for later use.

X-ray diffraction measurements

The Na-MMT and surfactant-modified montmorillonites were pressed in stainless steel sample holders. X-ray diffraction (XRD) at low angle section patterns were recorded using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) on a Philips PANalytical X'Pert PRO Diffractometer operating at 40 kV and 40 mA with variable divergence slit and 0.125° antiscatter, between 0.5° and 10° (2θ) at a step size of 0.0167° ($2\theta \text{ s}^{-1}$). The distance between the interlamellar, the so-called basal spacing was calculated by Bragg-reflections from data determined by X-ray diffraction measurements.

Thermogravimetric analysis

Thermogravimetric analysis and differential scanning calorimetry of the surfactant-modified montmorillonites were obtained using a TA Instruments Inc. SDTQ600 high-resolution thermoanalyser. Approximately 20 mg of finely ground sample was placed in an aluminum oxide pan and heated over a temperature of 50–900 °C at a scanning rate of 10 °C min⁻¹ under high-purity nitrogen atmosphere with a gas flow rate of 40 cm³ min⁻¹. All the samples were dried at 90 °C in vacuum during 24 h before the analysis.

Results and discussion

Powder X-ray diffraction analysis

With the cation exchange of the sodium ion for the cationic surfactant, expansion of the montmorillonite layers occurs. This expansion is readily measured by X-ray diffraction. The d(001) spacings calculated by Bragg-reflections from data determined by X-ray diffraction measurements were shown in Fig. 1. The Na montmorillonite has a d(001) spacing of 15.30 Å while the montmorillonite-CTAB is 23.66 Å which is paraffin-monolayer arrangement of CTAB in the interlayer space of montmorillonite [35]. After the montmorillonite is exchanged with Gemini12 at the 2.2CEC level, d(001) spacing is observed at 20.48 Å. This implies a pseudotrilayer arrangement of Gemini12 in the interlayer space of montmorillonite. But as for montmorillonite-Gemini14, it shows double peaks at 35.84 and 19.36 Å, the peak at 35.84 Å should correspond to paraffin-bilayer arrangement with tilt angle of carbon chains, the peak at 19.36 Å reflects paraffin-monolayer arrangement which means the alkyl chains assume a tilted upright

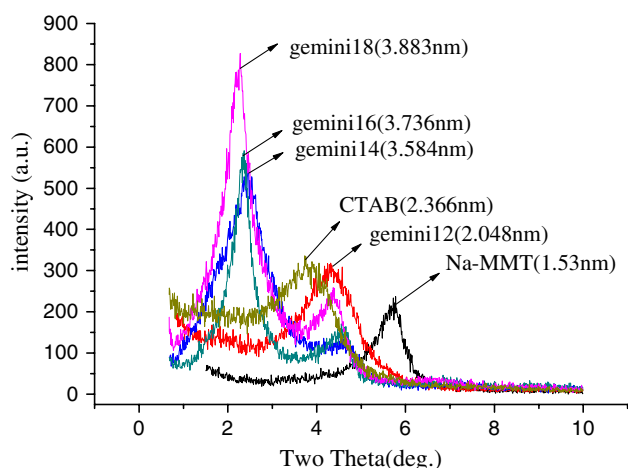


Fig. 1 X-ray diffraction patterns of Na-montmorillonite and surfactant-modified montmorillonite

position to the aluminosilicate surface [6, 7]. The former peak is stronger in intensity which means paraffin-bilayer arrangement takes bigger portion in this organoclays. With the increasing alkyl chain length, montmorillonite-Gemini16, montmorillonite-Gemini18, they also show double peaks at 37.36, 19.40 and 38.83 Å, 20.20 Å, respectively. That is to say, the d(001) spacing increases with the increasing of alkyl chain length of gemini surfactant intercalated into the montmorillonite. Compared montmorillonite-Gemini16 with montmorillonite-CTAB, although the size of surfactant Gemini16 is almost two times big as the CTAB, if look Gemini16 as two CTAB moleculars, the d(001) spacing of the montmorillonite-Gemini16 should be 47.2 Å, but from the experiment data it is 37.36 Å, so it can also be concluded that montmorillonite-Gemini16 arrangements from paraffin-monolayer to paraffin-bilayer.

Thermogravimetric analysis

The thermal stability of organoclay can be determined by the use of thermogravimetric techniques. Figure 2 displays

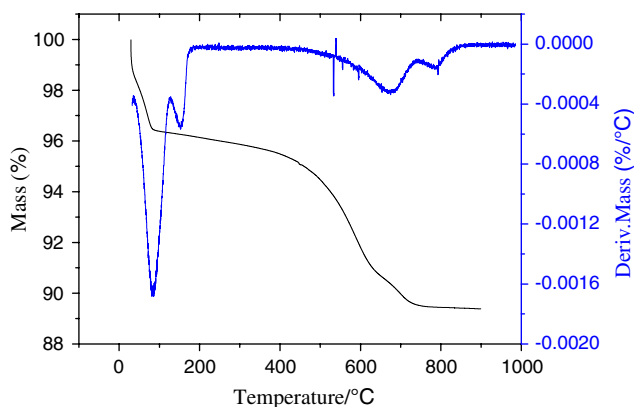


Fig. 2 TG and DTG of Na-montmorillonite

the TG and DTG results for the Na-montmorillonite without intercalation with the surfactant. Figures 3, 4, 5, 6 and 7 show the TG and DTG for montmorillonite-CTAB, montmorillonite-Gemini12, montmorillonite-Gemini14, montmorillonite-Gemini16 and montmorillonite-Gemini18. Mass loss percentage during different steps determined from these TG patterns is shown in Table 1.

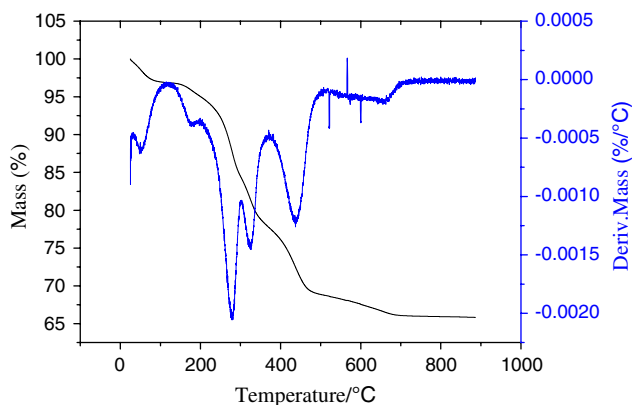


Fig. 3 TG and DTG montmorillonite-CTAB

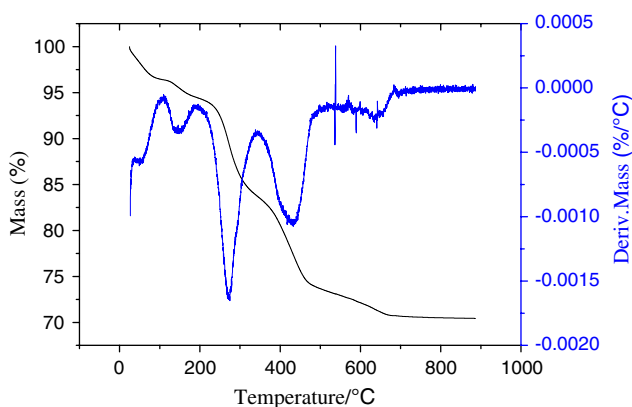


Fig. 4 TG and DTG montmorillonite-Gemini12

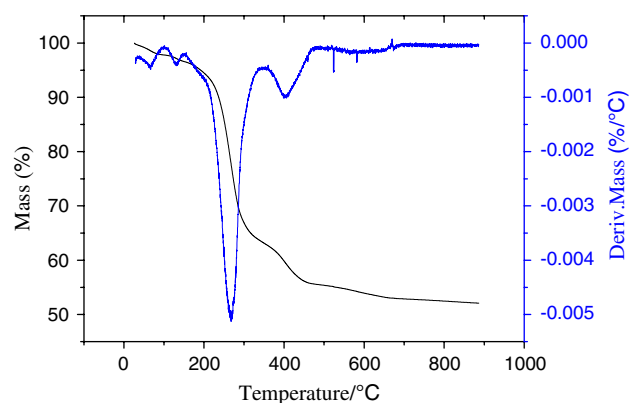


Fig. 5 TG and DTG montmorillonite-Gemini14

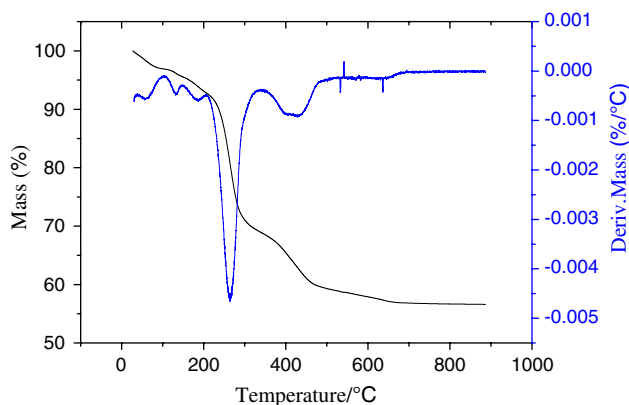


Fig. 6 TG and DTG montmorillonite-Gemini16

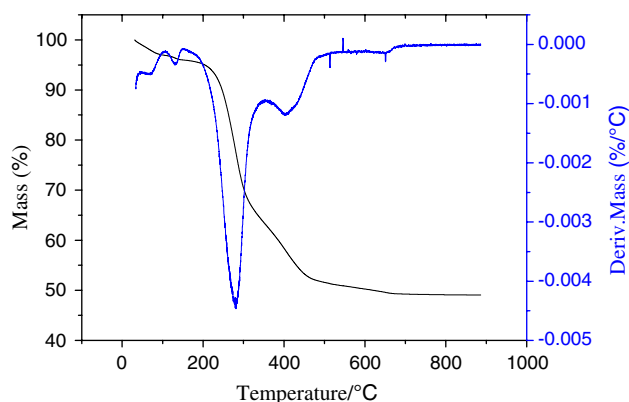


Fig. 7 TG and DTG montmorillonite-Gemini18

It is noted that the DTG of the unmodified montmorillonite has three mass loss steps at between ambient and 85 °C, secondly from 85 to 183 °C, the third from 500 to 820 °C. These three mass loss steps are attributed to desorption of water from clay, dehydration of water adsorbed by metal cations such as Na^+ and Ca^{2+} , and dehydroxylation of the structural OH units of the montmorillonite respectively [15, 36].

Four steps of the mass loss steps are observed for the montmorillonite-CTAB. The first step from the ambient to

95 °C temperature range and is attributed to the desorption of water. The second step occurs from 125 to 185 °C, the very small peak is assigned to the loss of hydration water from the Na^+ ions. The third step in the temperature of 190–500 °C should be attributed to the decomposition of the surfactant. It is found that there are three peaks in this range, the peaks at 210–290, 300–355, 380–480 °C correspond to the decomposition of the external surface, physically adsorbed surfactant, interlayer-adsorbed surfactant molecules, and intercalated surfactant cations, respectively [5, 37, 38]. The fourth mass loss step between 600 to 710 °C is assigned to the loss of structural hydroxyl groups from within the clay.

For the montmorillonite-Gemini12, there is one step that is different from the montmorillonite-CTAB, the third step just has two peaks at 210–330, 350–480 °C, this may be formulated as the big size of the gemini surfactant molecule is difficult to be adsorbed to the interlayer. The second reason is that of the strong electrostatic interaction of polar head group of the gemini surfactant, more surfactants are inclined to adsorb to the external surface of the clay, so the intensity of the peak around 210–330 °C is much bigger than the montmorillonite-CTAB. With the increasing of alkyl chain length of gemini surfactant, the intensity of the peak around 210–330 °C is becoming stronger and 350–480 °C weaker, respectively.

Conclusions

Montmorillonite has been successfully modified using a series of gemini surfactant. Small angle X-ray diffraction analysis results show that the $d(001)$ spacings of montmorillonite-Gemini14, montmorillonite-Gemini16, montmorillonite-Gemini18 can reach above 35 Å compared with the 23.66 Å of the montmorillonite-CTAB at 2.2CEC. The thermogravimetric analysis shows four-step degradation which corresponds to residual water desorption, dehydration, followed by decomposition of the organic

Table 1 Results of the TG of Na-MMT and surfactant modified organoclays

	Step 1		Step 2		Step 3		Step 4	
	Mass loss (%)	Temperature (°C)	Mass loss (%)	Temperature (°C)	Mass loss (%)	Temperature (°C)	Mass loss (%)	Temperature (°C)
A	3.53	85	0.25	85–183			5.09	500–820
B	2.98	95	1.29	125–185	27.51	190–500	1.49	600–710
C	3.19	81	1.94	110–193	20.76	195–500	2.76	515–720
D	3.07	100	3.02	110–187	32.55	210–470	2.58	490–690
E	2.02	102	2.36	107–185	39.27	195–483	2.30	513–687
F	3.08	105	1.38	112–190	42.91	205–477	0.82	527–680

A, B, C, D, E, F are stand for Na-MMT, MMT-CTAB, MMT-Gemini12, MMT-Gemini14, MMT-Gemini16, MMT-Gemini18, respectively

modifier and the dehydroxylation of the organo-montmorillonite. In addition, DTG enables two different structural arrangements of gemini surfactant molecules intercalating the montmorillonite to be proposed. These organically modified montmorillonites have potential utility in the preparation of polymer nanocomposites and in other possible applications. We therefore feel that the organoclays prepared in this study can be used to prepare nanocomposites with polar polymers in order to render good level of dispersion, improved mechanical and other types of properties.

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