Preparation and characterization of 3-aminopropyl-triethoxysilane grafted montmorillonite and acid-activated montmorillonite

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3-aminopropyltriethoxysilane grafted montmorillonites were synthesized with montmorillonite, acid-activated montmorillonites and 3-aminopropyltriethoxysilane in ethanol-water mixture. The resulting products were investigated using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TG). XRD patterns demonstrated that silane was intercalated into the montmorillonite gallery, indicated by increasing basal spacings. These intercalated silanes probably adopt bilayer arrangement models within the montmorillonite and acid-activated montmorillonites interlayer spaces. TG and DTG curves indicate that acidification results in a decrease of the thermal stability of the resultant montmorillonites. Silane grafting leads to a surface property transformation of montmorillonite from hydrophilicity to lipophilicity and an increase of the thermal stability of the condensed silanes.

Montmorillonite is one of the most common 2:1 type clays and widely distributed on the earth surface. Due to its nano-micron size, high surface areas and cationic exchangeable capacity[1], reagents with special function groups can be intercalated into and/or grafted onto the clay interlayer spaces or external surfaces to modify and adjust the surface performance of the resultant clay surfaces. Recently, the preparation and application of clay-based nanocomposites have accelerated the development of material science. For example, hydrophobic modification of the montmorillonite (e.g., organic intercalation)[2] can enhance the optical, thermal[3], rheological, and mechanical properties[4] of the resultant materials. Previous studies have demonstrated that montmorillonite surfaces can be converted from the hydrophilic to the hydrophobic with an improvement of loaded organic carbon content within the organoclays, resulting in an increased adsorption capacity of organic pollutants[5,6].

Hydrophobic modification of the montmorillonite

present great application prospect on the preparation of clay-based nanocomposites and the treatment of contaminated environments. Organoclays are usually synthesized by modifying clay with surfactants (e.g., alkyl ammonium cations) via ion exchange. In this case, most surfactants are intercalated into the clay gallery while part are adsorbed on external surface[7−9]. And the clay 'broken' edges with a number of (–SiOH) and (–AlOH) still display hydrophilic, leading to the difficulty for bulk organic molecules to be intercalated into clay gallery[1]. Recently, to improve the performance of clay-based nanocomposite, grafting clays with silanes has attracted great attention and was demonstrated to be a successful technique[10−13]. In the course of silane

grafting, the density of (–SiOH) and (–AlOH) on clay surface has a key role, i.e., the high density of (–SiOH) and (–AlOH) makes silanes easy to be grafted onto clay external surfaces and 'broken' edges. Previous studies have shown that acid-activation could result in the formation of more broken bonds on the clay surface, an increase of specific surface area more available holes[14,15]. This implies that acid-activation can enhance the reactivity of clay surface with silanes.

Hence, in this study, both montmorillonite and acid-activated montmorillonites were used to investigate the grafting mechanism and the factors control the grafting reaction. The microstructure and surface properties of the grafting products were studied using various techniques. The new insights from this study are of high importance for the synthesis of clay-based nanocomposites and the utilization of clays.

1 Experimental

1.1 Preparation of samples

Montmorillonite $(Na_{0.009}Ca_{0.193}Mg_{0.064})(Al_{1.440}Fe_{0.086} Mg_{0.475})(Si_{3.96}Al_{0.04})O_{10}(OH)_{10}\cdot nH_2O$ used was primarily Ca-MMT from Nanhai Mining Ltd., China. Ca-MMT was added into Na_2CO_3 solution with a mass ratio of Ca-MMT:Na_2CO_3 = 92:8 and was stirred for 3h using JSF-400 stirrer. Drops of HCl were then added into the suspension to dissolve the CO_3^{2-}. The suspension was washed several times with deionized water until chloride free and was dried at 105℃ in vacuum oven (DZF-6020). The product was ground and sieved through 200 mesh for further use. The Na_2CO_3 treated montmorillonite is designated as Na-MMT.

Silane. The silane used in this study is 3-aminopropyltriethoxysilane (APS). Figure 1 shows the schematic structure of the APS.
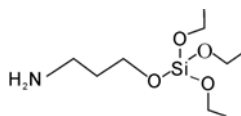

Figure 1   The schematic structure of APS.

Preparation of acid-activated montmorillonites. The acid-activation method follows that reported in the literature[16]. The acidification productions were marked as MMT-2.5%, MMT-5%, MMT-7.5%, MMT-10%, MMT-12.5%, respectively. MMT-2.5% denotes that montmorillonite was acid-activated by H_2SO_4 with a concen-

tration of 2.5%. The other samples were marked in the same way.

Preparation of silane grafted montmorillonites. APS (2 g) was first introduced into the mixture of ethanol/water (75/25 by volume, 200 mL), and then Na-MMT (2.5 g) or acid-activated montmorillonites (2.5 g) were dispersed in the above-mentioned mixture and sheared for 8－12 h at 80℃. The resultant products were washed using the mixture of ethanol/water for 8－12 times in order to remove the residual silane and dried at 50℃ in a vacuum oven. The products of APS grafted montmorillonites were marked as MMT-APS, MMT-2.5%-APS, MMT-5%-APS, MMT-7.5%-APS, MMT-10%-APS and MMT-12.5%-APS, respectively.

1.2 Characterization

Fourier transform infrared spectrum (FTIR) using the KBr pressed disk technique was obtained on a Bruker Vector 33 Fourier transform infrared spectrometer. 32 scans were collected for each measurement over the spectral range of 400－4000 cm^{-1}. X-ray diffraction (XRD) patterns were obtained using Bede D1 system diffractometer (CuK$_\alpha$ radiation under target voltage of 35 kV and current of 30 mA), the scan range of 1－60° with a scanning speed of 4°/min. Thermogravimetric analysis (TG) were performed on the NETZSCH STA 409PC thermobalance. Samples were heated from 30－900℃ at ramp 15℃/min under a N_2 flow 60 mL/min.

2 Results and discussion

2.1 XRD analysis

Figure 2 shows the XRD patterns of Na-MMT and the acid-activated montmorillonites. The basal spacing $(d_{(001)})$ for the Na-MMT is 1.26 nm. After acid-activation under different acid concentrations, the intensity of the (001) reflection is still clearly and $d_{(001)}$ is increased to ca. 1.51 nm, indicating that the acid-activation has little influence on the layered structure of montmorillonite.

Figure 3 displays the XRD patterns of silane grafted Na-MMT and acid-activated montmorillonites. As shown in Figure 3, the basal spacings of the silane grafted Na-MMT and acid-activated montmorillonites are obviously bigger than that of the montmorillonites. After deducting the thickness of phyllosilicate's TOT layer (ca. 0.96 nm) from the $d_{(001)}$ of the grafting products, the gallery height are 0.99 nm (MMT-APS), 1.16
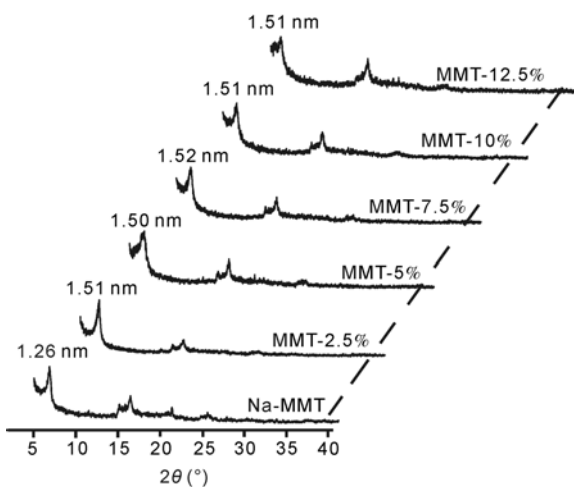
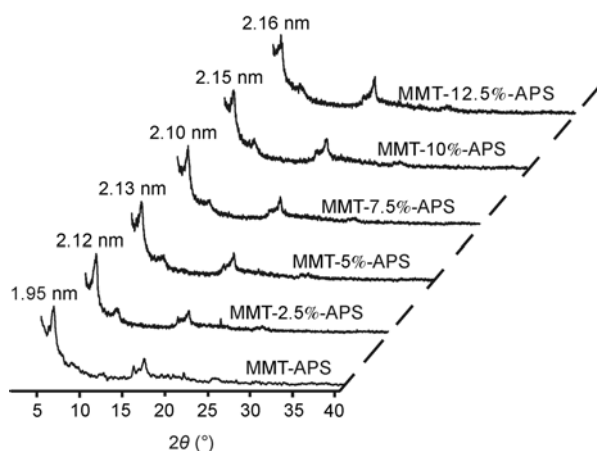**Figure 2** XRD patterns of Na-MMT and the acid-activated montmorillonites.

Figure 3 XRD patterns of silane grafted Na-MMT and acid-activated montmorillonites.

Figure 4 FTIR spectra of Na-MMT and the acid-activate montmorillonites.

nm (MMT-2.5%-APS), 1.17 nm (MMT-5%-APS), 1.14 nm (MMT-7.5%-APS), 1.19 nm (MMT-10%-APS) and 1.2 nm (MMT-12.5%-APS), respectively. I.e. the height of organic phase is ca. 1.1nm, indicating that APS has been intercalated into the montmorillonite gallery. As the height of APS molecule is ca. 0.46 nm, the gallery height of the grafting products suggests that APS adopts a bilayer model within the interlayer spaces of montmorillonite[7,17,18].

2.2 FTIR analysis

To give more evidence of successful grafting, the FTIR analysis of the grafting products was performed. Figure 4 is the infrared spectra of Na-MMT and the acidactivated products. In Figure 4, the peak at 3623 cm^{-1} corresponds to the hydroxyl stretching vibration 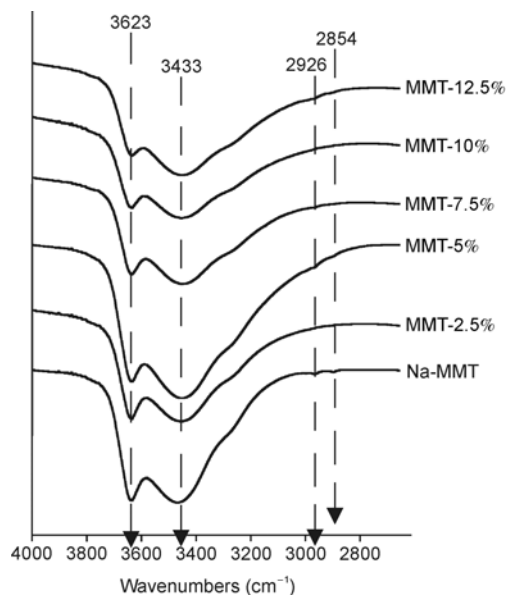and the OH units bond to the aluminum and/or magnesium in the octahedral sheets. The peak at 3433 cm^{-1} corresponds to the −OH stretching vibration of adsorbed water. The intensity decrease of the hydroxyl stretching vibration with the increase of the acid concentration suggests that part of hydroxyl lost with the dissolution of metals in the octahedral sheet[19]. Figure 5 shows the infrared spectra of silane grafting products. The new peaks occurring at 3370−3360 cm^{-1} and 3310−3300 cm^{-1} are attributed to antisymmetric stretching of N−H bond, and the two at 2926 cm^{-1} and 2854 cm^{-1} corresponds to the antisymmetric and symmetric stretching vibrations of −CH$_2$. This indicates the existence of APS in the grafting products. As shown in Figure 5, the intensities of the peaks corresponding to APS are obviously increased from Na-MMT-APS to the grafted acid-activated montmorillonites. This suggests that acid-activation is in favor of APS loaded into montmorillonite, due to the acid-activation resulting in the formation of more broken bonds, larger specific surface area and more available holes[14,16]. All these are in favor of condensation reaction between APS and montmorillonite and raising the adsorbing efficiency for APS[18,20]. Here, it can be seen that the content of APS in the grafting products can be improved by pre-treating montmorillonite with acid.

2.3 TG analysis

Thermogravimetric analysis (TGA) was provided as a simple method to measure the content of silanes and
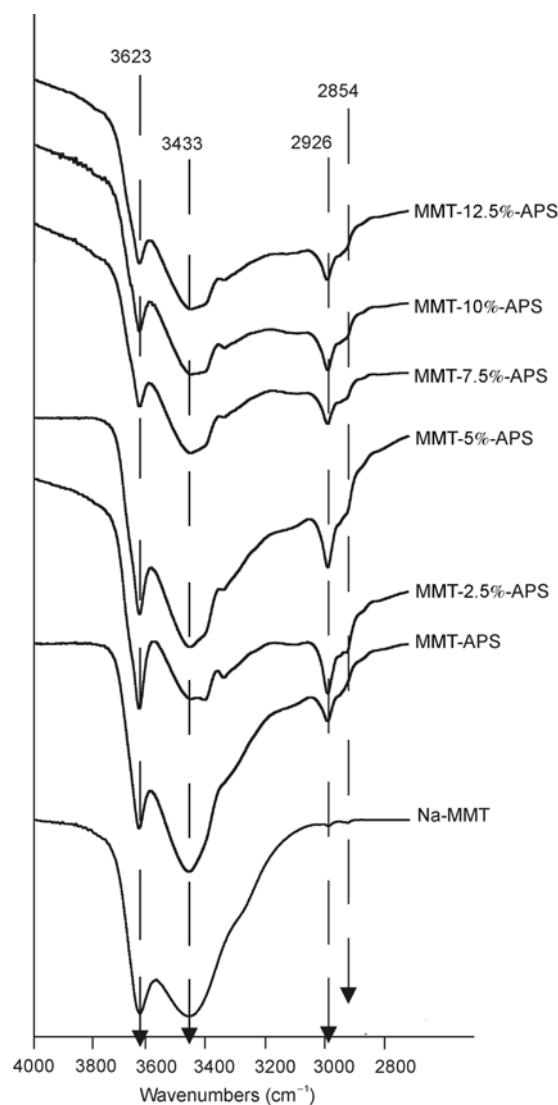
Figure 5 FTIR spectra of the grafted Na-MMT and the grafted acid-activate montmorillonites.

physisorbed water. Table 1 and Figure 6 are the TG and DTG results of Na-MMT and the acid-activated montmorillonites. The DTG curve of Na-MMT only displays two peaks at ca. 56 and 639℃, corresponding to the loss of the physically adsorbed water and the dehydroxylation of montmorillonite, respectively. There is a small

mass loss (ca. 0.98%) in the range of 150－440℃ for Na-MMT, which is attributed to the mass loss of the bonded water within the gallery. Hence, a greater mass loss than ca. 0.98% could be attributed to the evaporation and decomposition of silane for silane grafted samples in this temperature range.

From Figure 6, it can be found that the temperature corresponding to the loss of physically adsorbed water and interlayer water is prominently increased for acid-activated montmorillonites, compared with that of Na-MMT. In the course of acid activation, parts of octahedral cations are dissolved from the octahedral sheet of montmorillonite and the permanent charge of montmorillonite increases. This results in an increase of electrostatic interaction between montmorillonite and water molecules, causing an increase of the temperature of the adsorbed water. However, Figure 6 shows that the dehydroxylation temperature of the acid-activated montmorillonites is decreased whereas the mass losses corresponding to adsorbed water and dehydroxylation are decreased when compared with that of Na-MMT. The decrease of the mass loss of adsorbed water is mainly due to H^+ replacing the interlayer hydrated cations of montmorillonite in the acid-activation course. And the amount of structural hydroxyl was decreased due to their removal during acid-activation[19]. The removal of octahedral cations (e.g. Al^{3+}, Fe^{3+}, Mg^{2+}) and hydroxyls results in the formation of Lewis and Bronsted centers and decreases the thermal stability of montmorillonite[16,19].

Table 2 and Figure 7 show the TG and DTG results of the grafted Na-MMT and the grafted acid-activated montmorillonites. The decomposition of silane grafted montmorillonites can be separated into 5 steps (as shown in Table 2). The corresponding temperature ranges are 63－114℃, 340－355℃, 429－437℃, 533－554℃, 632－670℃, respectively. For Na-MMT and acid-activated montmorillonites, there is no obvious mass loss in the range 200－600℃. Thus, the mass

Table 1 The results and the mass loss of Na-MMT and the acid-activate montmorillonites

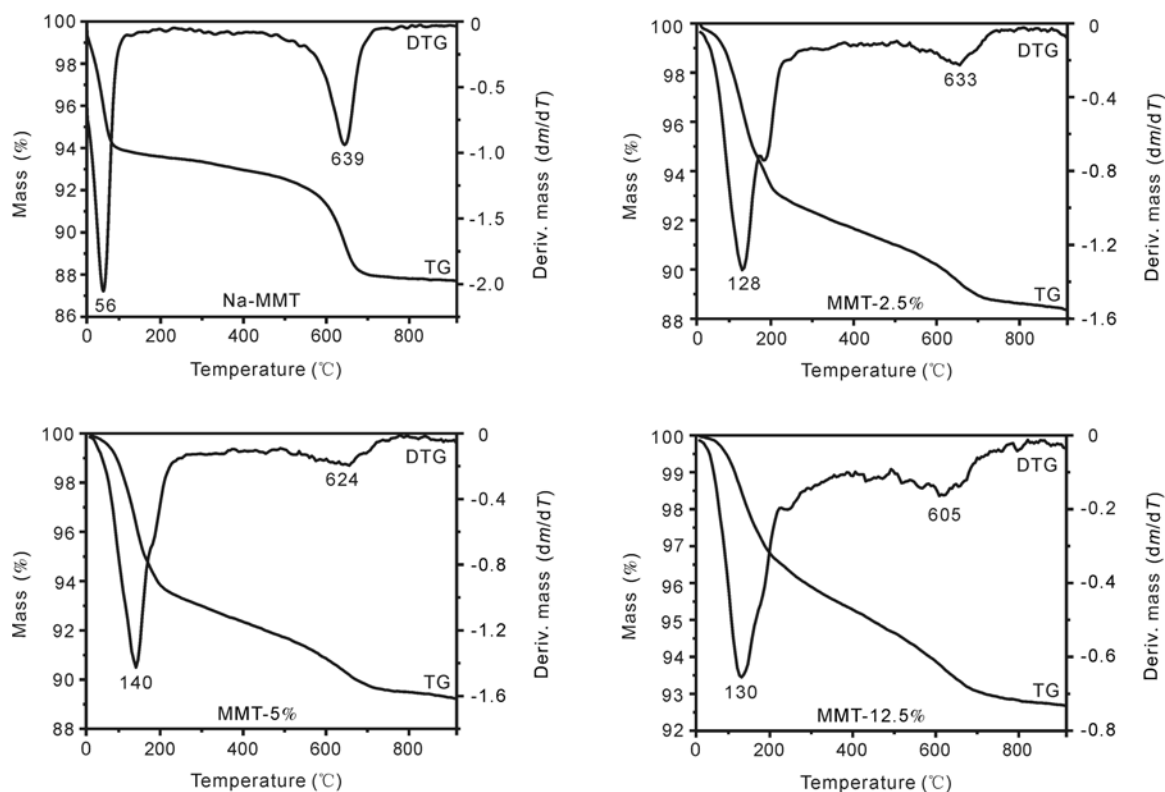| Sample name	First step		Fifth step	
	T (℃)	Mass loss (%)	T (℃)	Mass loss (%)
Na-MMT	56	6.68	639	5.26
MMT-2.5%	128	6.76	633	2.25
MMT-5%	140	6.53	624	2.14
MMT-7.5%	125	6.18	621	1.90
MMT-10%	126	4.31	607	1.60
MMT-12.5%	130	3.49	605	1.61

Figure 6 TGA and DTG curves of Na-MMT and the acid-activate montmorillonites.

Table 2 The results and the mass loss of the grafted Na-MMT and the grafted acid-activate montmorillonites

Sample name	First step		Second step		Third step		Fourth step		Fifth step	
	T (℃)	Mass loss (%)	T (℃)	Mass loss (%)	T (℃)	Mass loss (%)	T (℃)	Mass loss (%)	T (℃)	Mass loss (%)
MMT-APS	63	3.31	346	1.30	429	6.96	533	0.80	632	3.22
MMT-2.5%-APS	108	2.08	340	3.16	431	7.37	546	2.66	670	0.85
MMT-5%-APS	114	2.49	349	2.85	435	7.06	554	2.68	640	0.82
MMT-7.5%-APS	105	1.81	345	3.01	435	6.51	547	2.65	663	0.92
MMT-10%-APS	103	1.88	346	2.75	436	6.65	546	3.24		
MMT-12.5%-APS	110	2.26	355	2.63	437	5.95	550	3.22		

losses between 200−600℃ are attributed to the inter-calated and grafted APS. The mass loss stages in 340−355℃ and 429−437℃ correspond to the decomposition of the intercalated APS while the stage in 533−554℃ corresponds to the decomposition of the grafted silane[18]. As reported in Table 2, the content of APS in the silane grafted montmorillonites can be remarkably improved by using the acid-activation method. The acid-activation results in larger specific surface area and more available holes. This can enhance the adsorption capacity of montmorillonite to APS[14]. Meanwhile, in the case of the mixture of ethanol and water, ethoxy groups undergo hydrolysis. This leads to condensation between silane and clay surface hydroxyl groups, and polymeri-zation among silane molecules. In the case of polymerization, different polymers with various sizes can be formed, such as linear, monocyclic, polycyclic and 'cagelike'[21,22]. Only the polymers with suitable size can be intercalated into the clay interlayer space. According to the results of XRD analysis, after acidification the basal spacings $d_{(001)}$ is increased and 'house-of-cards' structure is formed in the suspension[23,24]. In this kind of structure, silane molecules not only exist in the interlayer space, which can carry out intercalation reaction, but also occupy interspaces between tactoid-like particles. This interspaces offer larger specific surface area, more available holes and favorable sites for the adsorption of APS onto montmorillonites.
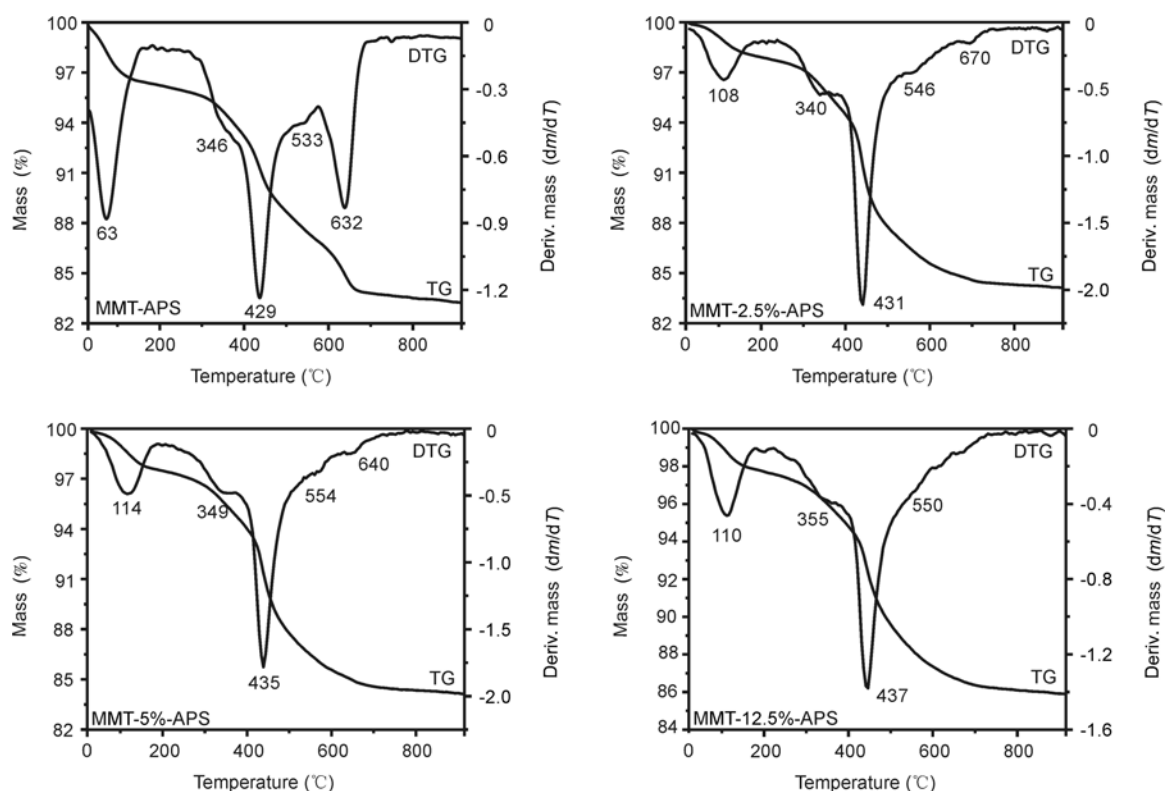
Figure 7 TGA and DTG curves of the grafted Na-MMT and the grafted acid-activate montmorillonites.

From Tables 1 and 2, it can be found that, after grafting reaction, the temperature of losing physically adsorbed water of the acid-activated montmorillonites is decreased to 108℃(MMT-2.5%-APS), 114℃(MMT-5%-APS), 105℃(MMT-7.5%-APS), 103℃(MMT-10%-APS), 110℃(MMT-12.5%-APS), respectively. This should be attributed to the intercalation of APS into the clay gallery and the condensation reaction between the clay surface hydroxyl groups and APS. Both intercalation and condensation can change the clay hydrophilic surface to hydrophobic surface, weakening the interaction between montmorillonites and polar water molecules.

3　Conclusion

In this paper, silane grafted montmorillonite and acid-activated montmorillonites were synthesized using APS in the mixture of ethanol/water. The results show that the basal spacings of silane grafted montmorillonites are significantly larger than that of Na-MMT and acid-activated montmorillonites. This demonstrates that the silane has been intercalated into montmorillonites interlayer space. Based on the interlayer height of the silane grafted montmorillonites and the configuration of APS, these intercalated APS adopt bilayer arrangement. The results of FTIR and TG analysis of the silane grafted montmorillonites indicate that the content of APS in silane grafted acid-activated montmorillonites is obviously bigger than that in silane grafted Na-MMT.

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