

# Grafting of swelling clay materials with 3-aminopropyltriethoxysilane

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## Abstract

The grafting reaction between a trifunctional silylating agent and two kinds of 2:1 type layered silicates was studied using FTIR, XRD, TGA, and <sup>29</sup>Si CP/MAS NMR. XRD patterns clearly indicate the introduction of 3-aminopropyltriethoxysilane ( $\gamma$ -APS) into the clay interlayer. In the natural montmorillonite,  $\gamma$ -APS adopts a parallel-bilayer arrangement, while it adopts a parallel-monolayer arrangement in the synthetic fluorohectorite. These different silane arrangements have a prominent effect on the mechanism of the condensation reaction within the clay gallery. In natural montmorillonite, the parallel-bilayer arrangement of  $\gamma$ -APS results in bidentate (T<sup>2</sup>) and tridentate (T<sup>3</sup>) molecular environments, while the parallel-monolayer arrangement leads to monodentate (T<sup>1</sup>), as indicated by <sup>29</sup>Si CP/MAS NMR spectra. This study demonstrates that the silylation reaction and the interlayer microstructure of the grafting products strongly depend on the original clay materials.

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## 1. Introduction

During the past 50 years, there has been increased interest in the synthesis of nanocomposite materials by embedding nanosized inorganic particles into polymers [1]. Since the optical, thermal, rheological, and mechanical properties of these materials strongly depend on the techniques used for their elaboration, a variety of synthesis strategies have been reported, with the aim of controlling the dispersion of the inorganic component within the polymer matrix on the nanoscale. Among the wide range of nanostructured materials, effort has more recently focused on the elaboration of polymer/layered silicate nanocomposites.

The application of layered silicates relies on their ion exchange properties and swelling ability. Access of guest molecules to host matrix could be a rate-limiting step in the intercalation reaction of swelling clays. Especially when

guest molecules are highly hydrophobic and bulky, they would have a low possibility of approaching hydrophilic reaction sites. This kind of organic molecules is difficult to be intercalated into hydrophilic clays by conventional ion exchange methods, which employ clay suspensions with single solution phases. Recently, their potentials have been tremendously expanded by the intercalation of a variety of biologically active organic substances [2–5]. Hydrophobic modification of the clay intra-surface allows many hydrophobic guest molecules to be easily intercalated.

More recently, it has been demonstrated that the interaction between hydrophobic molecules and clay surfaces could be greatly enhanced by simple grafting of hydrophobic groups onto the layer surfaces [6,7]. In previous studies of the interaction between silane and swelling clay materials, three basic models (interlayer, external surface, and “broken” edge grafting) have been proposed. The interlayer grafting happens within the clay gallery and results in prominent increase of the basal spacing of the clay [8–10]. The intercalation and silylation convert the hydrophilic inter-

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layer surface to an organophilic surface. For the external surface [7] and “broken” edge [6] graftings, the silylation occurs on the external surface and “broken” edge, separately. The former has no effect on the basal spacing of the clay, whereas the later increases the basal spacing, based on the assumption that the silylation reaction produces silane polymers able to penetrate the external part of the interlaminate space and push the clay sheets apart [6]. Successful grafting greatly enhances the intercalation of bulky hydrophobic molecules into clay materials. Obviously, in these reports, the locations for silylating reactions are very different. In addition, we find that researchers paid great attention to the effect of silanes with different numbers of functional groups, whereas little attention was paid to the effect of the used clay materials. Based on our knowledge about clay minerals, the mineralogical properties (for example, swelling ability, ion exchange property) have significant effects on the interaction between clays and other chemicals. Hence, in this study, grafting of different clay materials with the same silylating agent was performed, to elucidate the effect of clay minerals on the silylating reaction.

Among the various swelling clay materials, synthetic fluorohectorite (SOMASIF ME100) and natural montmorillonite (OPTIGEL-757) are the most widely used in the synthesis of polymer/layered silicate nanocomposites. However, as far as is known, no study has been performed on these two clay materials grafted with silane. It is of great importance for synthesis of polymer/layered silicate nanocomposites and/or improvement of their properties.

In this work, we report the grafting of two 2:1 type swelling clay materials with a trifunctional silylating agent (3-aminopropyltriethoxysilane) and the characterization of the resultant products using FTIR, XRD, TGA, and  $^{29}\text{Si}$  CP/MAS NMR. The aim of this work is to elucidate the effect of clay materials on the silylation reaction and the interlayer microstructure of the grafting products. This is a strategic step for synthesis of polymer/layered silicate nanocomposites.

## 2. Experimental

### 2.1. Materials

Two kinds of 2:1 type swelling clay materials, SOMASIF ME100 (ME) and OPTIGEL-757 (NANOFIL), were used in this study. SOMASIF ME100 (ME) is a synthetic fluorohectorite produced by the CO-OP Chemical Co., Japan. The cation exchange capacity (CEC) of synthetic fluorohectorite is 70 meq/100 g, and its interlayer spacing is 0.96 nm. Its structural formula can be expressed as  $\text{Na}_{2x}\text{Mg}_{3.0-x}\text{Si}_4\text{O}_{10}(\text{F}_y\text{OH}_{1-y})_2$  ( $x = 0.15\text{--}0.5$ ,  $y = 0.8\text{--}1.0$ ). OPTIGEL-757 (NANOFIL) is a kind of natural montmorillonite provided by SÜD-CHEMIE Co., Germany, and its formula is  $\text{Na}_{0.19}\text{K}_{0.20}\text{Ca}_{0.04}(\text{Mg}_{0.36}\text{Fe}_{0.10}\text{Al}_{1.44})\text{Si}_4\text{O}_{10}(\text{OH})_2$ . The CEC of natural montmorillonite is 91

meq/100 g. The trifunctional silylating agent 3-aminopropyltriethoxysilane ( $\gamma$ -APS), with a purity of 99% (from Aldrich), was used as received. The chemical formula of  $\gamma$ -APS is  $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$ . The two original clays, SOMASIF ME100 (synthetic fluorohectorite) and OPTIGEL-757 (natural montmorillonite), are denoted as H-0 and M-0, respectively.

### 2.2. Grafting process

The grafting reaction was carried out in a mixture of water/ethanol (25/75 by volume). A quantity of 3 g of  $\gamma$ -APS was first introduced into 1000 ml of the mixture of water/ethanol and the temperature was kept at 80 °C. Then 10 g of clay was added into the above-mentioned solution and the grafting reaction was realized, under shearing, for 5 h at 80 °C. The reaction product was filtered and washed six times using the mixture of  $\text{H}_2\text{O}$ /ethanol and dried at 80 °C for 6–8 h. The resultant product was ground and placed in a sealed container for characterization. The grafted products prepared from H-0 and M-0 are denoted as H-2 and M-2, respectively.

### 2.3. Characterization

X-ray powder diffraction (XRD) analysis was performed on a Siemens D500 diffractometer equipped with a back monochromator and a copper cathode as the X-ray source ( $\lambda = 0.154$  nm). The basal spacings were calculated from the  $2\theta$  values using the EVA software.

Fourier transform infrared (FTIR) spectra using the KBr pressed disk technique were performed on a Nicolet SX2 Fourier transform infrared spectrometer. The spectra were collected for each measurement over the spectral range 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

Thermogravimetric analysis (TGA) was performed on a TGA2950 thermobalance. Samples were heated from 30 to 800 °C for M-0 and M-2 and to 950 °C for H-0 and H-2 at a heating rate of 20 °C/mn under helium atmosphere (25 ml/min) in order to quantify and distinguish the amount of silane in the resultant products of grafting reaction.

$^{29}\text{Si}$  cross-polarization magic-angle-spinning nuclear-magnetic-resonance (CP/MAS NMR) spectra were gained on a Bruker DSX-300 spectrometer operating at 59.63 MHz. The contact time was 5 ms, the recycle delay 1 s, and the spinning rate 5 KHz. Tetramethylsilane (TMS) was used as the external reference.

## 3. Results and discussion

A lot of previous studies [11,12] have shown that hydroxyl groups on the silica surface, resulting from hydrolysis, act as active sites in the grafting reaction between silane and silica. For 2:1 type layered silicates, they have a kind of

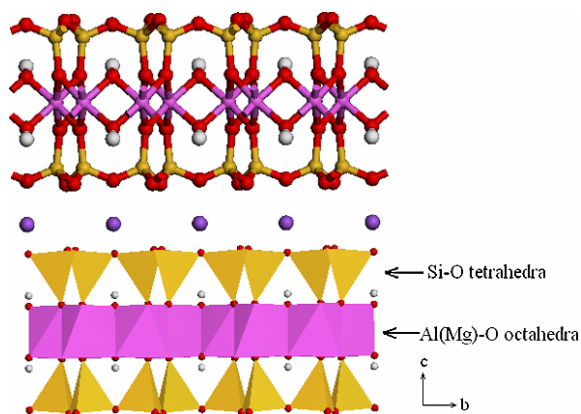


Fig. 1. Idealized structure of 2:1 type layered silicate. (Top: stick and ball style; bottom: polyhedron style.)

“sandwiched” structure; i.e., one Al(Mg)-O<sub>4</sub>(OH)<sub>2</sub> octahedral sheet binds with two Si-O tetrahedral sheets, as shown in Fig. 1. Since the extensively existing structural defects in the Si-O tetrahedral sheet and the layer edges with “broken” bonds, these sites will be active, similar to the Si atom environment in silica, and combine with silane during grafting reaction.

Fig. 2 displays the FTIR spectra of M-0, M-2, H-0, and H-2. A weak and broad band at ca. 2936 cm<sup>-1</sup> was recorded in the FTIR spectra of M-2 and H-2 (Fig. 2). This band corresponds to the CH<sub>2</sub> stretching mode of  $\gamma$ -APS, indicating the existence of silane in the grafted products. The XRD patterns of the clay materials before and after grafting are shown in Fig. 3. The basal spacings for M-0 and H-0 are 1.18 and 1.21 nm, respectively. After grafting reaction, the basal spacing is increased to 1.77 nm for M-2 and to 1.45 nm for H-2 (Fig. 3). The broad (001) reflection of H-2 and M-2 reflects the variety of layer height in the grafted products. The increase of the basal spacing indicates that  $\gamma$ -APS has been intercalated into the gallery of both clay materials. The estimated gallery heights for M-2 and H-2 are 0.81 and 0.49 nm. In the solution of water/ethanol mixture, silane is easy to hydrolyze [13], and this is also confirmed by our <sup>29</sup>Si MAS NMR spectrum (see below). After hydrolysis, the configuration of  $\gamma$ -APS is different from the original one and the height of the aminopropyl group is ca. 0.4 nm, similar to that of the alkyl chain [14]. Accordingly, the gallery heights of 0.81 and 0.49 nm indicate the parallel-bilayer and parallel-monolayer arrangement of  $\gamma$ -APS within the galleries of M-2 and H-2, respectively. Since the grafting reaction conditions for M-2 and H-2 are identical, their different gallery heights reflect the original clays having a significant effect on the gallery structure of the resultant products. In addition, our present study demonstrates that M-0 is more expandable than H-0 as shown by the XRD patterns of the grafted products.

Both of the DTG curves of H-0 and M-0 display two peaks at 47 and 901 °C for H-0 and at 62 and 625 °C for M-0 (Fig. 4), corresponding to loss of the physically adsorbed water and dehydroxylation of clay, respectively. As

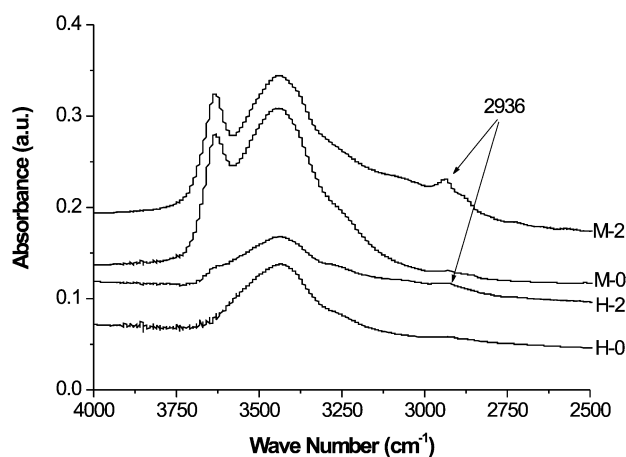


Fig. 2. FTIR spectra (2500–4000 cm<sup>-1</sup>) of natural montmorillonite (M-0) and synthetic fluorohectorite (H-0) before and after grafting.

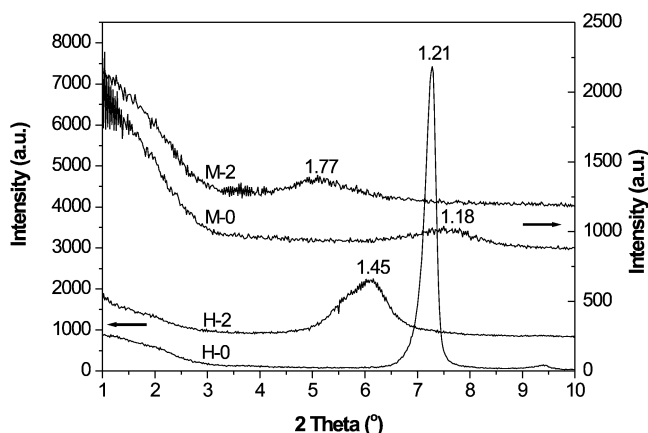


Fig. 3. XRD patterns of natural montmorillonite (M-0) and synthetic fluorohectorite (H-0) before and after grafting.

shown by the TGA curve of H-0, there is not weight loss during 200–600 °C. This means that H-0 does not undergo any thermally induced changes in this temperature range. However, for M-0, there is a slight weight loss (ca. 1 wt%) in the range 200–500 °C, possibly corresponding to the loss of the bonded H<sub>2</sub>O within the gallery. The DTG curve of H-2 (Fig. 4) displays five peaks at 63, 209, 347, 426, and 550 °C, respectively. The peak at 63 °C corresponds to loss of the physically adsorbed water. As shown by the TGA curve, H-0 is thermally stable in the temperature range 200–600 °C. Hence, the weight loss in this region should be attributed to the evaporation and/or decomposition of silane. The peak at 209 °C corresponds to the physically adsorbed  $\gamma$ -APS, while the peak around 550 °C to the decomposition of the grafted silane [15]. In addition, the peaks at 347 and 428 °C, similar to those derived from the decomposition of the intercalated cationic surfactants within the clay interlayer [16], should be attributed to the intercalated silane. For M-2, the DTG curve displays four peaks at ca. 62, 330, 426, and 535 °C, respectively. The peak at 62 °C corresponds to the loss of the physically adsorbed water, while the peaks at 330 and 426 °C correspond to the intercalated silane. However, the

peak at ca. 625 °C corresponding to dehydroxylation in the DTG curve of M-0 does not occur in the DTG curve of M-2. Hence, the broad peak at ca. 535 °C in the DTG curve of M-2 could be due to the cooccurrence of the decomposition of the chemically bound silane and the dehydroxylation of the clay. The TGA curves of the two clays used before and after grafting indicate that there are 6.0 and 6.9% (wt%)  $\gamma$ -APS within the galleries of M-2 and H-2, respectively. This reflects that the quantity of silane within the gallery is not the key factor for their arrangement. Here, it could be found that the used clay materials have a more prominent effect on the arrangement of silane within the gallery rather than the amount of silane.

$^{29}\text{Si}$  CP/MAS NMR spectrum provides supporting evidence for the silylation of silane onto the clay surface.  $^{29}\text{Si}$  CP/MAS NMR spectrum of M-0 (Fig. 5) displays two signals at  $-92.1$  and  $-108.3$  ppm, corresponding to  $\text{Q}^3[\text{Si}(\text{OSi})_3\text{OM}]$  (M stands for Al, Mg, etc.) and  $\text{Q}^4[\text{Si}(\text{OSi})_4]$ , respectively [17]. The former is characteristic of Si atoms, in layered silicates, while the latter relates to Si atoms in quartz, which is an impurity in the clays. There is no signal of  $\text{Q}^2$  in the  $^{29}\text{Si}$  CP/MAS NMR spectrum, attributed to isolated silanol groups present at the silicate sheet edges. This is similar to those of montmorillonites reported in the literature [17], but different from that of laponite, in which the signal of  $\text{Q}^2$  was recorded [6]. After grafting, two additional  $^{29}\text{Si}$  signals at  $-59.8$  and  $-66.7$  ppm are recorded in the  $^{29}\text{Si}$  CP/MAS NMR spectrum of M-2 in addition to the two signals of  $\text{Q}^3$  and  $\text{Q}^4$  occurring in the  $^{29}\text{Si}$  NMR spectrum of M-0. The two signals at  $-59.8$  and  $-66.7$  ppm correspond to the units of  $\text{T}^2[\text{Si}(\text{OSi})_2(\text{OR}')\text{R}]$  ( $\text{R} = \text{CH}_2\text{CH}_2\text{-CH}_2\text{NH}_2$ ,  $\text{R}' = \text{H}$  or  $\text{CH}_2\text{CH}_3$ ) and  $\text{T}^3[\text{Si}(\text{OSi})_3\text{R}]$ , respectively [6,8–11,13]. This demonstrates the successful grafting  $\gamma$ -APS onto the clay surface. For H-0,  $^{29}\text{Si}$  CP/MAS NMR spectrum displays a signal centered at  $-89.3$  ppm, corresponding to  $\text{Q}^3[\text{Si}(\text{OSi})_3\text{OM}]$ . In the  $^{29}\text{Si}$  CP/MAS NMR spectrum of H-2, a strong  $^{29}\text{Si}$  signal at  $-43.6$  ppm and a weak one at  $-53.0$  ppm are recorded. The former corresponds to  $\text{T}^1[\text{Si}(\text{OSi})(\text{OH})_2\text{R}]$  and the latter to  $\text{T}^1[\text{Si}(\text{OSi})(\text{OCH}_2\text{CH}_3)_2\text{R}]$  [11]. The higher signal intensities of the  $\text{T}^1[\text{Si}(\text{OSi})(\text{OH})_2\text{R}]$  unit suggests that most silane molecules have been hydrolyzed in the solution of water/ethanol mixture. This conclusion supports our proposal about the silane arrangement within the gallery based on the XRD patterns. In addition, the coexistence of  $\text{T}^1[\text{Si}(\text{OSi})(\text{OH})_2\text{R}]$  and  $\text{T}^1[\text{Si}(\text{OSi})(\text{OCH}_2\text{CH}_3)_2\text{R}]$  units gives good explanation of the obviously broadened (001) reflection of H-2.

Our present study demonstrates that the intercalation of silane firstly happens during grafting reaction and the arrangement of the intercalated silane strongly depends on the properties of layered silicates. This is similar to the intercalation of cationic surfactant into clay interlayer. Then, the condensation reaction between silane molecule and Si–O tetrahedral sheet of clay (and/or among silane molecules) occurs. The condensation reaction strongly depends on the arrangement of silane molecules within the gallery. For M-2,

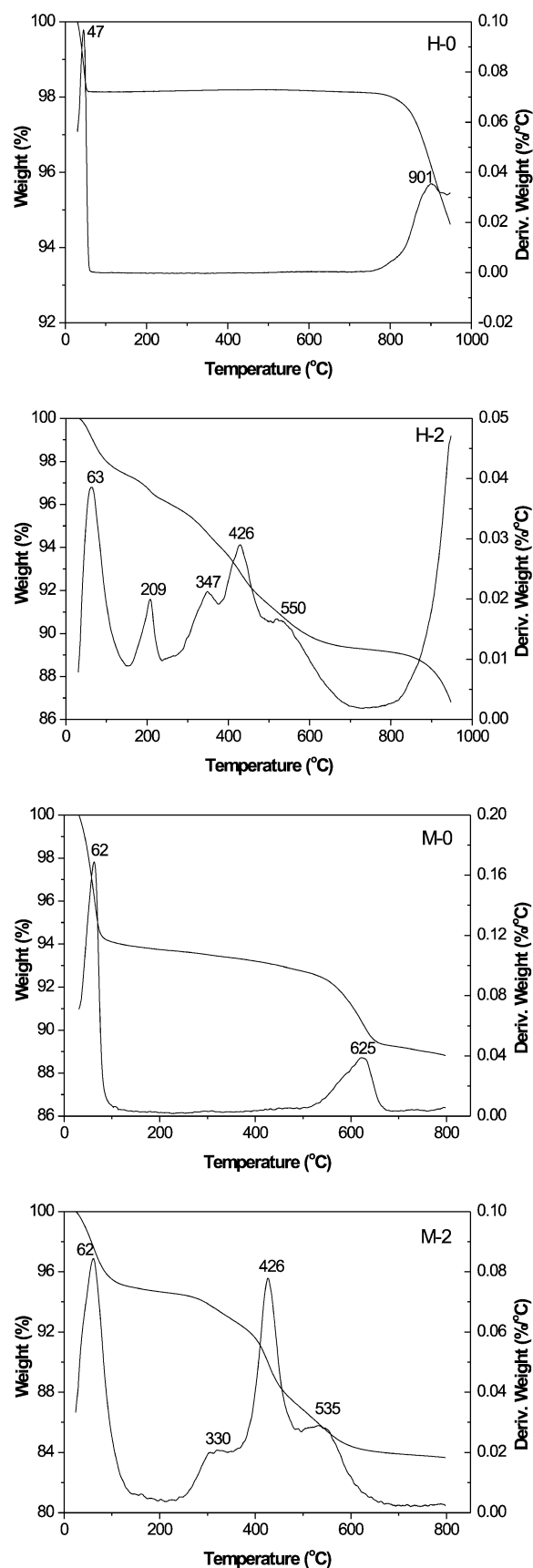


Fig. 4. TGA and DTG curves of natural montmorillonite (M-0) and synthetic fluorohectorite (H-0) before and after grafting.

the arrangement of  $\gamma$ -APS is a parallel bilayer and the condensation between silane molecules is easy to happen. However, the arrangement of  $\gamma$ -APS in H-2 is a parallel mono-

layer. Both of the experimental results [5,18] and our molecular modeling of organoclays indicate that, in the case of a parallel monolayer, the organic molecules or cations within the gallery are individually separated to lower the energy of the hybrid. Accordingly, there is little possibility for condensation between silane molecules in the case of parallel monolayer. This could well explain the different  $T^n$  ( $n = 1, 2, \text{ and } 3$ ) units occurring in M-2 and H-2 as indicated by the  $^{29}\text{Si}$  CP/MAS NMR spectra. Fig. 6 shows a hypothetical diagram for the intercalation of  $\gamma$ -APS into clay interlayer and silylation of  $\gamma$ -APS onto clay surface, and the possible structural models for  $T^1$ ,  $T^2$ , and  $T^3$  units.

Our proposed model is different from that reported by Herrera et al. [6] in spite of the similar basal spacing of the grafted products. Herrera et al. [6] suggested that the silane molecules could only react at the “broken” edges of the clay layer rather than with the intralayer surface. To elucidate this point, the experiment of grafting surfactant-modified-clay (SOMASIF MAE, provided by CO-OP Chemical Co., Japan) with  $\gamma$ -APS was performed. However, the characterization of TGA and  $^{29}\text{Si}$  CP/MAS NMR demonstrates that there is no silane grafted onto the organoclay. In addition, molecular dynamics simulation demonstrates that, in organ-

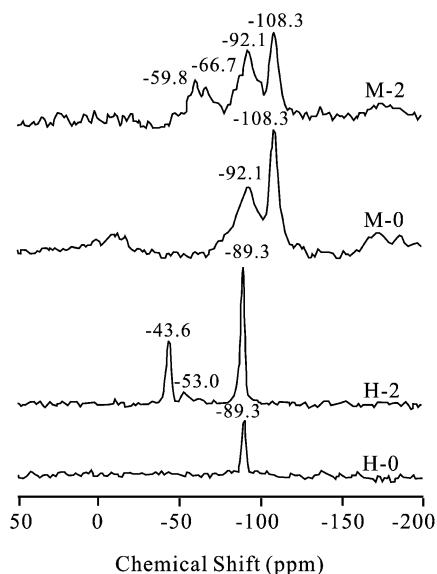


Fig. 5.  $^{29}\text{Si}$  MAS NMR spectra of natural montmorillonite (M-0) and synthetic fluorohectorite (H-0) before and after grafting.

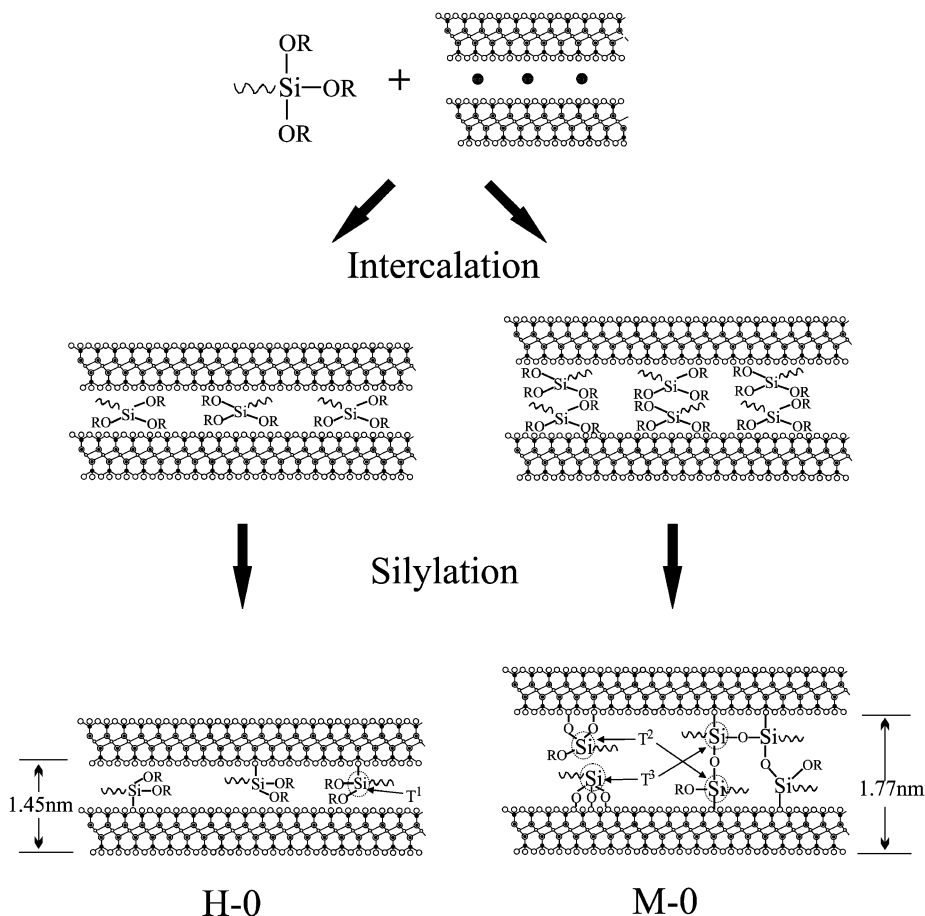


Fig. 6. The hypothetical diagram for the intercalation and silylation of  $\gamma$ -APS into clay interlayer and the possible structural models for  $T^1$ ,  $T^2$ , and  $T^3$  units.

oclays, the alkyl chains within the layer lie almost parallel to the clay surface whereas those out of the layer structure are essentially perpendicular to the surface [19]. This means that the “broken” edge of the clay layer is “protected” by the alkyl chains and there is little possibility of condensation reaction between the “broken” edges of the clay layer and silane molecules. Our present study has shown that the intercalation of silane molecules into the clay interlayer happens before the condensation between silane molecule and clay layer surface. Hence, it is suggested that the condensation occurs between silane molecule and the intralayer surface as shown in Fig. 6 rather than between silane molecule and the “broken” edges of the clay layer.

#### 4. Conclusions

In summary, our present study demonstrates that the grafting reaction between the trifunctional silylating agent and the two 2:1 type layered silicates includes two basic steps: First, the silane molecules are intercalated into the clay interlayer; then, the condensation reaction happens between silane molecules and clay layer surface. The silane molecules adopt a parallel-bilayer arrangement model in natural montmorillonite (OPTIGEL-757) and a parallel-monolayer arrangement in the synthetic fluorohectorite (ME). The different arrangements of silane molecules in the interlayer result in the various  $T^n$  units such as  $T^1[\text{Si}(\text{OSi})(\text{OR}')_2\text{R}]$ ,  $T^2[\text{Si}(\text{OSi})_2(\text{OR}')\text{R}]$  and  $T^3[\text{Si}(\text{OSi})_3\text{R}]$  during condensation. Consequently, it may lead to the different surface properties of the resultant products. This study clearly demonstrates that the interlayer structure of the grafted products and the molecular environment of the grafted silane strongly depend on the used clay materials. This is of high importance in the synthesis of polymer/layered silicate nanocomposites and improvement of their properties.

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