# Factors Affecting the Grafting of Aminopropyltriethoxysilane in Swelling Clay Materials

A. M. Shanmugharaj*, Kyong Yop Lee**, and Sung Hun Ryu*, †

*Industrial Liaison Research Institute and*
*College of Environment and Applied Chemistry*
**Center for Media Transport System*
*School of mechanical Engineering and Industrial System Engineering*
*Kyung Hee University, Yongin Kyunggi-Do 449701, South Korea*

# Clay의 Aminopropyltriethoxysilane 그라프트에 영향을 미치는 인자

A. M. Shanmugharaj* · 이 경 엽** · 류 승 훈*, †
*경희대학교 환경응용화학대학 산학협력연구원
**경희대학교 테크노공학대학 유체이동센터
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**ABSTRACT** : Functionalization of montmorillonite clay has been done using 3-aminopropyltriethoxy silane using water as a dispersing medium. Qualitative evidence of the presence of silane attached to the clay surface has been identified using Fourier transform infrared spectroscopy (FT-IR). Increase in silane concentration decreases the adsorbed/intercalated ratio calculated using differential thermo-gravimetric analysis (DTG). Average d-spacing calculated using X-ray diffraction initially increases with silane concentration and decreases slightly at higher silane concentration. The influence of processing temperature on the silane functionalization of clay has also been investigated and it shows that chemical grafting of silane on the clay surface is observed with increasing processing temperature.

요 약 : Monmorillonite 클레이를 물을 분산제로 이용하여 3-aminopropyltriethoxy 실란 기능화를 실시하였다. 실란의 그라프트 여부는 FT-IR을 이용하여 정성분석하였다. 실란의 농도가 증가함에 따라 흡착/삽입 비가 감소함을 알 수 있었다. X-ray를 이용하여 평균 d-간격을 측정한 결과 초기에는 실란농도가 증가하다 다소 감소하였다. 기능화 공정온도의 영향을 살펴본 결과 온도가 증가함에 따라 화학적인 그라프트가 증가함을 알 수 있었다.

*Keywords : montmorillonite, 3-aminopropyltriethoxysilane, solvent surface energy, adsorption, intercalation*

† 대표저자(e-mail : shryu@khu.ac.kr)

# Ⅰ. Introduction

The polymer nanocomposites, which consist of fine dispersions of nanoplatelets are of great interest for both scientific and practical industrial reasons due to their remarkable mechanical, thermal and chemical properties as well as optical, electronic and magnetic applications.[1-7] Better performance of polymer layered silicate nanocomposites is directly correlated with the exfoliation/dispersion of the nanoclay layers within the polymeric matrix. However, exfoliation of clay is difficult to achieve, due to strong electrostatic attractions between the silicate layers and the intergallery cations. The degree of exfoliation and intercalation of the clay platelets in the polymer matrix, as well as the orientation of the clay particles, have been found to have important implications for the final property of the nanocomposite. For instance, polymers which contain exfoliated clay particles have better mechanical properties than those which have intercalated clay structures.[8] Exfoliation of polymer layered silicate nanocomposites depends on several factors such as clay type, organic modifier and polymeric matrix. A crucial factor for succeeding exfoliated structures is the organic modification of the silicate layers so that they can be miscible or compatible with the hydrophobic polymeric matrix.

Clay minerals such as naturally occurring montmorillonite clay is a layer expanding silicate mineral, consisting of aluminosilicate layers stacked one above the other. In general, clay minerals consist of nanoplatelets with a length of about 0.5-1 $\mu$m and a thickness around 1 nm, leading to a large aspect ratio (500-1000). Each layer of the montmorillonite has a small net negative charge due to isomorphous substitution of ions in the framework. This charge is generally compensated by interlayer hydrated cations, which are easily exchanged for other cations. Cationic exchange between the silicate layers with long chain alkyl ammonium cations reduces their surface hydrophilicity favoring the interaction with the polymeric chains.[9,10] Consi-

derable amount of work has been reported on the interlayer swelling of the clay minerals.[11,12] The extent of swelling depends on the length and molecular dynamics of the alkyl chain and the cation-exchange capacity (CEC) of the clay.[13] The influence of solvents on the swelling capacity of pure sodium montmorillonite clay (MMT) has been reported by Burgentzle et al.[14]. Recently, Herrera et al.[15] reported the influence of aminosilane on the interlayer swelling of the laponite clay using toluene as a dispersing medium. They observed the interaction between the silanol groups with the broken edges of clay platelets. In contrary, Hongsping et al.[16] reported the intercalation of aminosilane between the clay platelets of montmorillonite clay swollen in water/ethanol mixture. In the previous paper, we reported that the solvent surface energy plays a crucial role in the grafting or intercalation of silane between the clay platelets.[17]

The objectives of this study are to investigate the influence of silane concentration and processing temperature on the chemical functionalization of montmorillonite clay with 3-aminopropyltriethoxy silane in two solvent mediums.

# Ⅱ. Experimental

## 1. Materials

Montmorillonite clay, Cloisite Na$^{\oplus}$, was obtained from the Southern Clay Products Inc., USA. 3-Aminopropyl triethoxysilane, ethylene glycol and hydrochloric acid were obtained from Aldrich Chemical Company Inc., USA.

## 2. Functionalization of montmorillonite

One gram of clay was dispersed in the 100 ml of solvent at 25 ℃ using a mechanical stirrer. Known amount of 3-aminotriethoxy silane dissolved in 100 ml of solvent was added to the clay dispersion at a constant stirring condition and stirring was continued for 30 minutes. It was then filtered off and dried at 60 ℃ under vacuum condition. Alterna-

tively, clay was dispersed in hydrochloric acid/water mixture at 25 ℃ using mechanical stirrer and calculated amount of 3-aminopropyltriethoxysilane in water was added to the clay dispersion. It was then filtered off and washed with hot water followed by drying at 60 ℃ under vacuum condition. Samples were designated as $C_{xs/y}$, where C represents the MMT and the suffixes s represent the 3-amino propyltriethoxysilane, x represents the silane concentration, and y represents the dispersing medium. Distilled water was used as dispersing medium.

### 3. Characterization

About 0.01 gms of clay was mixed with 1 gm of potassium bromide (KBr) and pelletized in the hydraulic press at 10 KPa for FTIR analysis. FTIR spectra were taken in the range of 4000 to 400 cm$^{-1}$ using Perkin-Elmer 2000 spectrophotometer operated in the transmission mode. The resolution was kept at 4.0 cm$^{-1}$ and the number of scans was 32. Thermogravimetric analysis has been carried out using Perkin Elmer TGA in the temperature range

of 50 to 800 ℃ at a scanning rate of 10 ℃ min$^{-1}$ under nitrogen environment. X-ray diffraction have been performed using Macscience X-ray diffractometer equipped with a back monochromator operating at 40 KV and a copper cathode as the X-ray source ($\lambda$ = 1.54 A$^0$).

## Ⅲ. Results and Discussion

Clay minerals, which consist of tetrahedral Si-O sheets, posses significant amount of broken edges and structural defects in Si-O silicate edges that makes it active and undergoes grafting reaction with multifunctional silanes.[18] Figure 1 displays the FT-IR spectrum of the pure clay ($C_{0/0}$) and specific regions of the FT-IR spectra of the 3-aminopropyl triethoxysilane modified clay functionalized in water as the dispersing medium. The peak at 3635 cm$^{-1}$ corresponds to the hydroxyl stretching that is bonded to the aluminum and magnesium (Al (Mg) OH or Al (Al) OH) in $C_{0/0}$. The peaks at 3400 cm$^{-1}$ and at 1630 cm$^{-1}$ are due to the -OH stretching and
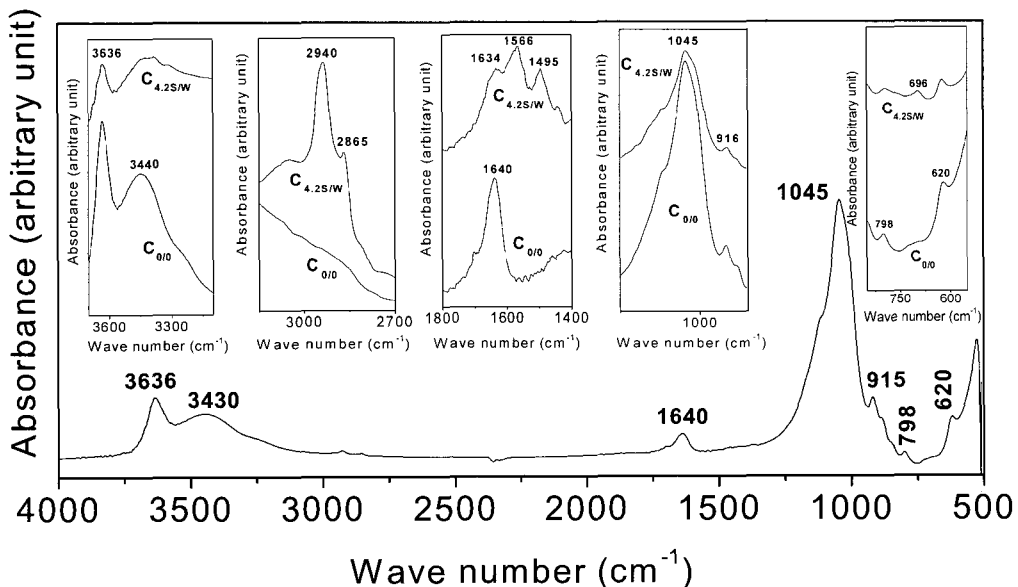


Figure 1. FT-IR spectra of pure and silane functionalized MMT's

bending vibrations of the adsorbed water, respectively. The broad peak over the range of 1200 to 1000 $cm^{-1}$ with the peak maximum at 1045 $cm^{-1}$ is due to the Si-O stretching of silicates present in the clay. The bending vibrations of Al (Al) OH and Mg (Mg) OH in $C_{0/0}$ occurs at 916 $cm^{-1}$ and 800 $cm^{-1}$, respectively. Aminosilane functionalization of the clay ($C_{1.0S/W}$) exhibits new peaks at 2930 $cm^{-1}$ and at 2850 $cm^{-1}$ that are corresponds to the -CH asymmetric and symmetric stretching of -$CH_2$ group confirming the presence of silane on the clay surface. Also, new peaks at 1566, 1496 and 690 $cm^{-1}$ that corresponds to the -$NH_2$, -$CH_2$ bending vibrations and -CH out of plane deformation further support this fact.

To picture out the nature of grafting between the silane and clay on using solvents such as water or HCl/water mixture as dispersing medium, peaks due to Al (Al) OH stretching, -$NH_2$ stretching and Si-O-Si stretching for the modified clays have been examined. The peak intensity at 3635 $cm^{-1}$ decreases in the case of modified clays indicating the hydrogen bonded interaction between the hydrolyzed silane with -OH group in Al (Al) OH group. Also, silane functionalization exhibits a drastic decrease in peak intensity at 3431 $cm^{-1}$ (stretching of water band) with peak broadening along with the appearance of small peak at 3291 $cm^{-1}$ (-NH stretching of $NH_2$ group) for modified clay ($C_{4.2S/W}$). The peak intensity at 3431 $cm^{-1}$ significantly changes on varying the dispersing medium as observed in our earlier report.[17] The probable reason could be the interaction of free hydroxyl groups in aminosilane resulting in surface grafting reaction between the silanol -OH groups and Al (Al) OH groups as reported by various researchers.[15-17] This is further supported by the decrease in peak intensity at 1640 $cm^{-1}$ with the shift in frequency for water bending vibration (1640 to 1634 $cm^{-1}$). The broad peak in the range of 1200 to 950 $cm^{-1}$ in $C_{0/0}$ is attributed to the overlap of Si-O stretching and Si-O bending vibrations. However, significant broadening of peak for the modified clays at 1045 $cm^{-1}$ indicates the interaction of the
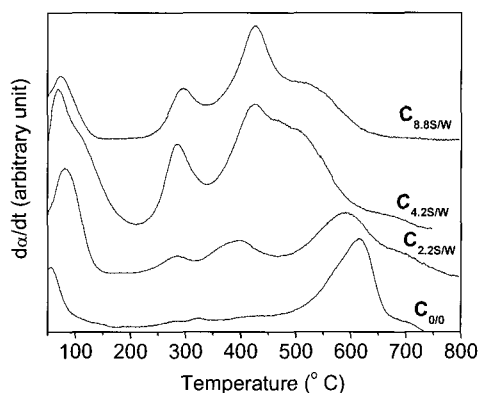


**Figure 2.** DTG curves of silanized MMT's with varying silane concentration.

silane with the platelet face.

To gain more knowledge on the influence of silane concentration and temperature on the reaction mechanism between the silane and MMT, thermal analysis was carried out to determine the amount of grafted silanes.

Figure 2 shows the differential thermogravimetric results of silanized MMT's with varying silane concentration using water as the dispersing medium. The weight loss of functionalized MMTs is more than that of pure MMT. The initial degradation of the pure clay below 100 ℃ is attributed to the vaporization of free water (between the pores and aggregates) and water bonded to the cations by hydrogen bonding or free solvents present between the pores.[18] The multiple degradation peaks between the temperature range of 200-600 ℃ is attributed to the degradation of silane molecules adsorbed/ intercalated between the clay platelets.[17] The major weight loss above 600 ℃ is due to the dehydroxylation of aluminosilicate groups.[10] Figure 2 also shows differential thermogravimetric results of $C_{S/W}$ with varying silane concentration. It is interesting to note the peak height at around 250 ℃ and at 395 ℃ increases on increasing the silane concentration from 2.2 ($C_{2.2S/W}$) to 4.2 ($C_{4.2S/W}$) and remains almost similar at higher silane concentration ($C_{8.8S/W}$). Also the peak at 395 ℃ shifts to higher temperature (425 ℃) on increasing the silane concentration from 2.2

($C_{2.2S/W}$) to 8.8 mmol/g ($C_{8.8S/W}$). It is quite interesting to note that intensity of the peak due to dehydroxylation of aluminum silicate layer (around 600 °C) decreases on loading silane, which is attributed to the chemical interaction between the silane and hydroxyl groups of aluminosilicate layers. This degradation peak completely vanishes at higher silane concentration (4.2 g/mol and 8.8 g/mol), which indicates the involvement of all hydroxyl groups in the chemical reaction with the adsorbed silane molecules. Also, the peak intensity of broad hump at around 490 °C decreases at higher silane concentration ($C_{8.8S/W}$). Earlier reports reveal that the peak at 450-550 °C is attributed to the chemically grafted and chemically intercalated silanes.[17] The decrease in peak intensity at 490 °C at higher silane concentration reveal that the excess silane molecules will remain as free silanes or it may react with the adjacent silane molecules due to the non-availability of the hydroxyl groups of aluminosilicate layers for chemical interaction.

X-ray diffraction patterns of the pure and functionalized MMT with various silane concentrations were shown in Figure 3. $C_{0/0}$ shows a sharp peak at around $2\theta = 7.0°$ that correspond to a $d$-spacing value of 12.6 Å. However, introduction of silane results in the shifting of peak towards lower $2\theta$ value with appearance of secondary peak at higher $2\theta$ values. From Figure 3, it is quite evident that the silane concentration has significant influence on the average d-spacing of the MMT. The appearance of secondary peak is attributed to the formation of aggregates, which is being referred as tactoids.[17] The intensity of the secondary peak increases with increase in silane concentration from 2.2 ($C_{2.2S/W}$) to 4.2 ($C_{4.2S/W}$) and decreases slightly at higher silane concentration ($C_{8.8S/W}$). Earlier report reveals that the intensity of secondary peak depends on the surface energy of solvent used.[17] Since in the present case, polar solvents like water was used as dispersing medium, the polar component of surface energy leads to hydrogen bonding with edge platelets and thereby resulting in the formation of tactoids.
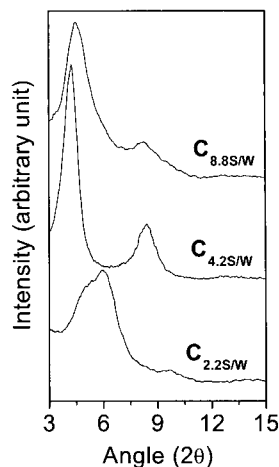


**Figure 3.** X-ray diffraction patterns of various silanized MMT's.
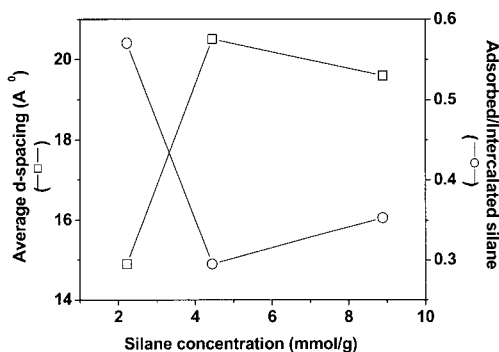


**Figure 4.** Influence of silane concentration on average d-spacing and adsorbed/intercalated ratio.

The influence of silane concentration on the average d-spacing and the ratio of adsorbed/intercalated silane are shown in Figure 4. The average d-spacing values increases and adsorbed/intercalated silane decreases at lower silane concentration. However, it remains constant at higher silane concentration. At lower silane concentration, silane molecules may adopt lateral monolayer orientation as proposed by Hengzhen et al.[19]. The higher adsorbed to intercalated silane at lower silane concentration is due to the interaction of silane with the broken edges of the clay platelets. The increase in average d-spacing with significant decrease in adsorbed/
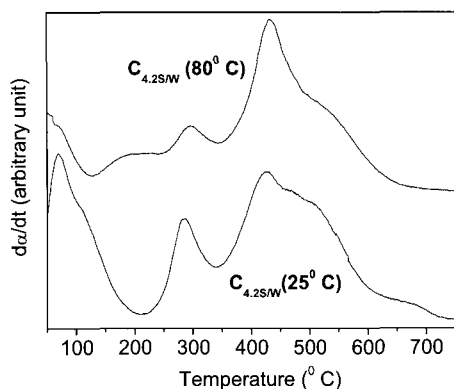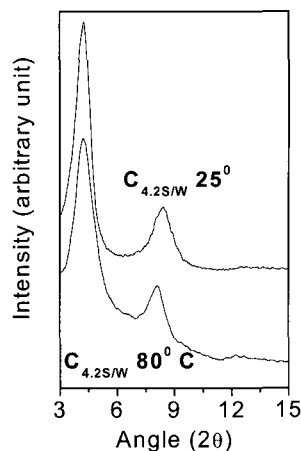
**Figure 5.** DTG curves of silanized MMT's processed at 25 and 80 ℃.
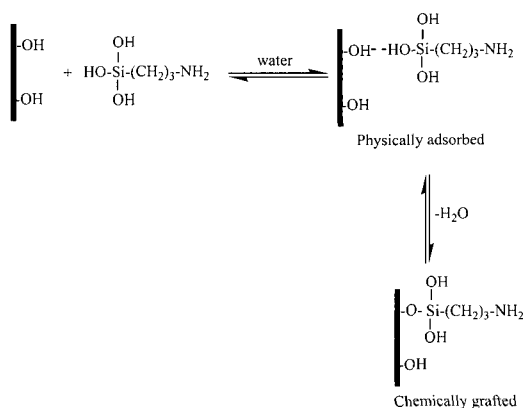


**Figure 6.** Proposed reaction scheme of adsorbed and chemically grafted silane.



**Figure 7.** X-ray diffraction patterns of silanized MMT's processed at 25 and 80 ℃.

intercalated silane at higher silane concentration may be attributed to the lateral bilayer orientation or paraffin like gallery structures due to the presence of excess silane molecules between the clay platelets.

Figure 5 shows DTG results of silane grafted MMT processed at two different temperatures (25 and 80 ℃). On increasing the processing temperature, it is interesting to note that the intensity of peak due to adsorbed silane decreases with the shifting of peak towards higher temperature. Also, the peak due to intercalated silane increases significantly on increasing the processing temperature. It is expected that the chemical interaction between silane and clay

is a thermoreverisble reaction as shown in the reaction scheme (Figure 6). On increasing the processing temperature, the reaction will precede forward leading to a chemically grafted silane molecules. This is supported by the positive shift in degradation peak in DTG curve. X-ray diffraction results of silane functionalized clay at two different temperatures are shown in Figure 7. From X-ray diffraction results, it is quite evident that there is no significant variation in peaks that corresponds to intercalation and tactoids on increasing the processing temperature.

## IV. Conclusions

The influence of trifunctional silane concentration on the properties of swelling clay materials dispersed in water medium has been investigated. The appearance of new peaks at 2930 and at 2850 $cm^{-1}$ that corresponds to the -CH asymmetric and symmetric stretching confirms the silane on the surface. The decrease in peak degradation temperature observed in DTG curve that corresponds to the dehydroxylation of aluminosilicate groups indicates the effective grafting of silane molecules with increase in silane concentration. X-ray diffraction studies of the silane functionalized clay corro-

borate two peaks that correspond to the intercalated and tactoid formation. Average d-spacing increases with silane concentration upto 4.2 mmol/g and decreases slightly at higher silane concentration, which is due to the decrease in adsorbed/intercalated ratio calculated using DTG analysis.

## Acknowledgement

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