

## Controlled silylation of montmorillonite and its polyethylene nanocomposites

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### Abstract

An alkylammonium modified montmorillonite, Cloisite 20A, was reacted with trimethylchlorosilane in order to replace the edge hydroxyl groups of the clay. Since the reaction will liberate HCl, reactions were performed both in the presence and absence of sodium hydrogencarbonate. Without sodium hydrogencarbonate, the proton, which was generated in situ, could replace a portion of the alkylammonium ions and further react with trimethylchlorosilane. The product, TMS-20H, has a smaller basal spacing than Cloisite 20A itself. If the proton was trapped by the hydrogencarbonate ions, only the edge silanol groups react with trimethylchlorosilane. The product, TMS-20A, maintained the same basal spacing as the precursor. The presence of the edge trimethylsilyl groups were confirmed by thermogravimetric analysis and infrared spectroscopy. Intercalated polyethylene nanocomposite could be fabricated by melt blending polyethylene with TMS-20A, while only microcomposites could be formed using TMS-20H. The structure of the hybrid was characterized by X-ray diffraction and transmission electron microscopy.

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### 1. Introduction

Layered silicates are very important in research and have many applications because of their unique structure; montmorillonite (MMT) is one of the most widely used layered silicates. The montmorillonite minerals occur as very small micron sized particles and they are extremely fine-grained and thin-layered. The structure of montmorillonite has been well defined. The building blocks [1] of montmorillonite are silicon—oxygen tetrahedra ( $\text{Si}_2\text{O}_5^{2-}$ ) and aluminum octahedra  $\text{Al}(\text{OH})_6^{3-}$ . The repeat unit contains two tetrahedral and one octahedral layer. The MMT layer has permanent negative charge because of the isomorphous substitution of, for instance,  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  or, rarely,  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$ . These net negative charges are balanced by charge-balancing cations such as sodium, potassium et al. between the clay layers in the gallery space. These ions are loosely bound to the silicate layers and exchangeable, which provide the common way to modify the silicates with organic cation to form an organic–inorganic complex [2]. The layer of

the MMT has a thickness about 1 nm and a length of 100 nm or a little more. Broken bonds on the edge are common phenomena for layered silicates and lead to the formation of hydroxyl groups [3,4], which can be utilized for chemical modification. The first attempt may be traced back to 1941 when Berger [5] found that hydroxyl groups of montmorillonite could be methylated with diazomethane. Deuel [6] also tried to make ester derivatives of montmorillonite. Ruiz-Hitzky [7] reported their efforts on the preparation of stable organic derivatives of several silicates using organochlorosilanes. It was found that the organochlorosilanes could only be grafted to the external surfaces of the silicates when the reactions took place in anhydrous petroleum ether. Further, they [8] showed that organochlorosilane could be grafted onto the internal surface of the silicate when the silicate was expanded by dimethylsulfoxide. In this case, the sodium silicate was changed to silicic acid by acid treatment [9,10]. The grafted organosilane is reported to show high thermal stability and does not degrade below 400 °C. The topic of modification of clays by various reagents has been treated in detail in a book by Utracki [11].

In summary, there are two ways to modify the layered silicates, covalent bond formation on the edges and ion exchange with organic cation. Yankgisawa [12] has blended these two methods together by reaction of the edge hydroxyls

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of organically-modified clays. Layered silicates, such as magadiite and kenyaite, were first modified by ion exchange with dodecyltrimethylammonium (DTMA) ion. Then the DTMA-silicates were further reacted with diphenylmethylchlorosilane (DPMCS), which could react with internal silanol groups, because the interlayer space of the silicate was expanded by the DTMA. Other organochlorosilanes were also successfully used to perform the same reaction [13,14] and similar reactions could be extended to another synthetic layered silicate, octosilicate [15].

Surface modification plays a very important role in polymer/clay nanocomposite formation. Sodium MMT modified by a small amount of (3-aminopropyl)trimethoxysilane was reported to facilitate the high extent of exfoliation of epoxy/clay nanocomposites [16] while trimethylsilylated clay can significantly retard the intercalation of a polar polymer, such as poly(styrene-*co*-acrylonitrile), into the clay gallery [17]. On the other hand, ion exchanged MMT has been used extensively in fabricating polymer/silicate nanocomposites [2,18,19]. Nanocomposites based on silicates can exhibit a remarkable improvement of many properties, such as enhanced mechanical properties, gas permeability and flame properties, compared with virgin polymers and usually less than 10% silicate is required to realize this improvement.

Polyethylene (PE) is one of the most widely used polyolefins. Due to its non-polar backbone, it is difficult to obtain nanocomposites without further modification of the organically-modified silicates. Immiscible/intercalated structure is the common morphology when organoammonium treated MMT is melt blended with polyethylene [20]. Better dispersion could be achieved using polyethylene-graft-maleic anhydride [21,22] as a compatibilizer, which can enhance the intercalation of the polymer chain with the silicate gallery.

In this paper, we describe a modified montmorillonite based on Yankgisawa's [12] method. Cloisite 20A, a montmorillonite modified with dimethyl dihydrogenatedtallow ammonium ions, was used and silylated both in the presence and the absence of a base, which led to two different trimethylsilyl derivatives and one of these can be directly melt blended with polyethylene to form nanocomposites.

## 2. Experimental

### 2.1. Materials

Trimethylchlorosilane (TMSCl), sodium hydrogencarbonate ( $\text{NaHCO}_3$ ) and HPLC grade acetone were obtained from Aldrich Chemical Company and used as received. Cloisite 20A was supplied by Southern Clay Products, Inc. Low-density polyethylene (LDPE) Petrothene NA960000, was supplied by Equistar Chemicals Company.

### 2.2. Trimethylsilylation of Cloisite 20A

A 10 g portion of Cloisite 20A was placed in a 500 ml three-neck round bottom flask charged with 300 ml of anhydrous acetone. The system was stirred under nitrogen for 20 min,

then 50 ml of trimethylchlorosilane was added at one time to the suspension and the system was gently refluxed for 72 h. The product was collected by filtration, washed with acetone, then with acetone/ $\text{H}_2\text{O}$  (50:50). After drying in a vacuum oven at 80 °C for 12 h, the product, TMS-20H, was ground to a powder. A small amount of TMS-20H was dispersed in a saturated saline solution for 24 h to remove the ammonium ions; the same process was repeated three times. The product, TMS-MMT, was filtered and air-dried. After grinding to a powder, the sample was analyzed by FT-IR.

### 2.3. Trimethylsilylation of Cloisite 20A in presence of $\text{NaHCO}_3$

A 10 g portion of Cloisite 20A and 42 g of  $\text{NaHCO}_3$  were placed in a 500 ml three-neck round bottom flask charged with 300 ml of anhydrous acetone. The system was vigorously stirred under nitrogen, and then a 50 ml portion of trimethylchlorosilane was added drop wise to the suspension over 3 h and the system was gently refluxed for 8 h. The product was collected by filtration, and then washed with acetone/ $\text{H}_2\text{O}$  (50:50). After drying in a vacuum oven at 80 °C for 12 h, the product, TMS-20A, was ground to a powder.

### 2.4. Preparation of LDPE—layered silicate nanocomposites

LDPE with modified montmorillonite were premixed in a beaker, then melt blended in a Brabender Plasticorder with a chamber of 50  $\text{cm}^3$  at 185 °C for 15 min at 60 rpm to obtain a well-mixed system. Three loadings of the organically-modified montmorillonite in polyethylene were used, 1, 3 and 5%. Upon completion of the melt blending, the molten complex was removed from the chamber and allowed to cool to room temperature.

### 2.5. Instrumentation

Fourier transform infrared spectroscopy, FT-IR, was performed on a Nicolet Magna-IR 560 spectrometer at a resolution at 4  $\text{cm}^{-1}$ . Powder X-ray diffraction measurements, XRD, were conducted on a Rigaku Geiger Flex, 2-circle powder diffractometer equipped with  $\text{Cu K}\alpha$  generator ( $\lambda = 1.5404 \text{ \AA}$ ) at 50 kV and 20 mA, scanning from 1 to 10° at 0.1° step size. Samples of montmorillonite for XRD were obtained by filtration while samples of polyethylene/MMT hybrids were compression molded at 180 °C to 15 mm  $\times$  10 mm  $\times$  1 mm plaques. Transmission electron microscopy (TEM) image was obtained at 100 kV with a JEOL 100CX transmission electron microscope. The samples for transmission electron microscopy were prepared by sectioning the sample blocks on a RMC PowerTome XL ultramicrotome with a RMC CRX cryosectioning attachment. The thin sections, approximately 70–80 nm thick, were cut at  $-125 \text{ }^\circ\text{C}$  with a diamond knife. The thin sections were picked up on a 300 mesh copper grid and stained with ruthenium tetroxide vapors. Thermogravimetric analysis (TGA) was carrying out on a SDT 9600 unit under nitrogen flowing (60–80 ml/min) at a scan rate of 20 °C/min. The sample was first equilibrated at 100 °C then heated up to

800 °C. Temperatures are reproducible to  $\pm 3$  °C while the fraction of non-volatile is repeatable to  $\pm 2\%$ . TGA/FTIR was performed on Cahn TG 131, which is connected to a Mattson Research grade FTIR with 60–80 ml/min of nitrogen flowing and a heating rate of 20 °C/min.

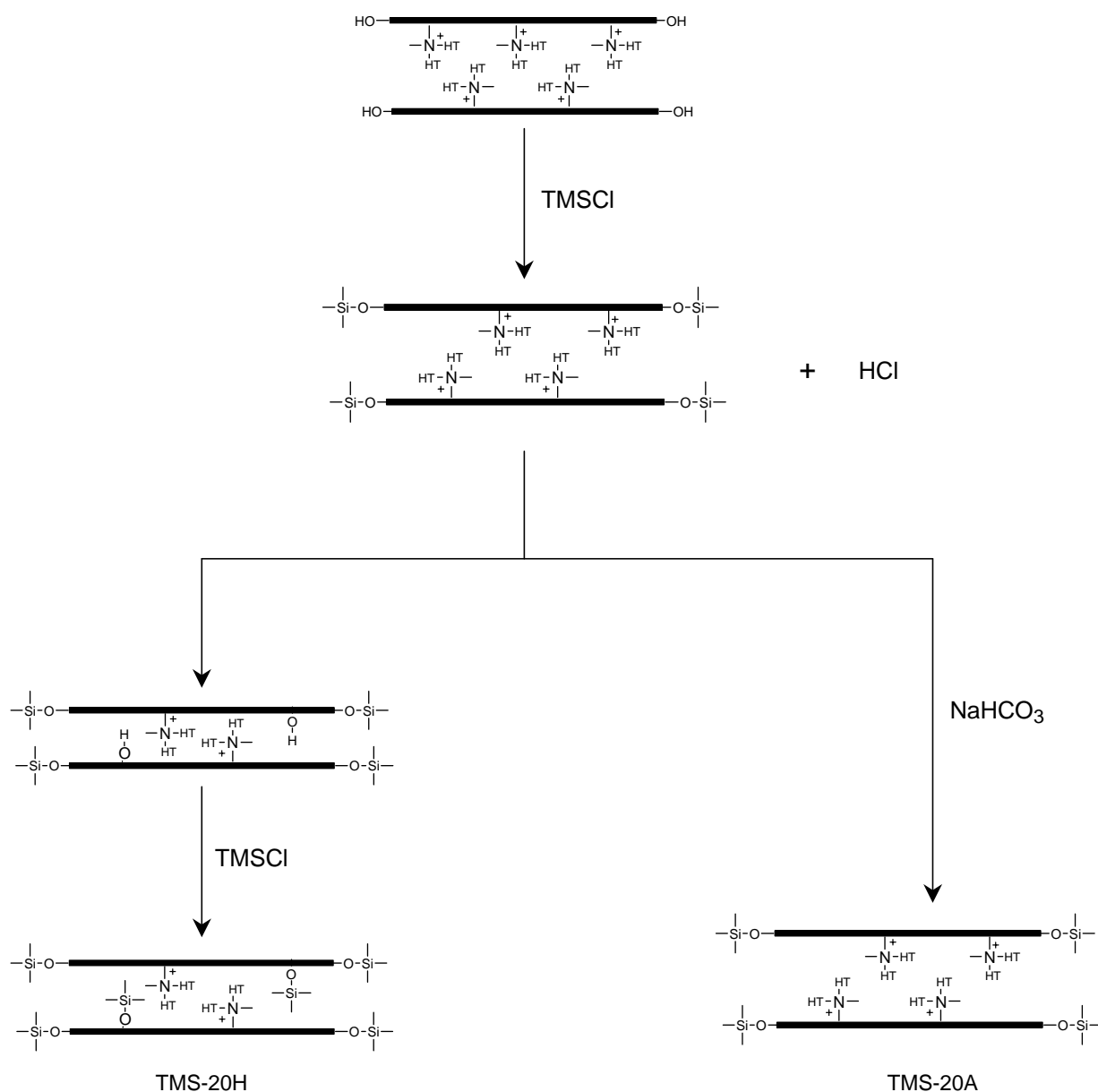
### 3. Results and discussion

The most recent work on silylation of layered silicates was done using magadiite [12,14] and octosilicate [15,23,24]. Zhao [25] et al. reported their work on silylation of sodium montmorillonite and their evidence for successful silylation was a very weak C–H vibration in the infrared spectrum. In this paper, instead of using sodium montmorillonite, an organically-modified montmorillonite was reacted with trimethylchlorosilane. The organic derivative of montmorillonite was

examined by TGA, XRD and FT-IR. The results strongly suggest that trimethylsilyl group has been successfully grafted to the surface of montmorillonite.

#### 3.1. Synthesis of trimethylsilyl derivatives of Cloisite 20A

Endo's [15] work on silylation of dodecyltrimethylammonium (DTMA) modified octosilicate showed that most of the DTMA ions were released during the reaction. The author proposed that DTMA ions were first replaced by the protons, which were generated by the condensation reaction between silanol groups and trimethylchlorosilane, then the newly formed silanol groups, which are at the internal surface of the silicate, could further react with trimethylchlorosilane. The detailed mechanism has been provided by Yankgisawa [26]. The TMS-octosilicate had a smaller basal spacing than DTMA modified



Scheme 1. Schematic diagram of the trimethylsilylation of Cloisite 20A.

octosilicate but still larger than sodium octosilicate. In another words, the proton is very crucial in this reaction. Here, Cloisite 20A, an organically-modified montmorillonite containing two hydrogenated tallow (HT) chains, was reacted with trimethylchlorosilane. The reaction product retained about one-half of the organoammonium ions, as shown by thermogravimetric analysis. If the proton is removed as it is generated, only the external silanol group can react with TMSCl and the organoammonium ions should be retained. The reaction mechanism is shown in Scheme 1. In order to determine if the TMS capped silanol groups are stable or exchangeable, the two organic derivatives were exchanged with the 20A salt. TGA shows that no additional ammonium cations were added, which indicates that there are no exchangeable ions, except 20A ammonium ions, present in the clay.

### 3.2. Characterization of trimethylsilyl derivatives of Cloisite 20A

Thermogravimetric analysis (TGA) was performed on the materials to obtain their organic content and information on their degradation. Ruiz-Hitzky [8] and Ogawa [14] mentioned that the organosilyl groups grafted to the silicates were highly thermal stable and started to decompose only at 400 °C. Fig. 1 provides the TGA curves, and their derivatives, for 20A and its silylated derivatives. From these TGA curves, the pertinent information has been extracted. The onset temperature of degradation, as measured in a TGA at a ramp rate of 20 °C/min, for Cloisite 20A is about 240 °C and the alkylammonium content is 30%. TMS-20A shows the same onset temperature while TMS-20H exhibits a higher onset temperature, 270 °C.

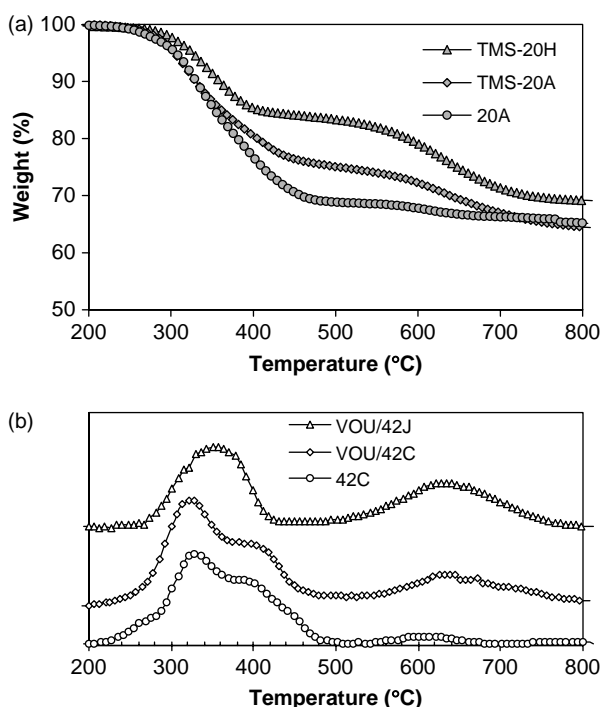


Fig. 1. TGA curves and its derivative for 20A and its silylated derivatives. (a) TGA curves (b) Derivatives of the TGA curves.

Comparing the derivatives of the TGA curves for the three systems, there is a clear similarity between Cloisite 20A and TMS-20A. Both show one major peak at about 330 °C with a shoulder at higher temperatures, based on previous work on the thermal degradation of organically-modified clays, this may be attributed to the release of olefin and amine [27]. In the region of 600 °C, a mass loss has been previously assigned to the loss of structural hydroxyl water from MMT [1]. Previous work on silylated clays has also suggested that the loss of the trimethylsilyl groups occurs in this temperature region, so this is likely the reason for a larger mass loss at high temperatures for the two silylated clays [28]. The TGA curve for TMS-20H is quite different with the lower temperature peak not showing a shoulder.

TMS-20H contains only 16% alkylammonium, meaning that one-half of the ammonium ions are lost during the silylation. TMS-20A contains 24% alkylammonium, this is 80% of the original amount of surfactant, which is present in Cloisite 20A. Hendrick [29] and Spencer [30] found that 20% of the cation exchange capacity of montmorillonite resides on the edges of the platelets and this result is in good agreement with that.

The second step of the degradation, which starts at 400 °C, is the loss of the trimethylsilyl group, which was suggested by Ruiz-Hitzky's DTA result [8]. The trimethylsilyl group is released very slowly between 400 and 500 °C and more quickly between 500 and 700 °C. TGA-FTIR spectra in this region do not show a difference for Cloisite 20A and its two silylated derivatives, probably because the amine continues to evolve in low amount, and the silicon-carbon stretching vibration cannot be observed.

The X-ray diffraction patterns for Cloisite 20A and its silylated derivatives are shown in Fig. 2. Cloisite 20A shows a strong peak at 3.6°, corresponding to a basal space of 2.4 nm. There is almost no change in the peak position for TMS-20A, which shows a strong diffraction at 3.7°. The released ammonium ions have negligible effect on the basal spacing, which has been also noted by Utracki [11]. For TMS-20H, where 50% of the ammonium ions have been lost, the peak appears at a new position, 4.6°, corresponding to a basal space

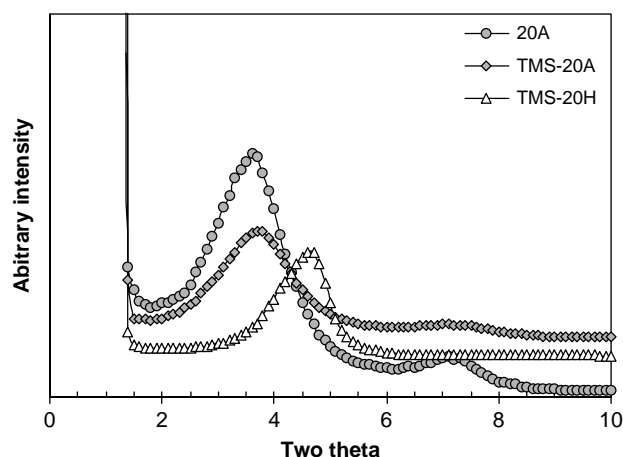


Fig. 2. X-ray diffraction patterns of 20A and its derivatives.

of 1.9 nm. The smaller amount of ammonium ions leads to a significant reduction in the basal spacing.

These silicates were further characterized by FT-IR. Due to the presence of ammonium ions, there is no difference observed in the FT-IR for 20A and its silylated derivatives and only the 20A spectrum is shown in Fig. 3. In order to obtain evidence for the trimethylsilyl group, TMS-20H was dispersed in saturated saline solution three times to exchange the ammonium ions. The FT-IR spectrum of the product after removal of ammonium ions, TMS-MMT, is also shown in Fig. 3. Peaks in  $3400\text{--}3600\text{ cm}^{-1}$  region are due to the silanol groups [15,26,31]. The very strong absorption at  $1050\text{ cm}^{-1}$  may be assigned to the Si–O stretch. The  $3000$  and  $1500\text{ cm}^{-1}$  regions, which are attributed to C–H stretching and bending, respectively, from the organic portion of the clay, are of interest. The characteristic peaks of alkylammonium occur at  $2926\text{ cm}^{-1}$ ,  $\nu_{\text{as}}(\text{CH}_3)$ ;  $2852\text{ cm}^{-1}$ ,  $\nu_{\text{as}}(\text{CH}_2)$ ; and  $1470\text{ cm}^{-1}$ ,  $\delta_{\text{s}}(\text{CH}_2)$ . For TMS-MMT, the absorption at  $1470\text{ cm}^{-1}$  is totally lost, indicating the absence of alkylammonium. Two relatively weak absorption bands at  $2926$  and  $2855\text{ cm}^{-1}$  can only arise from trimethylsilyl groups in the silicate.

### 3.3. Characterization of polyethylene composites

Previous work [20] has shown that Cloisite 20A is not well dispersed in polyethylene by melt blending. It is believed that the strong electrostatic attraction between the silicate layers hinders the intercalation of polymer into the clay gallery [32] and the edge hydroxyl groups on the clay surface may also be part of the reason for the immiscibility between polymer and clay [17]. Can the miscibility be improved by the silicate surface modification? The XRD patterns of polyethylene nanocomposites containing TMS-20A are displayed in Fig. 4, where TMS-20A is shown as a reference and the data is listed in Table 1. The XRD pattern for polyethylene containing TMS-20H is shown in Fig. 5, along with TMS-20H as a reference. TMS-20A has a strong peak at  $3.7^\circ$ , indicating a 2.4 nm basal spacing. When 5% TMS-20A is dispersed in the polyethylene matrix, the reflection becomes broad and the peak shifts to  $3.0^\circ$ , a 2.7 nm basal spacing. With 3% TMS-20A, the peak shifts to

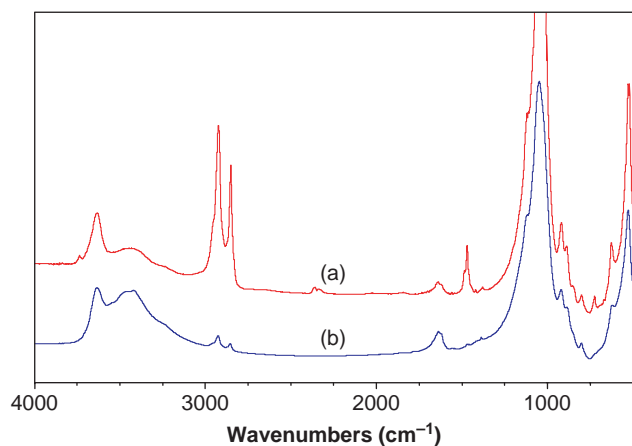


Fig. 3. FT-IR spectra of (a) 20A and (b) TMS-MMT.

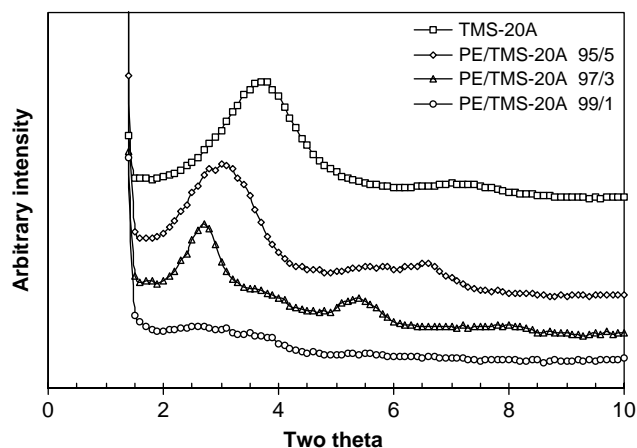


Fig. 4. XRD patterns for TMS-20A and its polyethylene nanocomposites.

$2.7^\circ$ , a 3.3 nm basal spacing. No peak can be seen when the loading of TMS-20A is 1%. The trend is very clear. The  $d$ -spacing increases when PE is combined with the clay, probably because the PE enters the gallery space and forces the galleries apart. With less silicate in the composite, there is more chance for polyethylene chains to intercalate into the gallery [33]. Based on XRD alone, this appears to be intercalated nanocomposite. As shown in Fig. 5, the XRD shows the same peak position for TMS-20H and its polyethylene composite; there is no intercalation process at any silicate loading. The lack of a change in the  $d$ -spacing probably means that the polymer does not enter the gallery space. Only a microcomposite can be formed even though the surfaces of the silicate are modified by trimethylsilyl groups.

Table 1  
XRD data for TMS-20A and its PE nanocomposites

Composition		$2\theta$ ( $^\circ$ )	Basal spacing (nm)
PE	TMS-20A		
–	100	3.7	2.4
95	5	3.0	2.7
97	3	2.7	3.3
99	1	–	–

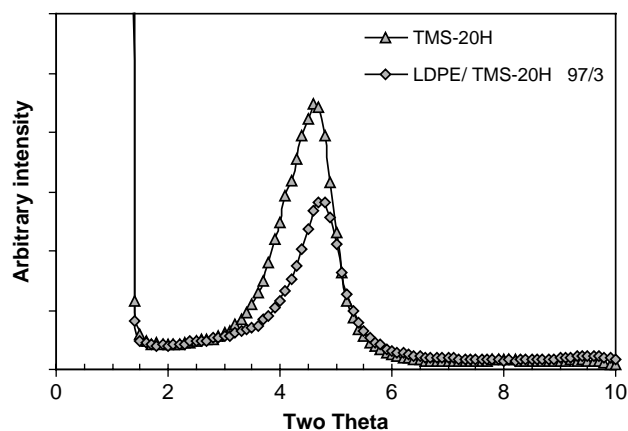


Fig. 5. XRD patterns for TMS-20H and its polyethylene microcomposites.



Apparently in the case of TMS-20H, the gallery space is not sufficiently organophilic, perhaps due to the reduced amount of surfactant, to permit the entry of the polymer. Comparing Cloisite 20A and TMS-20A, it is likely that removal of the edge

hydroxyl is necessary to render the clay sufficiently organophilic for facile nanocomposite formation; apparently both edge modification and a organophilic gallery space are required to form a PE nanocomposite.

The utilization of X-ray diffractions alone is not enough to determine the morphology of a nanocomposite; transmission electron microscopy (TEM) is required and has been used [34]. TEM images of the polyethylene and TMS-20A nanocomposites at 3% clay loading were obtained and are shown in Fig. 6. Well-dispersed clay and few clay tactoids are obvious in the low magnification image while intercalated clay layers are evident in the high magnification images. The polyethylene nanocomposites based on TMS-20A have an intercalated structure and the hybrid shows much better nano-dispersion than that obtained by the melt blending of PE with Cloisite 20A [20].

#### 4. Conclusions

The condensation reaction between trimethylchlorosilane and Cloisite 20A clay can be controlled by the presence of sodium hydrogencarbonate to capture the proton liberated by the condensation reaction. If the proton is not removed, the trimethylsilyl group can be grafted to both external and internal surfaces. The product, TMS-20H, has a smaller basal spacing than that of Cloisite 20A clay. The internal surface graft reaction was eliminated by capturing the proton with a base and the product, TMS-20A, has the same basal spacing as the 20A clay. Nanocomposites can only be fabricated by melt blending polyethylene with TMS-20A. Both the edges and the gallery space must be rendered organophilic to permit the entry of non-polar polymers, such as polyethylene, into the gallery space of the clay.

#### References

- [1] Van Olphen O. An introduction to clay colloid chemistry; 1977.
- [2] Ruiz-Hitzky E, Aranda P, Serratos JM. In: Auerbach SM, Carrado KA, Dutta PK, editors. Handbook of layered materials. New York, NY: Marcel Dekker, Inc.; 2004. p. 91–154.
- [3] Shi H, Lan T, Pinnavaia TJ. Interfacial effects on the reinforcement properties of polymer-organoclay nanocomposites. *Chem mater* 1996;8:1584.
- [4] Yariv S, Cross H. Organo-clay complexes and interactions; 2002.
- [5] Berger G. The structure of montmorillonite. Preliminary communication on the ability of clays and clay minerals to be methylated. *Chem Weekblad* 1941;38:42–3.
- [6] Deuel H, Huber G, Iberg R. Organic derivatives of clay minerals. *Helv Chim Acta* 1950;33:1229–32.
- [7] Ruiz-Hitzky E, Fripiat JJ. Organomineral derivatives obtained by reacting organochlorosilanes with the surface of silicates in organic solvents. *Clay Clay Miner* 1976;24:25–30.
- [8] Ruiz-Hitzky E, Rojo JM. Intracrystalline grafting on layer silicic acids. *Nature* 1980;287:28–30.
- [9] Eugster HP. Hydrous sodium silicates from Lake Magadi, Kenya: precursors of bedded chert. *Science* 1967;157:1177–80.
- [10] Lagaly G, Beneke K, Weiss AZ. Magadiite, H-magadiite. II. H-magadiite and its intercalation compounds. *Am Miner* 1975;60:650–8.
- [11] Utracki LA., Clay-containing polymeric nanocomposites, Rapra technology, Shawbury, Shrewsbury, Shropshire, UK, 2004, p. 85–198.

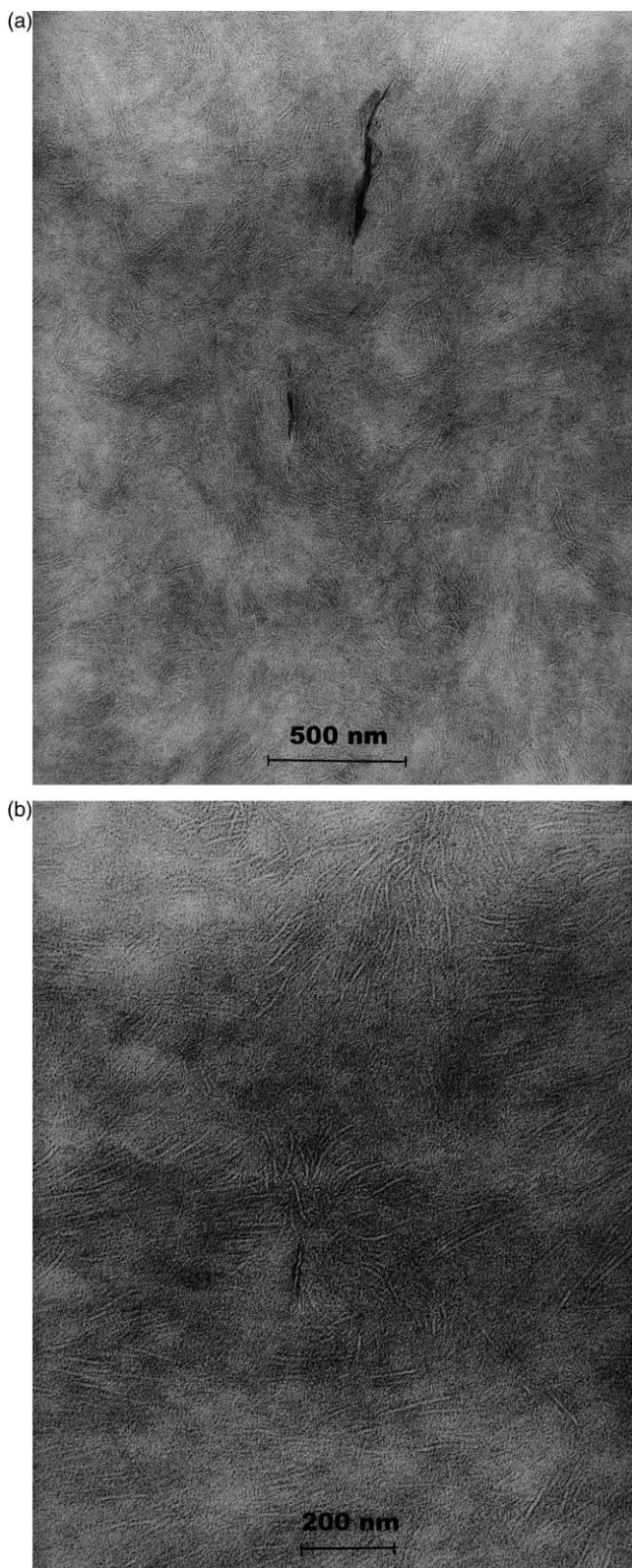


Fig. 6. TEM images of PE nanocomposite at 3% clay loading.

- [12] Yanagisawa T, Kuroda K, Kato C. Organic derivatives of layered polysilicates. II. Reaction of magadiite and kenyaite with diphenylmethylchlorosilane. *Bull Chem Soc Jpn* 1988;61:3743–5.
- [13] Ogawa M, Okutomo S, Kuroda K. Control of interlayer microstructures of a layered silicate by surface modification with organochlorosilanes. *J Am Chem Soc* 1998;120:7361–2.
- [14] Ogawa M, Miyoshi M, Kuroda K. Perfluoroalkylsilylation of the interlayer silanol groups of a layered silicate, magadiite. *Chem Mater* 1998;10:3787–9.
- [15] Endo K, Sugahara Y, Kuroda K. Formation of intercalation compounds of a layered sodium octosilicate with *n*-alkyltrimethylammonium ions and the application to organic derivatization. *Bull Chem Soc Jpn* 1994;67:3352–5.
- [16] Wang K, Wang L, Wu J, Chen L, He C. Preparation of highly exfoliated epoxy/clay nanocomposites by ‘slurry compounding’: process and mechanisms. *Langmuir* 2005;21:3613–8.
- [17] Lee S, Kim J. Surface modification of clay and its effect on the intercalation behavior of the polymer/clay nanocomposites. *J Polym Sci Part B Polym Phys* 2004;42:2367–72.
- [18] Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Mat Sci Eng* 2000;28:1–63.
- [19] Ray SS, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Prog Polym Sci* 2003;28:1539–641.
- [20] Zhang J, Wilkie CA. Preparation and flammability properties of polyethylene-clay nanocomposites. *Polym Degrad Stab* 2003;80:163–9.
- [21] Liang G, Xu J, Bao S, Xu W. Polyethylene/maleic anhydride grafted polyethylene/organic-montmorillonite nanocomposites. I. Preparation, microstructure, and mechanical properties. *J Appl Polym Sci* 2004;91:3974–80.
- [22] Zhai H, Xu W, Guo H, Zhou Z, Shen S, Song Q. Preparation and characterization of PE and PE-g-MAH/montmorillonite nanocomposites. *Eur Polym J* 2004;40:2539–45.
- [23] Mochizuki D, Shimojima A, Kuroda K. Formation of a new crystalline silicate structure by grafting dialkoxysilyl groups on layered octosilicate. *J Am Chem Soc* 2002;124:12082–3.
- [24] Mochizuki D, Shimojima A, Imagawa T, Kuroda K. Molecular manipulation of two- and three-dimensional silica nanostructures by alkoxysilylation of a layered silicate octosilicate and subsequent hydrolysis of alkoxy groups. *J Am Chem Soc* 2005;127:7183–91.
- [25] Zhao C, Feng M, Gong F, Qin H, Yang M. Preparation and characterization of polyethylene-clay nanocomposites by using chlorosilane-modified clay. *J Appl Polym Sci* 2004;93:676–80.
- [26] Yankisawa T, Kuroda K, Kato C. Organic derivatives of layered polysilicates. I. Trimethylsilylation of magadiite and kenyaite. *React Solid* 1988;5:167–75.
- [27] Zu J, Morgan AB, Lamelas FJ, Wilkie CA. Fire properties of polystyrene-clay nanocomposites. *Chem Mater* 2001;13:3774–80.
- [28] Herrera NN, Letoffe J-M, Putaux J-L, David L, Bourgeat-Lami E. Aqueous dispersions of silane-functionalized laponite clay platelets. A first step toward the elaboration of water-based polymer-clay nanocomposites. *Langmuir* 2004;20:1564–71.
- [29] Hendricks SB, Nelson RA, Alexander LT. Hydration mechanism of the clay mineral montmorillonite saturated with various cations. *J Am Chem Soc* 1940;62:1457–64.
- [30] Spencer WF, Gieseking JE. Organic derivatives of montmorillonite. *J Phys Chem* 1952;56:751–3.
- [31] Okutomo S, Kuroda K, Ogawa M. Preparation and characterization of silylated—magadiites. *Appl Clay Sci* 1999;15:253–64.
- [32] Shi H, Lan T, Pinnavaia TJ. Interfacial effects on the reinforcement properties of polymer-organoclay nanocomposites. *Chem Mater* 1996;8:1584–7.
- [33] Becker O, Varley R, Simon G. Morphology, thermal relaxations and mechanical properties of layered silicate nanocomposites based upon high-functionality epoxy resins. *Polymer* 2002;43:4365–73.
- [34] Morgan AB, Gilman JW. Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and X-ray diffraction: a comparative study. *J Appl Polym Sci* 2003;87:1329–38.