Synthesis and Characterization of Covalently Functionalized Laponite Clay

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Received February 10, 2005. Revised Manuscript Received March 28, 2005

Covalently functionalized Laponite clay was synthesized through a condensation reaction of the clay's silanol groups with mono- and trifunctional alkoxy silanes. Most of the work focuses on primary-amine-containing modifications because that group offers a wide range of derivitization options. Various 3-aminopropyltrimethoxy silane (APS) treatments yielded 4−14 wt % of organic material bound to the clay. APS-treated clay was further reacted to yield attached methacrylate, benzophenone, and tertiary bromine groups capable of polymerization, photoinitiation, and atom transfer radical polymerization initiation, respectively. Studies using a monoalkoxy analogue of APS, aminopropyldimethylethoxysilane (APES), are consistent with the hypothesis that multifunctional alkoxy silanes can cause the clay sheets to link together, hindering the clay's dispersibility and the efficiency of subsequent surface ion-exchange reactions. The attached amines were further reacted to 40 and 80% conversion in the APS- and APES-treated Laponites. Quantification studies show that there are about 200 siloxane-reactive sites per clay sheet at a concentration of 11 mequiv per 100 g of clay. All products were characterized with thermogravimetric analysis and solid-state ^{13}C NMR to study the organic content and composition. ^{29}Si solid-state NMR was also used to compare the treated clay with untreated sodium Laponite. Changes in the ^{29}Si spectra were consistent with the expected silanol reaction.

Introduction

Over the past several years, much research has focused on polymer-clay nanocomposites.[1,2] Systems in which clay is well dispersed in a polymer matrix generally exhibit positive effects such as significant increases in mechanical properties and decreases in flammability at relatively low loadings, ca. 5 wt %.[3,4] Generally, the critical part of creating such a system is exfoliating the clay sheets and dispersing them throughout the polymer matrix to maximize interaction between the clay surface and the polymer. Most methods to date have focused on exchanging cations in the clay galleries with long-chain aliphatic quaternary ammonium or phosphonium compounds.[5−7] This substitution increases clay gallery spacing and creates a more favorable organophilic environment for polymer penetration and interaction. Another route to forming hydrophobic clay uses trialkoxysilanes as the silicon source during clay synthesis.[8,9] Also, sol−gel reaction in the presence of dispersed organically modified montmorillonite was used to form delaminated clay structures.[10] All of these clays, modified in some form, can then be used in polymer matrix nanocomposites. The two common methods of exfoliating clay in a polymer matrix include in situ polymerization and polymer mixing methods by melt compounding or solvent casting.[11] Both generally involve organically surface-modified clay.

Another possible modification is reaction of the silanol groups, which are assumed to be on the edge of the clay sheets.[12,13] This route uses chloro or alkoxy silanes with reaction presumably involving edge SiOH groups. Little work has been done on edge-modified clay, perhaps because the edge area is small relative to the surface for most clays. The treatment of Montmorillonite with trichloro and trialkoxy silanes has been reported, resulting in organic loadings of up to 25 wt %, with the intended application of hazardous material remediation.[12] They observed no increase in the clay's basal spacing, suggesting the organic compounds are bound to the outer clay edges. Methacrylate-terminated alkoxy silanes were also used to treat the edge of Laponite for applications in emulsion polymerizations.[14] They observed that trialkoxy silanes linked the clay sheet together, making them nondispersible, while monoalkoxy silane-

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10.1021/cm050306a CCC: $30.25

treated clays were dispersible in water. In another report, protonated amino-alkoxysilanes and α,ω-alkoxysilanes were used to create clay monoliths by cross linking clay particles together through their edges.[15]

Laponite is a relatively uniform disc-shaped synthetic clay 25 nm in diameter and 1 nm thick, as claimed by the manufacturer.[13] It has an empirical formula of $Na^{+0.7}[(Si_8Mg_{5.5}Li_{0.3})\,O_{20}(OH)_4]^{-0.7}$ and a cation exchange capacity of 50−55 mmol per 100 g. Laponite particles suspended in dilute aqueous solution are approximately 40 nm in diameter and 3.5 nm thick.[16] By assumption that the manufacturer's clay dimensions are correct, its high ratio of edge to surface area (0.07) makes it an ideal candidate for further investigating edge modification, since easily observed amounts of organic material can be attached. We have been exploring synthesis of edge modified Laponite clay using alkoxy silanes possessing additional reactive groups such as primary amines, methacrylates, benzophenones, and tertiary bromines.[17] With such structures, polymer chains can be grafted to, or grown from, clay edges, creating starlike or fringed polymers with a nanosized inorganic core. We have recently reported the synthesis of polymer grown from covalently bound atom transfer radical polymerization (ATRP) initiators from Laponite clay.[18] Extension to combined edge and surface modification of clay via different synthetic routes opens up possibilities for multifunctional nanomaterials, an area we are actively exploring. Combining edge and surface treatments may also aid in exfoliation in nonpolar polymer systems and in dispersing clay in water or organic solvents for more efficient reaction and blending.

Results and Discussion

Alkoxysilane Deposition. Reaction of the silanol groups was accomplished through a condensation reaction with aminopropyltrimethoxy silane (APS), aminopropyldimethylethoxysilane (APES), or trimethoxypropylsilane (TPS), as shown in Figure 1. Most of these efforts focused on APS-modified Laponite, primarily because the primary amine group offers a wide range of derivitization options and APS is relatively inexpensive. It was found that the procedure for treating the clay with APS was critical in maximizing the amount of bound material. Table 1 summarizes the methods evaluated, which are based on literature procedures for silica treatment with alkoxysilanes in either dry toluene or aqueous solutions.[19,20] By use of extensively dried Laponite, the toluene procedure resulted in approximately 5% bound organics based on thermogravimetric analysis (TGA) weight loss data. A procedure used for treating glass fibers in water at pH 5 (added acetic acid) at 50 °C was also used. After APS treatment, the water was pH adjusted to 9 to deprotonate the bound amine groups. This resulted in bound organic contents of between 4 and 13%, depending on reactant concentration, ranging from 1.7 to 3.3 wt % clay and APS. Overall, the aqueous treatments yielded material with a higher clay-bound organic content, probably due to oligomerization of the APS upon addition to the water and during clay treatment.[21] The aqueous procedure carried out in the absence of acetic acid (self-catalyzed by APS) resulted in similar amounts of binding. On the other hand, the toluene treatment reduced the possibility of oligomerization and showed the lowest amount of binding but with a greater likelihood of forming thinner, more uniform coverage.

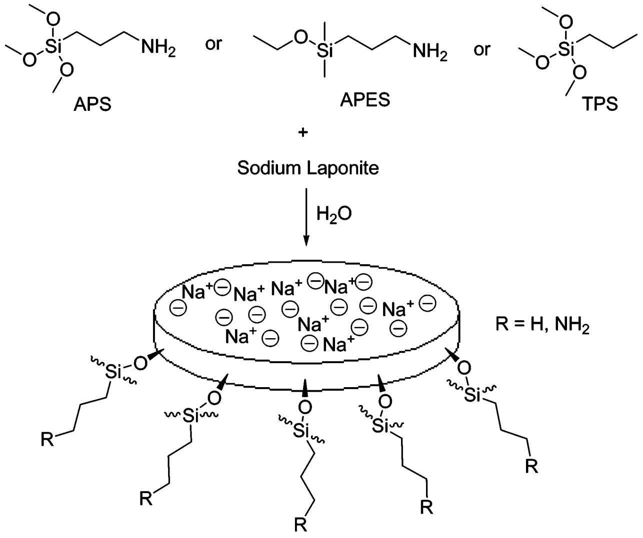

Figure 1. Schematic representation of a sheet of Laponite whose silanol groups have been reacted with alkoxy silanes.

Table 1. Organic Content of Laponite Treatments from TGA Analysis[a]

description	weight loss (150−600 °C)	amount organic[d]
sodium Laponite	4.6%	0.0%
Laponite/APS (toluene)	9.1%	4.5%
Laponite/APS (acetic acid, dilute)	8.8%	4.2%
Laponite/APS (acetic acid, concentrated)	17.2%	12.6%
Laponite/APS (no acid, concentrated)	13.5%	8.9%
Laponite/APS/AHM[b]	23.6%	19.0%
Laponite/APS/BBC[c]	25.4%	20.8%
Laponite/APS/BMB[b]	18.3%	13.7%
Laponite/TPS	10.5%	5.9%
Laponite/APES	N/A	1.3%
Laponite/APES/AHM	11.3%	6.7%
Aerosil/APS	10.3%	10.3%

[a] All TGA data was normalized at 150 °C to minimize variations in solvent and water loss. [b] APS clay with 8.9% organic content was used. [c] APS clay with 12.6% organic content was used. [d] A percentage (4.6%) was subtracted from the weight loss to account for the maximum possible amount of water loss.

Binding Mechanism of APS to Laponite. There are three obvious ways that APS can bind to Laponite: covalent bonds, ionic bonds, and physical adsorption. The goal here was to create covalent binding, and thus the mechanism was studied to determine if covalent binding was actually taking place. Physical and ionic binding were studied by treating

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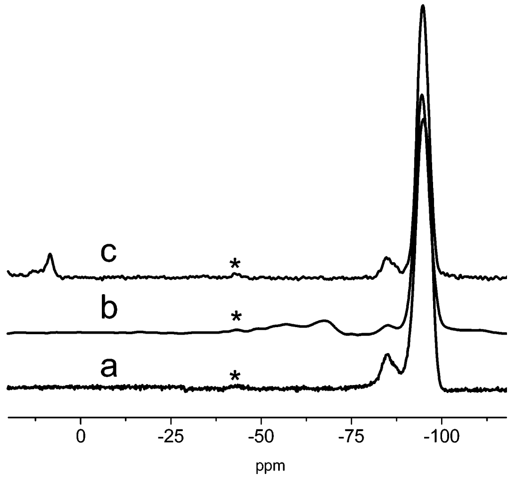

Figure 2. Solid-state ^{29}Si DP/MAS NMR spectra of (a) unmodified sodium Laponite, (b) APS-modified Laponite, (c) APES-modified Laponite. Spinning sidebands are denoted with an asterisk.

Laponite with control compounds, while covalent binding was directly studied by solid-state NMR.

One concern with APS treatment of Laponite is the possibility of ion exchange between protonated amine groups of the APS with sodium ions bound to the clay surface. The presence of organic molecules in clay galleries increases its interlayer spacing, which can usually be seen with wide-angle X-ray diffraction (WAXD). Sodium Laponite, due to its small size and disordered state, does not show a pronounced diffraction peak. None of the modified Laponites showed diffraction peaks, and this technique did not provide any information about ion exchange (data not shown). To verify that covalent binding was occurring, and not ionic surface exchange, sodium Laponite was treated with TPS, which has no amine group and thus no possibility of ionic interaction. This resulted in approximately 6% weight increase, in good agreement with the APS treatments, suggesting that most of the APS treatment results in chemically linked incorporation as opposed to ionic interaction. This result is also consistent with most or all of reaction taking place at the edge-localized SiOH groups.

Another test was performed to be sure that no ion exchange or strong physical binding was occurring and to develop an effective procedure for washing the clay. 1,3-Diaminopropane was added to a dispersion of Laponite in water and allowed to stir for several hours. A sample of clay was collected via centrifugation, redispersed in clean water, and collected again via centrifugation. This process was repeated two times. The water wash was inadequate at removing the diaminopropane, since its presence was seen by TGA. Another sample was collected and washed by the same procedure but using a 60% methanol in water mixture. This washing removed all organic material detectable with TGA. It has been found with other treatments that a polar organic solvent is required to efficiently remove amine-containing compounds.

Further evidence of successful covalent modification is seen in Figure 2, which illustrates quantitative ^{29}Si solid-state direct-polarization magic-angle spinning (DP/MAS) NMR analysis of unmodified sodium Laponite, APS-modified Laponite, and APES-modified Laponite. There are at least three types of silicon in Laponite: completely condensed silicons bonded through oxygen to three other silicons and one magnesium, an incompletely condensed silicon attached to an oxygen anion within the clay layer, and an incompletely condensed silicon attached to a hydroxyl on the clay sheet's edge. The NMR spectrum of unmodified Laponite shows a large peak at −95 ppm which represents the condensed silicons and a smaller peak with a shoulder at −85 ppm from the uncondensed silicons.[8,22,23] After APS treatment, the −85-ppm peak is clearly diminished, and the appearance of two broad peaks are observed at −67 and −56 ppm, corresponding to different condensation levels of the Si−O moieties in the bound APS.[24] On the basis of peak integration, the unmodified Laponite contained approximately 11% uncondensed silicons. After reaction with APS, the peak at −85 ppm represented only 4% of the silicons, indicating that about 65% of the uncondensed silicons had reacted. The remaining uncondensed silicons are either inaccessible (lying between the clay surface layers) or simply edge silanols that did not react. Figure 2c shows the ^{29}Si spectrum of APES-modified Laponite. APES is monofunctional and can only react with one silanol group. Again, the peak at −85 ppm diminished from 11 to 6.5%, indicating that 40% of the uncondensed silicons on Laponite reacted. The silicon of APES appears as a sharp peak at 8.5 ppm and accounts for 4% of the total spectrum integration, in good agreement with the observed decrease of 4.5% in the −85 ppm peak.

Further Clay Functionalization. Attaching primary amines to the edges of clay opens up a wide range of possible functionalization reactions. Thus, APS-treated clay was reacted to give attached methacrylate, benzophenone, and tertiary bromine groups capable of polymerization, photoinitiation, and ATRP initiation, respectively. Reaction schemes are shown in Figure 3. Methacrylate functionality was achieved through Michael addition of the clay-bound primary amines with 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM). The benzophenone group was attached via a reaction with 4-benzoyl-benzoyl chloride (BBC). Last, the reaction of 2-bromo-2-methylisopropionyl bromide (BMB) produced an amide-linked tertiary bromine capable of initiating ATRP.

Solid-state NMR results confirmed the chemical reactions expected. Figure 4 shows ^{13}C cross-polarization magic-angle spinning (CP/MAS) solid-state NMR spectra of the various clay derivatives, and Figure 5 shows ^{13}C solution NMR spectra of the alkoxy silane starting materials for reference purposes. Referring to Figure 4, APS-treated clay, shown in spectrum a, has three distinct aliphatic peaks. The absence of the silicon methoxy peak, which has a chemical shift of approximately 50 ppm, indicates complete hydrolysis. Spectra b, c, and d of Figure 4 are for the products of reaction of APS-treated clay with AHM, BBC, and BMB, respectively. These spectra have peaks consistent with the presence of the expected products, although their broadness can make interpretation difficult. In spectrum b, disappearance of the acrylate peaks at 128 and 132 ppm, retention of the methacrylate peaks at 126 and 136 ppm, and appearance of

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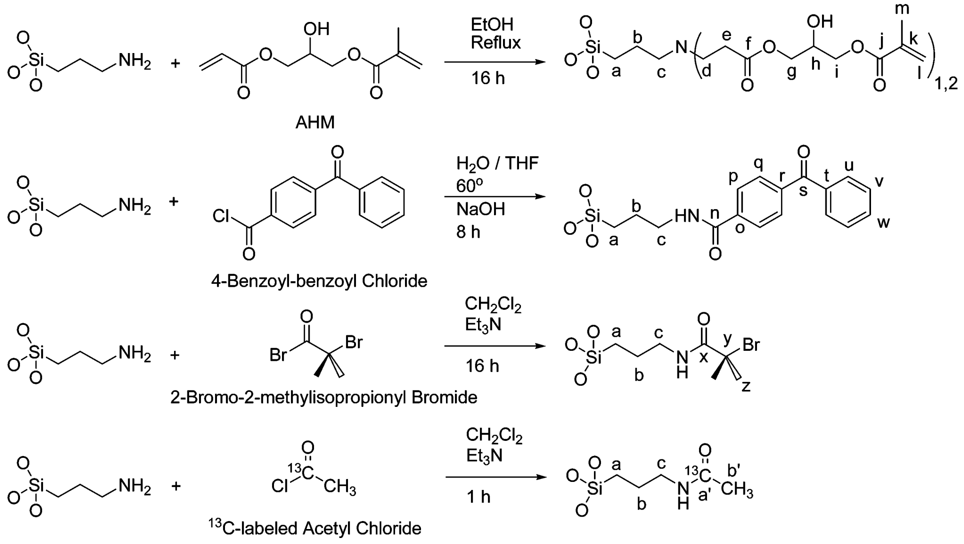

Figure 3. Reaction schemes for functionalization of APS-treated Laponite.

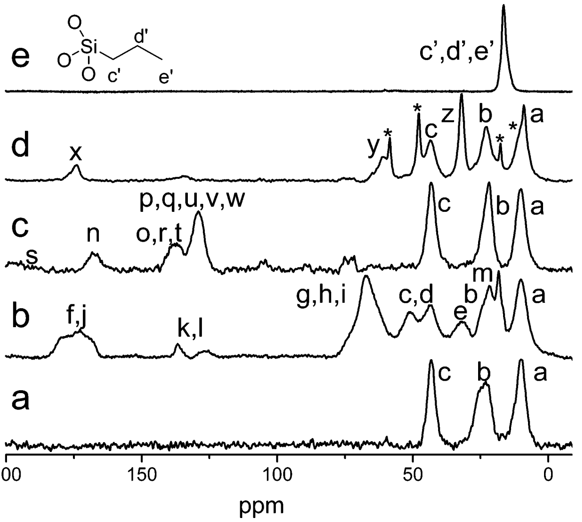

Figure 4. Solid-state ^{13}C CP/MAS NMR spectra of modified Laponite clays. Modifications are (a) APS (aqueous treatment), (b) APS with AHM, (c) APS with BBC, (d) APS with BMB (asterisk denotes triethylamine and solvent contamination), (e) clay with TPS.

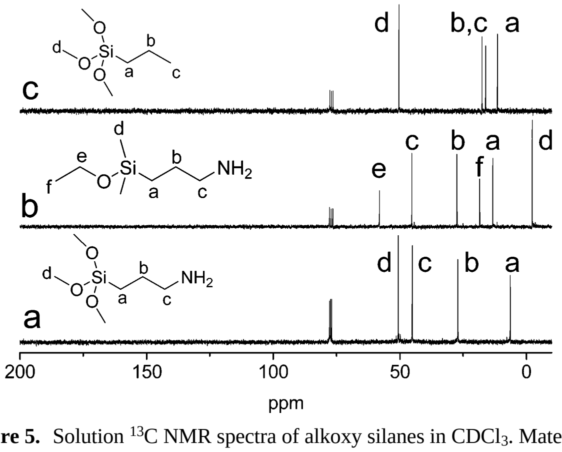

Figure 5. Solution ^{13}C NMR spectra of alkoxy silanes in $CDCl_3$. Materials are (a) aminopropyltrimethoxysilane (APS), (b) aminopropyldimethylethoxysilane (APES), (c) trimethoxypropylsilane (TPS).

aliphatic peaks at 31 and 43 ppm suggest a successful Michael addition reaction. Note that the carbonyl resonance is relatively broad, indicating both conjugated and nonconjugated ester groups. In spectrum c, the presence of ketone, carbonyl, and aromatic peaks at 197, 168, 138, and 129 ppm, respectively, confirms the presence of BBC. Because chemical shift changes are so small, it is difficult to confirm chemical reaction from solid-state NMR spectrum alone. Spectrum d shows the product of BMB reacted with APS-treated Laponite. Again, although the presence of BMB is evident, only slight chemical shift changes are expected and are difficult to observe in this spectrum. Also present in this sample is triethylamine (or the respective salt), observed at 10 and 50 ppm, which was used in the synthesis of this material and was not washed away during cleanup. There is also a small amount of contaminant, probably ethanol, observed at 18 and 58 ppm. Spectra e shows TPS-treated clay. Again, the absence of the methoxy peak indicates complete hydrolysis. Surprisingly, the three aliphatic carbons in TPS have very similar chemical shifts (verified by solution NMR of the starting material in $CDCl_3$) and thus appear as a single broad peak in the spectrum.

Quantitation of organic material bound to the edge of Laponite was accomplished with TGA weight loss data, shown in Table 1. As discussed earlier, the amount of bound APS depends on the treatment procedure and ranged from 4 to 12%. Subsequent reaction of the APS Laponite with the various reagents increased the organic content to ca. 20%, consistent with amine conversions of ca. 35%.

Amine Reactivity and Accessibility Studies. It is important to know about the reactive accessibility of the grafted amines, since there may be barriers to reaction in such an environment. This is a heterogeneous system, and the APS treatment has the ability to form oligomers and link the clay sheets together, both of which can sterically block access. Thus, the activity and accessibility of the APS- and APES-treated Laponite, and APS-treated Aerosil (fumed silica), were studied via acylation with ^{13}C-labeled acetyl chloride and quantitative solid-state ^{13}C DP/MAS NMR analysis (Figure 6). By comparison of the integral of the carbonyl region to the integral of the aliphatic region, amine end-group conversion with the labeled acetyl chloride can be determined. ^{13}C-labeled material was used to enhance the signal of the carbonyl carbon to achieve more accurate

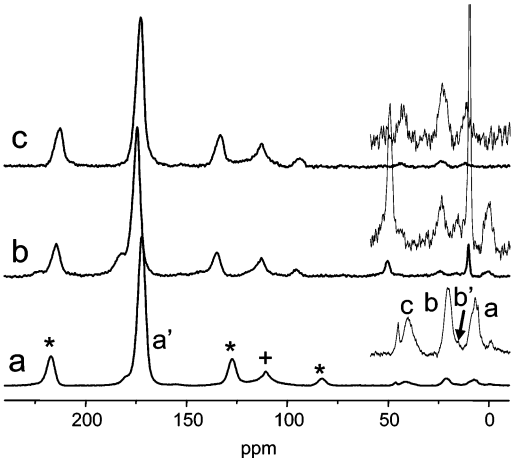

Figure 6. Quantitative solid-state ^{13}C DP/MAS NMR spectra of ^{13}C-labeled acetyl chloride materials. Materials are (a) APS-treated Laponite (aqueous treatment), (b) APES-treated Laponite, (c) APS-treated Aerosil. Spinning sidebands on the spectrum (a) are denoted with an asterisk. The Teflon NMR rotor signal is denoted with "+".

analyses. It is important to note that the spinning sidebands were integrated as well, since they quantitatively contribute to the total NMR signal.

From this analysis, APS-treated Laponite involved 46% amine conversion with acetyl chloride. This is in agreement with the reactions of APS-treated clay with AHM, BBC, and BMB which yielded 29, 34, and 40% conversion, respectively, as calculated from TGA weight loss. There are several possible reasons for lack of complete reaction of the amines, including isolation under an oligomeric layer of APS, hydrogen bonding with other amines and silanols,[25] entrapment of APS in the clay interlayers, or steric inhibition caused by adjacent groups which have already reacted. To explore these possibilities in greater detail, experiments were carried out using a monoalkoxy silane treated Laponite and APS-treated nonporous silica (Aerosil). A monoalkoxy silane has only one group that can react with the clay SiOH groups, eliminating the possibility of oligomerization interactions that would link APS groups and the clay sheets together. At most, exactly one APES molecule can bind to one silanol, creating a monolayer of amines on the silanol-functional areas of the clay. ^{13}C NMR analysis showed that 83 and 72%, respectively, of the amines bound to APES-treated Laponite and APS-treated Aerosil reacted with acetyl chloride.

It is interesting that, in the NMR spectrum of APES-treated Laponite, two peaks (10 and 50 ppm) are observed that are attributed to a triethylamine compound (triethylamine was used as acid scavenger in the acetyl chloride reactions). Amine salts can ionically bind to the surface of clay. These peaks were quite pronounced in the APES-treated Laponite, only slightly visible in the APS-treated clay, and absent in the Aerosil, indicating two possibilities. First, the surface of the APS-treated clay may not be completely accessible, probably due to the APS linking the sheets together. This behavior has been seen by others using trialkoxysilane treatments on Laponite.[14] Also, the low (40%) reactivity in the APS Laponite is probably due to nondispersability of the clay and amines trapped within the clay interlayer. This is supported by the fact that APS-treated Aerosil showed about 70% conversion. Possible structures of these treated materials are shown in Figure 7. Figure 7a depicts Laponite treated with APS, in which the sheets are linked together by a polymeric layer of APS, with APS molecules trapped in the clay interlayer. Figure 7b shows Laponite treated with APES, in which a monolayer of silane is grafted along the clay edge. Figure 7c shows Aerosil with a multilayer of condensed APS.

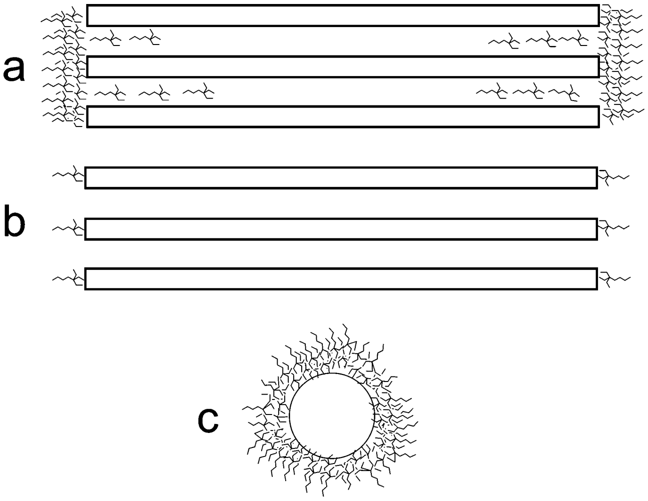

Figure 7. A depiction of possible structures of Laponite and Aerosil treated with trialkoxysilanes and monoalkoxysilanes. (a) Laponite treated with APS; (b) Laponite treated with APES; (c) Aerosil treated with APS.

Reactive Site Quantification. On the basis of data from the TGA studies done here, it is possible to estimate the number and distribution of reactive sites on the edges of Laponite. The volume of a single sheet of Laponite can be calculated as the volume of a cylinder. From the manufacturer's literature, each sheet of Laponite has an average diameter of 25 nm and height of 0.92 nm,[13] plus an intersheet gallery space of about 1.36 nm.[26] The density of Laponite could not be found in the literature, so Montmorillonite's density (2.86 g/cm^3)[27] was used for these calculations. With knowledge of the volume and density, the mass of a single Laponite sheet was estimated to be 3.20×10^{-18} g. Each APES can react with only one silanol, and its reaction with Laponite resulted in 1.3% bound organic material by weight. Each APES residue (at 116 g/mol) corresponds to 1.93×10^{-22} g after the reaction with the clay. Since there is 1.3% organic material on the clay, there is approximately 3.20×10^{-18} g $\times$ $(0.013/(1-0.013)) = 4.21 \times 10^{-20}$ g of organic material per sheet of clay. Dividing this number by the weight of each APES residue gives a value of 218 residues per sheet of Laponite. This implies that there are approximately 200 reactive sites per sheet of clay. By assumption that the sites are evenly distributed and only located on the clay edges, the average surface area per reactive site is 36.0 Å^2. This means that each reactive site occupies an equivalent square of about 6 Å × 6 Å, which seems reasonable based on the bond distances of silicon atoms in clay. It is also possible to calculate a molar-

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equivalent value of reactive sites per mass of clay, similar to a cation-exchange capacity value. In this case, based on a 1.3% weight gain from APES, there are 11 mequiv per 100 g of reactive SiOH sites in Laponite, compared to a cation-exchange capacity of 55 mequiv per 100 g. Although the edge accounts for only 7% of the clay's total surface area, it contains about 17% of functional/exchangeable sites.

Polymerizations with Methacrylate Laponite. Possible applications of edge-treated Laponite include compatibility modification for hybrid systems and polymer edge grafting. For example, AHM-treated clay may act as a multifunctional cross linker for free radical polymerization. Initial bulk polymerizations of MMA (methyl methacrylate) with added 10−50 wt % AHM-treated clay did not give cross-linked material. TGA analysis of the extracted clay showed a weight loss of about 50%, indicating that a small amount of polymer did bind to the clay, but no extensive cross-linked network formed. One possibility is that in AHM-treated Laponite, adjacent methacrylate groups are so close that radical propagation occurs between adjacent units much faster than with free monomer. This "zipping up" process would create a layer of polymerized AHM around the clay edge without significant reaction with polymerizing MMA.

Further experiments in which the benzophenone-treated Laponite will be used as a photoinitiator and cross-linking agent and the tertiary bromide for ATRP-initiating site are in progress. Other uses for these systems involve creating dual-functionalized clays, whereby one type of functional group is covalently linked to the edge while other groups are electrostatically bound to the clay surface. Thus, complementary groups may be attached to the same nanoparticle but in spatially separated nanoenvironments.

Conclusion

This work demonstrates a generic route to covalently modified Laponite clay with potential for incorporating a wide range of functionality. Evidence from solid-state NMR spectroscopy and TGA analyses indicate that the expected structures have been obtained. NMR studies of the accessibility of the amine groups on the functionalized clay indicate that about 40% are available in the APS Laponite vs 80% for the APES Laponite. The results are consistent with the hypothesis that trialkoxysilanes can link clay sheets together, reducing subsequent surface ion exchange capacity. Monoalkoxysilanes do not exhibit this behavior, and this type of treatment is recommended for nanocomposite applications. Quantitation studies indicate that there are approximately 200 reactive silanol sites per clay sheet, resulting in a bulk concentration of 11 mequiv per 100 g of Laponite.

Experimental Section

Materials. Laponite (RD grade) was obtained from Southern Clay Products, Inc. APES was purchased from Gelest, Inc. APS, TPS, AHM, BMB, MMA, thionyl chloride, 4-benzoyl-benzoic acid, and 1,3-diaminopropane were purchased from Aldrich Chemical Co. Aerosil 300, a nonporous silica,[28] was donated by Degussa. All materials were used as received unless otherwise noted.

Characterization. TGA analyses were performed on a TA Instruments SDT 2960 simultaneous DTA-TGA, at a rate of 20 °C/minute up to 800 °C under an air atmosphere. Solution NMR spectra were obtained on a Varian Mercury 300-MHz spectrometer. Solid-state NMR spectroscopy was performed on a Varian $^{\mathrm{UNITY}}$INOVA 400 spectrometer using a standard Chemagnetics 7.5-mm PENCIL-style probe. Samples were loaded into zirconia rotor sleeves, sealed with Teflon caps, and spun at rate of 4−4.5 kHz. The standard CP/MAS technique[29] was used with high-power proton decoupling implemented during data acquisition. In addition, the TOSS technique[30] was implemented to remove spinning sidebands. The acquisition parameters were as follows: ^{1}H 90° pulse width was 4.0 μs, the cross-polarization contact time was 1 ms, the dead time delay was 6.4 μs, and the acquisition time was 45 ms. A recycle delay of 3 s between scans was utilized. For quantitative ^{13}C and ^{29}Si acquisitions, DP/MAS, or Bloch Decay, techniques were used. The ^{13}C acquisition parameters were as follows: ^{13}C 90° pulse width was 4 μs, acquisition time was 45 ms, and recycle delay time was 40 s. The ^{29}Si acquisition parameters were as follows: ^{29}Si pulse width was 4 μs, acquisition time was 45 ms, and recycle delay time was 180 s.

Synthesis of BBC. 4-Benzoyl-benzoic acid (2.3 g 10 mmol) was mixed with 15 mL of thionyl chloride, and the mixture was refluxed overnight. After excess thionyl chloride was removed on a rotary evaporator, a mixture of benzene (7 mL) and petroleum ether (17 mL) was used to recrystallize BBC to give a white solid (1.4 g, 56% yield, mp 86−89 °C). H NMR ($CDCl_3$): 8.2−7.5 ppm (aromatic protons).

Treatment of Laponite with APS and TPS. Procedure 1. A 500-mL Erlenmeyer flask containing Laponite (5.0 g) in 150 mL of deionized water was stirred at 50 °C for 30 min. In a 250-mL Erlenmeyer flask, a solution of APS (5.0 mL, 28 mmol) and 150 mL of deionized water was prepared and the pH adjusted to 5 with acetic acid. This solution was heated to 50 °C and allowed to stir for 10 m. It was then poured into the Laponite dispersion, immediately causing the solution to turn cloudy and viscous. Stirring continued at 50 °C for 16 h. The pH was then adjusted to 9 with NaOH to neutralize the acetic acid and deprotonate the amines. The product was collected via vacuum filtration on a Buchner funnel as a white gel, washed with 500 mL water, then dried in a vacuum oven at 80 °C for 18 h. To remove residual contaminants, the product was ground to a fine power with a mortar and pestle, stirred in 150 mL of water, filtered and washed with 500 mL water, and dried in a vacuum oven at 80 °C for 18 h.

Procedure 2. This procedure was similar to procedure 1 except that the acid and base treatment steps were eliminated.

Procedure 3. This procedure was similar to procedure 1, except that the concentration of clay was increased and the scale of the treatment was decreased: Laponite (1.0 g) and APS (1.0 mL, 5.6 mmol) were mixed in a total volume of 30 mL of deionized water.

Procedure 4. Laponite was dried in a vacuum oven at 80 °C for 16 h, and APS and toluene were dried with molecular sieves. Laponite (3.3 g), APS (6.5 g, 36 mmol), and 110 mL of toluene were added to a 250-mL round-bottomed flask. The reactants were stirred and heated to reflux for 6 h. They were allowed to cool, collected via vacuum filtration on a Buchner funnel, and then transferred to a Soxhlet extractor and washed with toluene for 2 h. The product was dried in a vacuum oven at 100 °C for 16 h.

Procedure 5. Because of immiscibility, the TPS treatment was carried out in a 50/50 volumetric mixture of deionized water and ethanol. Thus, Laponite (1.0 g) was dispersed in 50 mL of a mixture

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of water and ethanol, stirred and heated to 50 °C. To this was added TPS (1.0 mL, 5.7 mmol), and the mixture stirred for 24 h; upon addition of the TPS, the mixture turned cloudy and viscous. The product was collected on a Buchner funnel, washed with 200 mL ethanol, and dried in a vacuum oven at 80 °C for 16 h.

Treatment and Washing of Laponite with 1,3-Diaminopropane. To a 250-mL Erlenmeyer flask was added Laponite (0.48 g) and deionized water (50 mL) and the mixture stirred for 20 min while being heated to 50 °C. To this flask was added 1,3-diaminopropane (1 mL) dissolved in water (10 mL). Upon addition, the solution turned slightly cloudy. After approximately 1 h of stirring, a 10 mL aliquot was removed and centrifuged. The supernatant was discarded, clean water added, and the clay redispersed. This procedure was repeated a total of two times. The remaining solution was centrifuged. The supernatant was discarded, 60% methanol in water was added, and the clay was redispersed. This procedure was repeated a total of three times.

Treatment of Laponite with APES. To a 500-mL Erlenmeyer flask was added Laponite (5 g) and deionized water (200 mL), and the mixture was stirred at 50 °C for 30 min. In a 150-mL Erlenmeyer flask was added APES (2.0 mL, 12.4 mmol) and 50 mL deionized of water, stirred for 30 min, and poured into the Laponite dispersion. Upon addition, the solution turned cloudy. It was allowed to stir at 50 °C for 16 h. The clay was collected via centrifugation, washed by dispersion in water followed by centrifugation, placed in a beaker, and dried under vacuum at 100 °C overnight. The clay was then dispersed in a 60% methanol/water mixture by stirring overnight. This mixture was centrifuged, the supernatant decanted, and dispersed again in 60% methanol/water. This procedure was repeated a total of five times to remove all unbound materials.

Treatment of APES−Laponite with AHM. To a 25-mL round-bottomed flask was added APES−Laponite (0.20 g), AHM (0.50 g, 2.3 mmol), and methylene chloride (5 mL). This mixture was stirred overnight, collected, and washed via dispersion and centrifugation two times with ethanol and two times with methylene chloride. The product was then dried in a vacuum oven at room temperature for 4 h.

Treatment of Aerosil with APS. To a 150-mL Erlenmeyer flask containing deionized water (65 mL) was added Aerosil 300 (2.16 g), and the mixture was stirred at 60 °C. To a 250-mL Erlenmeyer flask with deionized water (65 mL) was added APS (2.2 mL, 12.3 mmol), with stirring at 60 °C. The Aerosil mixture was added to the APS mixture, which was stirred at 60 °C overnight. The product was collected via centrifugation and washed by dispersion and centrifugation, 3 times in ethanol and 2 times in methylene chloride. The product was then dried at 80 °C under vacuum overnight.

Secondary Treatments of APS-Treated Laponite. Synthesis of Methacrylate Laponite. To a 25-mL round-bottomed flask was added APS-treated Laponite (0.50 g clay from procedure 2, 8.9% organic content), AHM (0.50 g, 2.3 mmol), and 5 mL of methanol. The flask was septum sealed and purged with argon for 10 min, then heated and stirred at 40 °C in an oil bath for 24 h. The product was collected via vacuum filtration on a Buchner funnel, washed with 100 mL methanol, and dried in a vacuum oven at 40 °C for 16 h.

Synthesis of Tertiary Bromine Laponite. In a septum-sealed and argon-purged 25-mL round-bottomed flask containing a mixture of APS-treated Laponite (0.50 g clay from procedure 2, 8.9% organic content), triethylamine (0.66 g, 6.5 mmol), and 10 mL methylene chloride, BMB (1.0 g, 4.3 mmol) was added dropwise. Upon addition of the BMB, the solution became hot and a precipitate formed. The reaction was stirred at room temperature for 16 h. The clay was collected in a Buchner funnel, washed with 100 mL of methanol, then transferred to a Soxhlet extractor, where it was washed with methanol for 16 h. The clay was collected and dried in a vacuum oven at 40 °C for 24 h.

Synthesis of BBC Laponite. APS-treated Laponite (0.8 g clay from procedure 3, 12.6% organic content) was dispersed in 40 mL of a 50/50 volumetric mixture of water and THF, stirred, and heated to 50 °C under a N_2 atmosphere. BBC (0.4 g, 1.6 mmol) dissolved in THF was added dropwise to the Laponite−APS suspension. NaOH (1 M solution) was added as needed to maintain a pH of 10. After addition of BBC, the reaction was stirred for 8 h. The product was collected on a Buchner funnel, washed once with 5 mL of deionized water and four times with THF, then dried in a vacuum oven at 60 °C for 24 h.

Synthesis of ^{13}C-Labeled Laponite. A solution of ^{13}C labeled acetyl chloride (0.25 g, 3.2 mmol) in 25 mL methylene chloride was prepared in a 50-mL flask. In a separate flask, APS-treated Laponite (2.03 g clay from procedure 3, 12.6% organic content) and triethylamine (0.44 mL, 3.2 mmol) were stirred rapidly in 150 mL of methylene chloride for 15 m. The two solutions were mixed and allowed to stir for 1 h. The solid was collected on a Buchner funnel and washed with 500 mL of distilled water. The sample was transferred to a beaker and dried in a vacuum oven at 50 °C for 2 days. The ^{13}C labeling reaction of APES-treated Laponite and APS-treated Aerosil follow similar procedures.

Synthesis of Poly(methyl methacrylate) and Laponite Composites. MMA (0.50 mL, 4.6 mmol), methacrylate-modified Laponite (0.10 and 0.50 g), and AIBN (30 mg, 0.2 mmol) were combined in a small test tube containing a stir bar. The test tube was septum sealed and purged with argon for 5 min. It was then heated with stirring to 60 °C in an oil bath for 16 h, resulting in solid polymer. To test for cross-linking, chloroform was added to the test tube and allowed to sit overnight. The clay was separated from the dissolved polymer via centrifugation, and the chloroform phase was decanted off. The clay was transferred to a Soxhlet extractor, washed with chloroform for 16 h, and dried in a vacuum oven at 60 °C for 16 h.

Acknowledgment. The authors thank NSF IGERT 0333136 for partial funding of this project. The authors thank Dr. William Jarrett for his assistance with the solid state NMR analysis.

CM050306A