Facile Processing of Clays into Organically-Modified Aerogels

Louis S. Somlai, Suneel A. Bandi, and David A. Schiraldi
Dept. of Macromolecular Science & Engineering, Case Western Reserve University, Cleveland, OH 44106

Lon J. Mathias
School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS 39406

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A facile process for the conversion of clay powders to organically modified clay aerogels (OMCAs) is reported. The resultant clay aerogels are of potential interest for a variety of applications, by themselves, or as a component in composite materials. Freeze-drying aqueous clay-surfactant solutions isolates these highly organized materials. Robust OMCAs are formed from clay-surfactant compositions that initially produce stable surfactant modified clay-water suspensions. Characterization of the OMCA by FTIR, WAXD, and TGA confirms the retention of surfactant after freeze-drying, while SEM and porosimetry data show a structural reorganization of clay sheet bundles. © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 1162–1168, 2006
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Introduction

The addition of small amounts of layered, smectic clays, when properly expanded or exfoliated, has been shown to increase thermomechanical properties of organic matrix polymers when combined through in situ polymerization of melt blending processes.[1] This technical development has led, in a very real way, to the existence of structural nanocomposites as a field of inquiry. The high aspect ratio and layered structure of clays, such as montmorillonite, are generally believed to be responsible for these nanocomposite property improvements. Because of their large, anionic surface areas, smectic clays can accept and exchange hydrated cations and other polar molecules within the interlayer position.[2] Surfactant ion exchange has been used to change the clay sheet surface chemistry and modify silicate interactions with polymers.[3] While working to incorporate new surfactants into clays for the modification of poly(ethylene terephthalate),[4] we observed the formation of unusual silicate structures that we subsequently identified as organically modified clay aerogels (OMCAs). These OMCAs are the first examples (to our knowledge) of surfactant modified clay aerogels.

Discovery and development of clay aerogels

The production of inorganic aerogels from silica and water was first reported by Kistler.[5,6] In this initial process, water was slowly removed from an aqueous silica mixture via a solvent exchange process using ethanol or ether to produce low density structures. The preparation of montmorillonite clay aerogels by freeze-drying clay hydrogels was reported by Mackenzie[7] and Call[8]; the resultant fibrous montmorillonite structures were described as possessing reasonable rigidity, but poor thermal stability at 110°C for extended time or when desiccated over phosphorus pentoxide. Similar processing of non-swelling clays, such as kaolin, only produced fine powders.

Weiss et al.[9] and Hoffman et al.[10] studied several clay-solvent combinations that produced rapid setting, thixotropic gels. These authors demonstrated that high vacuum sublimation of frozen thixotropic clay gels in water or benzene produced "gel skeletons" with remarkable elasticity (elastic compression up to 75% of their original volumes). Montmorillonite

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Correspondence concerning this article should be addressed to D. A. Schiraldi at das44@cwru.edu.

interlayer spacings, measured by X-ray diffraction, were shown to inversely correlate thixotropic and sedimentation volumes. Weiss proposed that high thixotropic volumes of montmorillonite solutions containing alkali ions were caused by a splitting of the montmorillonite crystal into thin layers.[9]

The effects of freeze-drying on the interlayer spacing of clay hydrogels was studied in greater depth by Norrish.[11] Although montmorillonite clay hydrogels were found to retain their shape and partial rigidity when water was removed, the interlayer spacing in sodium montmorillonite decreased from greater than 30 to 10 Å during freezing. Upon thawing, the original clay morphology was restored. Ice crystal formation was thought to be responsible for the collapse of the swollen structure, thus defining a mechanism for structural transformation, but the structure of the gel itself remained elusive.

Van Olphen proposed that particles within clay aerogels, produced using a freeze-drying process, are linked edge-to-face much like a "house of cards" owing to opposite surface and edge charges that exist in clays.[12] The author suggested ice crystals grow radially, pushing clay particles aside to promote parallel platelet alignment. The incorporation of polyelectrolytes into bentonite clay aerogels via freeze-drying of a polyelectrolyte-bentonite hydrogel was also studied by Van Olphen, who found the normally fragile aerogels to become stronger and tougher upon polyelectrolyte incorporation.[13]

The effects of process parameters, such as clay concentration and freezing rates, upon the size and shape of resultant clay aerogels was investigated by Nakazawa et al., who reported that decreases in clay concentrations and freezing rates resulted in pore shape changes from polygonal cells to thin lenses.[14] The authors proposed that pores remaining in the freeze-dried aerogel structure are "negatives" of the ice particles once formed and later sublimed. The aerogels produced by Nakazawa were stable to heat treatment up to 800°C, albeit with some shrinkage.[14]

A wide variety of applications of aerogels have developed over the past 20 years. The high surface area and low bulk density of such structures recommend them for use in sensors,[15] supported metal catalyst systems,[16] insulating materials,[17] as a general inorganic "glue" by which to attach a wide range of other materials,[18] and as an ultralight collection media for collecting particles from space.[19] In virtually every case, the aerogels used in these applications have been composed of silica, itself produced by sol-gel polymerization of silicon tetrachloride or silicon alkoxides. The structure of these silica aerogels has been well established and, to some extent, resembles a "string of beads."[20-23] A limited literature exists in which silica aerogels are combined with organic polymers to produce nanocomposite materials.[24-27] In none of these studies has the use of clay aerogels been investigated.

In the present study, montmorillonites, laponites, and synthetic fluoromica were ion exchanged using the hydrogen chloride-amine salt of monoaminated triethyleneglycol (MATEG-HCl). Isolation of MATEG-HCl modified clay from low viscosity hydrogels by freeze-drying yielded MATEG-HCl modified clay aerogels. A systematic study of process variables, such as clay type and concentration, surfactant type and concentration, shear rate, and freezing rate, on the resulting clay aerogel structure was undertaken. The MATEG-HCl modified OMCA structure was also characterized using TGA, FTIR, SEM, and porosimetry. Such modified clay structures are of interest for a wide range of applications ranging from polymer composites[28] and sound/thermal insulation to biological supports.[29,30]

Experimental Procedures

Materials and equipment

Unless otherwise indicated, solvents and reagents were purchased from Aldrich Chemical Company and used as received. Montmorillonite grades included: sodium-exchanged (PGW), 12-aminolauric acid exchanged (ALA), and octadecyltrimethyl quaternary amine salt (EXT) exchanged montmorillonite (cation exchange capacity (CEC) = 110 milliequivalents/100 g clay (MEQV)), which was used as received from Nanocor, Inc. An additional montmorillonite grade, Cloisite Na^+ (purified and sodium exchanged), Laponite D, Laponite S, and XLG, colloidal synthetic layered silicates (CEC = 60 MEQV), and synthetic fluorosilicate clay (CEC = 60 MEQV) were all used as received from Southern Clay Products. Fluoromica (CEC = 120 MEQV) was used as received from Unicoop Japan. Hectrabrite NT100, a highly purified bentonite clay (CEC = 120 MEQV), was used as received from The American Colloid Company. XTA-250, a purified monoaminated triethyleneglycol (MATEG), and an unpurified MATEG (XTG-512) were used as received from Huntsman Chemical Corporation. E-19–5 surfactant, a bis-2(2-hydroxyethyl) linear alkyloxypropylamine (12 to 15 carbon alkyl), and Q-19–5 surfactant, a methyl chloride quaternized form of E-19–5, were used as received from Tomah[3] Products. Deionized water was prepared using a Barnstead ROpure low-pressure reverse osmosis system plumbed to a Barnstead NANOpure ultrafiltration system (18 Mohm-cm resistivity).

A single speed Waring laboratory blender fitted with 1.25 L glass vessel, stainless steel rotor blade assembly, and lid was used for blending clays, water, and surfactant. A rotating lyophilization shell freezer (Virtis Freeze Mobile S2EL, 188-203 K temperature range) was used to freeze clay hydrogels in 2 L glass lyophilization shells. A Virtis Freeze Mobile 35EL freeze-dryer was used to sublime frozen clay hydrogels. In this way, half filled shells were rotated at 30 rotations per minute at a temperature of −80°C until frozen. Frozen shells were then evacuated 36 h using the freeze-dryer.

Clay aerogel preparation and characterization

The procedure of Kojima et al.[31] was modified as follows: to a 1.25 L glass blender vessel was added 250 mL deionized water and 3.57 g (4.3 mmol exchange sites) of Nanocor PGW clay. The mixture was blended 5 min, and then 0.86 mL of concentrated hydrochloric acid and 1.27 g (8.5 mmol) of purified MATEG (XTA-250) were added to yield a 2:1 surfactant: exchange site ratio. Blending was continued for an additional 5 min. The blender contents were transferred to a 2 L glass lyophilization shell with lid, and a second, identical batch of material was prepared and added to the same lyophilization shell. Hydrogels were frozen on a rotating lyophilization shell freezer with −80°C refrigerated ethanol bath, then freeze-dried. This procedure was followed for all other OMCA preparations.

Thermogravimetric analysis was performed using a TA Instruments SDT 2960 simultaneous DTA-TGA. WAXD data was obtained in transmission mode using a Siemens XPD-700P polymer diffraction system equipped with a two-dimensional, position-sensitive area detector. The sample-to-detector distance was 30 cm, yielding an angular scan from 4 to 10 degrees (2θ). An Electroscan E20 environmental scanning electron microscope (SEM) was used to collect scanning electron micrographs.

Results and Discussion

Preparation of organically modified montmorillonite clay aerogels

Combinations of surfactant and swelling clays that formed stable, translucent, low-viscosity surfactant-modified clay/water suspensions generally produced aerogel structures upon freeze-drying (Figure 1). As a result of freezing the clay suspension for 1h, highly ordered ice-clay patterns were observed through the lyophilization shell wall. After vacuum drying for approximately 48h, a soft, stacked-layer and highly ordered material was produced, with a sheet-like texture much different from the powdery nature of the starting clays. The starting, macroscopic clay particles of 5-50 μm diameter are comprised of multiple clay sheet aggregates. It is this sodium-exchanged form of montmorillonite clay that is normally used for the commercial preparation of organically modified clays. After the aqueous suspension/freeze-drying process, a sheet-like clay morphology was observed, indicating formation of patterned three-dimensional array structures. This structure was periodically revisited, and found to be stable for upwards of 4 years, standing under room temperature/humidity/fluorescent lighting conditions. The clay in these aerogels is not composed of individually exfoliated sheets—the dimensions are far too large to correspond to the galleries of montmorillonite. Instead, it appears that a simple geometric reorganization of the sheet stacks has taken place in which individual sheets have self-organized into layered arrays.

The aerogel structure shown in Figure 1 best resembles the "feather type" montmorillonite clay aerogel reported by Nakazawa.[14] Their feather type clay morphology had pores of 25 to 50 microns in diameter. Applying their line of thought to our system, we infer that the spaces between sheets are open passages previously filled with ice (Figure 2), although the interlayer voids in our aerogels are approximately 100 to 200 microns. The high vacuum freeze-drying process maintains the clay orientation during sublimation and avoids the liquid phase that could promote rearrangement and loss of aerogel structure.

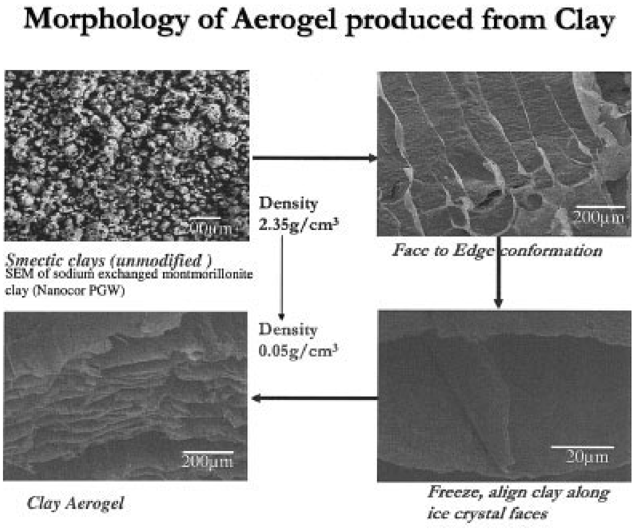


Figure 1. Morphology formation in clay aerogels.

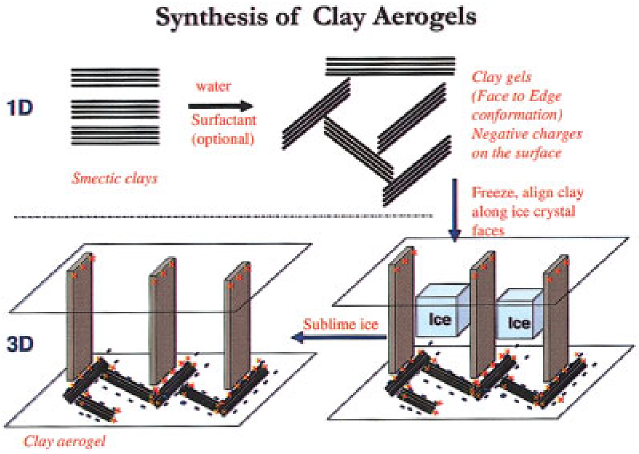


Figure 2. Synthesis of clay aerogels.

As shown in Table 1, a wide range of clay/surfactant systems was examined to determine the affects of composition and processing conditions on the final low bulk density clay structures. A range of different clays were observed to produce aerogels; sodium clays from different commercial sources and with different cation exchange capacities were found to perform equivalently under the freeze-drying process conditions. The final color of the OMCAs produced corresponded to the colors of the starting clays (montmorillonite OMCAs were beige in color while synthetic fluoromica OMCAs were white). In all cases, significant mixing of clay and water was necessary prior to freeze-drying to produce aerogel structures, likely reflecting a high shear requirement for break up of energetically favorable face-to-face clay sheet agglomerates. Quick, even, and efficient freezing was also found to be necessary to produce the aerogels.

Effects of clay:water ratio, surfactants, and process parameters on aerogel structure

The first entry of Table 1 lists optimized conditions for the production of organically modified clay aerogels. When a lower rate of shear is used (entries 2 and 3) in the presence or absence of surfactant, fragile foam-like structures, rather than OMCAs, are produced from the freeze-drying process. We believe that under such low shear mixing conditions, an insufficient degree of clay agglomeration is obtained, preventing the formation of well-developed three-dimensional aerogels.

Attempts at using a more economical, less pure sample of monoaminated triethyleneglycol surfactant (Table 1, entries 4 and 5) resulted in the production of expanded powders, rather than aerogels. Impurities within the surfactant, such as diaminated triethyleneglycol and triethyleneglycol, may have interfered with the initial hydrogel formation, potentially bridging multiple clay sheets. Control experiments with triethyleneglycol (Table 1, entry 6) produced discontinuous aerogel struc-

Table 1. Clay Processing Conditions (Per Batch) and Results

Sample	Clay	Shear	Freeze Dry	Acid	Surfactant	Structure
1	PGW 3.57 g	High	Normal	Yes	XTA-250 1.27 g	Aerogel
2	PGW 3.57 g	Low	Normal	Yes	None	Fragile foam
3	PGW 3.57 g	Low	Normal	Yes	XTA-250 1.27 g	Fragile foam
4	PGW 3.57 g	High	Normal	Yes	XTG-512 1.27 g	Expanded powder
5	PGW 3.57 g	High	Normal	Yes	XTG-512 1.27 g	Expanded powder
6	PGW 3.57 g	High	Normal	Yes	TEG 1.28 g	Discontinuous aerogel
7	PGW 3.57 g	High	Normal	Yes	XTA-250 1.27 g	Expanded powder
8	Lap-S 3.57 g	High	Normal	Yes	XTA-250 1.27 g	Expanded powder
9	Lap-XLG 3.57 g	High	Normal	Yes	XTA-250 1.27 g	Expanded powder
10	PGW 3.57 g	High	Normal	Yes	XTA-250 0.635 g	Aerogel
11	PGW 3.57 g	High	Normal	Yes	XTA-250 0.318 g	Aerogel
12	Cloisite 3.57 g	High	Normal	Yes	XTA-250 0.159 g	Aerogel
13	PGW 3.57 g	High	Normal	No	None	Aerogel
14	NT100 3.57 g	High	Normal	Yes	XTA-250 1.27 g	Fragile aerogel
15	ALA 3.57 g	High	Normal	No	None	Powder
16	EXT 3.57 g	High	Normal	No	None	Powder
17	PGW 3.57 g	High	Normal	Yes	E-19-5 2.67 g	Expanded powder
18	PGW 3.57 g	High	Normal	Yes	Q-19-5 3.10 g	Expanded powder
19	PGW 3.57 g + NT100 3.57 g	High	Normal	No	None	Aerogel
20	Lap-D 3.57 g	High	Normal	No	None	Fragile aerogel
21	Lap-S 3.57 g	High	Normal	No	None	Powder
22	Lap-XLG 3.57 g	High	Normal	No	None	Fragile aerogel
23	PGW 3.57 g	High	Freezer	No	None	Fragile, discontinuous aerogel-like structure
24	PGW 3.57 g	High	Freezer	Yes	XTA-250 1.27 g	Fragile aerogel
25	PGW 1.79 g	High	Normal	No	None	Powder
26	PGW 0.893 g	High	Normal	No	None	Powder
27	PGW 0.446 g	High	Normal	No	None	Powder
28	PGW 3.57 g	High	Slow	No	None	Dense flakes
29	PGW 5.36 g	High	Normal	No	None	Aerogel
30	PGW 7.14 g	High	Normal	No	None	Aerogel

Note: PGW = Nanocor PGW, XTA-250 (purified MATEG); Lap-S = Laponite S; Lap-D = Laponite D; Lap-XLG = Laponite XLG; Cloisite = Southern Clay Products Cloisite Clay; NT100 = American Colloid Company Hectabrite NT100; ALA = Nanocor aminolauric acid treated montmorillonite; EXT = Nanocor octadecylamine treated montmorillonite; High Shear = processed using Waring blender; Low Shear = processed using Erlenmeyer flask and stirbar at 65°C for 24 h; Normal = sample frozen on shell freezer at −80°C; Freezer = sample frozen in −80°C deep freezer (no sample rotation); Slow = sample frozen in a −5°C freezer (no sample rotation).

tures in which layer density varied along the cross-sectional profile.

When disk-like clays, such as Laponite D, S, and XLG, were treated with MATEG-HCl (Table 1, entries 7-9), powders were also produced. Fragile aerogels were formed in surfactant free aqueous dispersions of Laponite D and Laponite XLG (Table 1, entries 20 and 22). In the former case, MATEG-HCl surfactant may adversely affect the formation of a laponite gel. We further note that in the presence and absence of MATEG-HCl (Table 1, entries 8 and 21, respectively), Laponite S formed powders. The "as received" Laponite S has been pretreated with an inorganic polyphosphate peptiser. We suspect this agent is the source of interference in aerogel formation. Under conditions that appear to maximize stabilization of Laponite/water suspensions (Table 1, entries 21, 22), aerogel formation was observed as a result of freeze-drying. These Laponite aerogels were not as mechanically robust as those obtained with montmorillonite, likely reflecting the assembly of small disk units rather than longer, continuous sheets.

Sodium montmorillonite, bentonite, and fluorosilicate clays, as well as synthetic fluoromica, were found to process well into aerogels, in combination with a wide range of surfactant levels (0-25 wt% MATEG-HCl addition, base on starting clay; Table 1, entries 10-14). Most interesting was the absence of aerogel structure formation when starting clays modified with large, hydrophobic groups (aminolauric acid, tallow amine) or more hydrophobic surfactants (E-19–5, Q-19–5, and XTG-512) were added to the clay/water gel (Table 1, entries 15-18). In these cases, thixotropic solution behavior was not observed upon initial blending of starting materials, and powder products were produced. The hydrophobic nature of the surfactant used to modify the clays may adversely affect the modified clay-water suspension stability, minimizing ice/clay interactions during the freeze-drying process.

The effects of freezing process conditions on OMCA production were examined (Table 1, entries 1, 13 vs. 23, 24). Freezing samples in the absence of rotation produced a solid block of frozen clay hydrogel. An aerogel-like structure was obtained, but the alignment of clay platelets appears to have been disrupted as the final material shows a discontinuous cross-sectional profile. Under the same conditions, the presence of MATEG-HCl appears to improve the final morphology, but the aerogels produced were not as mechanically robust as those obtained using the rotating freezer. In the case of a slow freeze, using a conventional laboratory refrigerator, aerogels were not produced.

The concentration of clay in water was also found to be important. Clay concentrations of 1.4-2.9 wt% produced aerogel structures (Table 1, entries 29, 30), whereas less than or equal to 0.7 wt% did not (Table 1, entries 25-27). Clay concentrations above 2.9 wt% were viscous and difficult to blend. Hence, a balance between suspension viscosity and clay building block concentrations is needed in order to produce optimized clay aerogel structures.

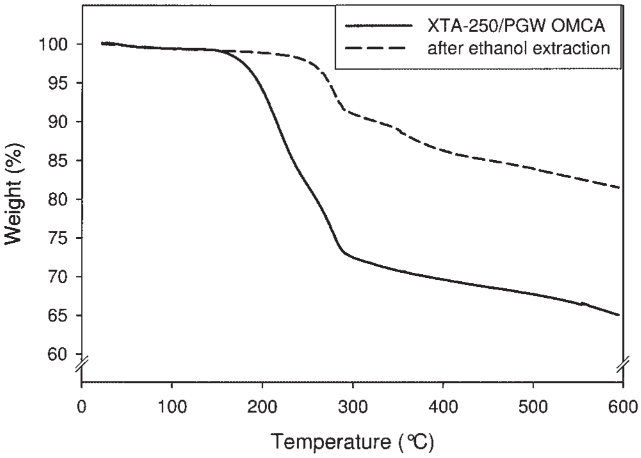


Figure 3. Thermogravimetric analysis of MATEG-HCl OMCA before (solid) and after (dashed) ethanol soxhlet extraction.

OMCA thermal analysis and percent ion exchange

Montmorillonite clay aerogels modified with MATEG-HCl were dried for 10 min at 150°C and quickly cooled to 50°C prior to heating at 2°C per min to 600°C. The thermogravimetic analysis (TGA) methods for organically modified clays developed by Xie et al.[32] were used to measure surfactant loss from clay. TGA was performed on freeze-dried MATEG-HCl modified aerogel and an ethanol extracted sample. Figure 3 shows a comparison of the TGA profiles. Soxhlet extraction on 5 g of XTA-250/PGW OMCA for 24 h using 250 mL ethanol removed excess surfactant from the aerogel and decreased residual mass. No change in OMCA structure was observed by SEM for the XTA-250/PGW system after the ethanol soxhlet extraction. The onset of mass loss temperature also increased, perhaps caused by elimination of excess unbound surfactant. Xie et al. described this behavior as a result of kinetics specific to surfactant degradation in organically modified clays.[32] A control sample, prepared without surfactant or acid, was used to estimate intergallery water loss (during the initial drying treatment involving drying at 150°C). Comparing weight lost to theoretical values for surfactant loading (CEC 120 MEQV), we calculate 100% ion exchange for the ethanol-extracted XTA-250/PGW OMCA sample.

MATEG-HCl OMCA: Fourier-transform infrared spectroscopy

Fourier-transform infrared (FTIR) spectroscopy confirmed the presence of surfactant in clay aerogel samples. Clays in general have several useful FTIR absorbances of note: 3600-3500 cm^{-1} for octahedral layer hydroxyl stretching (i.e., Mg$_3$-OH, FeMg$_2$-OH, or MgFe$_2$-OH), 1200-1000 cm^{-1} (Si-O tetrahedral layer stretching), 800 cm^{-1} (Al-O tetrahedral stretch vibration), and 500 cm^{-1} (complex Si-O-Si and Si-O-Al bending vibrations).[33] For comparison with clay and OMCA, a sample of MATEG-HCl was prepared by adding HCl 1:1 to MATEG. The sample was diluted in ethanol and dried over sodium sulfate. A thin film of MATEG-HCl was then cast onto a sodium chloride plate from the dried ethanol solution. FT-IR analysis (Figure 4) showed a strong, broad absorbance from 3300 to 3030 cm^{-1} (most likely due to N-H stretching of the hydrogen chloride amine salt), while strong absorbance at 1110 and 1070 cm^{-1} can be traced to C-O-C ether and C-C-O alcohol stretch. In addition, C-H stretches (2900 cm^{-1}) and C-O-C ether and C-C-O alcohol (1400-1500 cm^{-1}) absorptions can still be seen for the MATEG-HCl organically modified clay aerogel. The FTIR evidence confirms that MATEG-HCl is

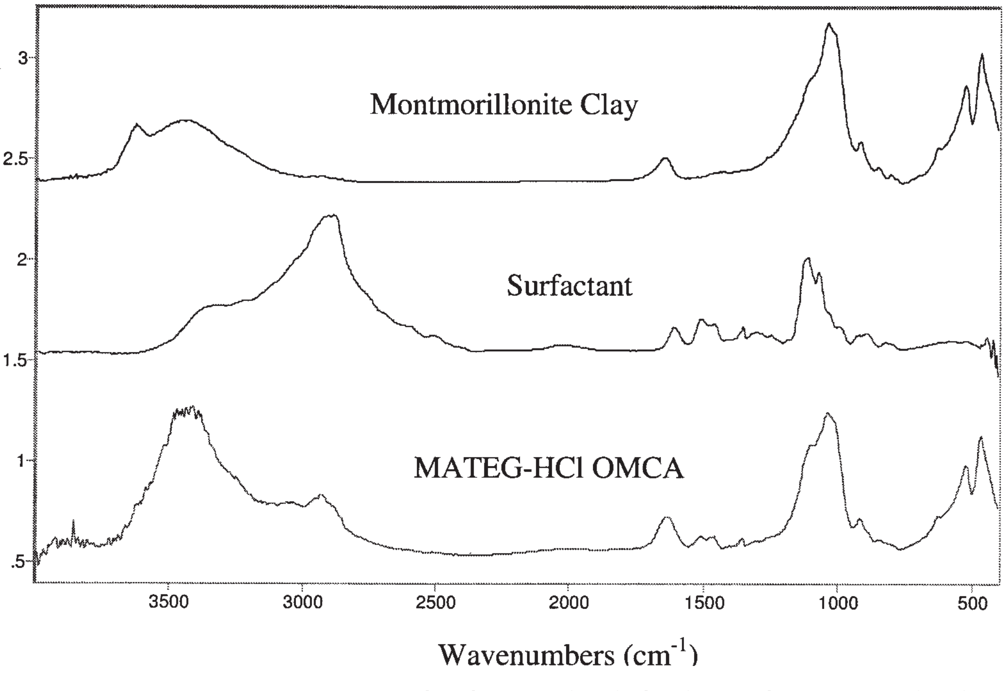
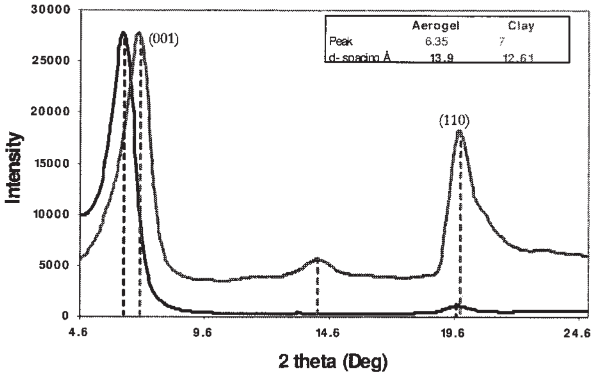


Figure 4. FTIR analysis of sodium montmorillonite (KBr), MATEG-HCl (NaCl plate), and MATEG-HCl modified montmorillonite clay aerogel (KBr).

WAXD of Sodium exchanged
Montmorillonite Clay and Aerogel



- As the clay is distorted into Aerogel structure, the d-spacing increases

Figure 5. Wide angle X-ray diffraction analysis of sodium exchanged montmorillonite clay (solid) and MATEG-HCl organically modified montmorillonite aerogel (dashed).

present in the OMCA and has not been removed by the freeze-drying process.

MATEG-HCl OMCA: wide angle X-ray diffraction

Small disks of montmorillonite clay and freeze-dried MATEG-HCl OMCA were prepared using a brass FTIR sample mold and introduced to an X-ray beam. An increase in the montmorillonite 001 spacing (from 12.6 to 13.9 Å) was observed (Figure 5), indicative of surfactant intercalation. We speculate that the MATEG-HCl surfactant may have adopted a more energetically favorable coiled conformation that would account for the small intergallery spacing increase in comparison to commercial hydrocarbon-tailed onium surfactants. In their study of freezing effects on the swelling of clay minerals, Norrish et al. reported variations in spacing that resulted from the orientation of the hydrogel as well as the effect of solution ionic strength.[11] They reported intergallery spacings of 18.0 to 20.1 Å for frozen montmorillonite gels and 10 Å for freeze-dried materials, indicative of decreased interlayer hydration and sheet collapse upon freeze-drying. Our OMCA clay sheets could not completely collapse due to the presence of intercalated MATEG-HCl surfactant. Examination of OMCAs by SAXS showed no diffraction peaks at smaller angles of 2θ.

OMCA surface area measurements and flammability

Van Olphen also described a mechanism for clay sheet reorganization in aerogels involving freeze-induced parallel alignment of clay particles.[12] Water-exfoliated clay sheets collapse during the freezing process to form thicker plates with decreased clay surface area. Not surprisingly, Brunauer-Emmett-Teller (BET) surface area measurements of our OMCAs, using nitrogen porosimetry, showed a 43% reduction (6.410 to 3.673 m^2/g) between as-received montmorillonite clay and MATEG-HCl OMCA.

Flammability of OMCAs and surfactant free aerogels was also studied. Heating clay to high temperatures liberates three different forms of water: surface bound water (below 110°C), interlayer or zeolite water (below 300°C), and crystalline water (400 to 800°C).[12] Placing a sample of clay aerogel in a propane-air flame for several minutes resulted in discoloration of MATEG-HCl OMCAs, but little visual change to the shape of the aerogel. During prolonged flame exposure (i.e., 30 minutes), the OMCA shrinks slightly as crystalline water is slowly released and clay sheets undergo what is assumed to be a non-reversible change in structural chemistry. The previously soft, cotton-like aerogel material is transformed into a more refractory material as a result of this prolonged treatment at high temperatures. From a composites viewpoint, the non-flammable and highly organized nature of OMCAs makes them excellent candidates for composite reinforcements and insulation; a preliminary report of the use of OMCAs in organic polymer composite materials suggests a wide array of potential applications.[28]

Conclusions

The development of aerogel technology can be tracked from Kistler's early beginnings to the organically modified clay aerogels of this current work. Structural changes, from montmorillonite clay starting material to organically modified aerogels presented herein, are supported by WAXD, SEM, and porosimetry, and demonstrate that a highly organized montmorillonite clay platelet realignment occurs during rapid and efficient freezing at low temperatures in blender-mixed clay hydrogels in the presence or absence of MATEG-HCl surfactant. Processing of the clay gels into aerogels is generally easier in the presence of organic surfactants, assuming that the levels used are modest and the surfactants relatively hydrophilic. The aerogels produced using the freeze-drying process in this work are similar to the feather type aerogels previously reported by Nakazawa. We emphasize the retention of aerogel structure even though the clay sheets have been modified with MATEG-HCl surfactant, which serves primarily as a processing aid. The aerogel materials described here may offer entirely new families of composite materials for structural, biological, catalytic, and sensor applications. In future work, surface modification of aerogels, to provide for catalytic, biocatalytic, and biocompatible interactions, will be explored. Modification of aerogel density, by altering clay concentrations in the initial aqueous gel, crosslinking to enhance mechanical strength, and careful thermal treatment to convert clay into ceramic, will be explored as means of producing inorganic structures to be used within structural composites. Support of rare earth metals and other electro/optical substances on and in the aerogel structure will be investigated for sensor/device applications.

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