Temperature-Responsive Clay Aerogel−Polymer Composites

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ABSTRACT: Polymer composites reinforced by hydrophilic clay aerogels were produced and found to possess interpenetrating cocontinuous structures, not the exfoliated structure often observed in clay nanocomposites. An efficient process for producing these clay aerogels was recently reported; in-situ polymerization of *N*-isopropylacrylamide within the clay aerogels was readily accomplished. The resulting composites have low densities, are stable, and exhibit a new synergistic effect of interpenetrating organic−inorganic phases in which the organic polymer prevents loss of aerogel structure in water by encapsulation, while the inorganic filler increases the structural integrity of the polymer. The composites undergo phase transition and show LCST behavior similar to unmodified poly(*N*-isopropylacrylamide) despite the presence of reinforcing clay aerogels. Reversible changes in morphology of the aerogel hydrogel composites are observed with varying degrees of hydration.

Introduction

The term "aerogel" is used to describe inorganic materials, largely composed of air, with bulk densities typically in the 0.01−0.1 g/cm^3 range. These materials, among the least dense forms of solid matter known, were first described by Kistler, who reported their preparation from silica.[1] A wide variety of applications for 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,[2] in supported metal catalyst systems,[3] in insulating materials,[4] as a general inorganic "glue" by which to attach a wide range of other materials,[5] and as an ultralight media for collecting particles from space.[6] 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 materials has been well established and to some extent resembles a "string of pearls".[7−10] A growing body of literature exists in which silica aerogels are combined with organic polymers to produce nanocomposite materials.[11−16] While the majority of aerogels described in the literature are silica-based, there are a limited number of references to clay-based aerogels (though in many cases, the authors did not use this nomenclature). The conversion of clay to clay aerogel through freeze-drying results in a rearrangement of clay sheets, creating a lightweight, fabric-like material. The production of low-density structures from clays was reviewed by Mackenzie,[17] with structural properties then reported by Call[18] and Weiss.[19] Materials with improved mechanical stability were reported by Norrish,[20] with the identification of a "house of cards" structure and stabilization by incorporation of polyelectrolytes made by Van Olphen.[21] The importance of processing conditions to the final stability of these was demonstrated by Nakazawa.[22] Clay can be modified with surfactants and then freeze-dried to form organically modified clay aerogels (OMCAs) in a highly robust processing method which was recently reported.[23]

Thermoresponsive hydrogels based on poly(*N*-isopropylacrylamide), PNIPAM, gels have been investigated intensively for their swelling and mechanical properties.[24,25] Increasing the extent of cross-linking within PNIPAM can induce rigidity in the material but results in reduced swelling/hydration capabilities. Polymer/clay nanocomposites have been an area of intensive investigation over the past decade.[26] Hydrophilic ordered clay has been added to improve their physical properties. Addition of clay to thermoresponsive polymers has gained interest as they have been shown to act as cross-linking agents, increasing the mechanical properties of the composites.[27,28] These improvements in properties are primarily driven by good dispersion and/or the ability of clay to exfoliate in the polymer. An alternative route for the incorporation of clays into organic polymers could be to preform clay matrices that do not require exfoliation and then fill or impregnate these clay structures with polymer (melt or solution) or monomers (which then could be polymerized in situ). In this manner, a three-dimensional, interpenetrating network of clay and polymer could be obtained. Clay aerogels could serve as the source of such three-dimensional clay networks. The approach of preconverting clay into an aerogel is appealing in its simplicity, its ability to be adapted to a wide range of polymeric matrixes, and from the absence of thermodynamic and kinetic barriers present when polymerization reactions are conducted within the more traditional swelled clays.[29] By using a clay aerogel as the inorganic filler, no exfoliation of clay sheets would be required, and polymerization reactions could potentially proceed in a normal manner. To this end, early work by Nakazawa has shown that aerogel composites can be produced with gelatin.[30]

In the present study, we focus on preparing thermoresponsive, cocontinuous clay aerogel/polymer networks which preserve the structure of the aerogel within an organic matrix. This preservation of structure would be achieved by physical encapsulation of the aerogel within a cross-linked organic polymer.

Experimental Section

Materials and Methods. *N*-Isopropylacrylamide (NIPAM), azobis(isobutyronitrile) (AIBN) initiator, toluene, and ethylene

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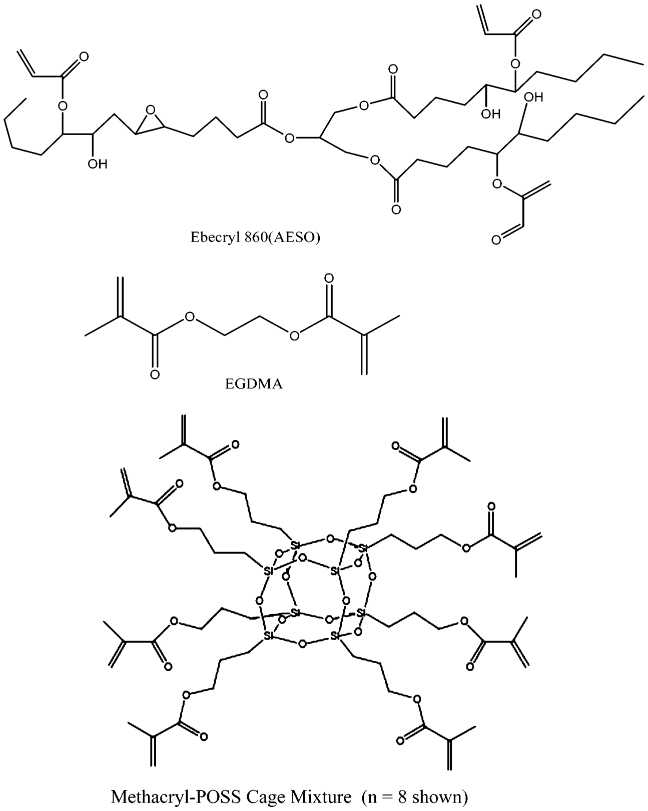


Figure 1. Molecular structures of cross-linkers used in PNIPAAm gels.

glycol dimethacrylate (EGDMA) cross-linking agent (*f* = 2) were purchased from the Aldrich Chemical Co. and used as received. Other cross-linking agents (Ebecryl 860) epoxidized soy bean oil acrylate containing three vinyl end groups (*f* = 3) and (methacryloxypropylpolysilsesquioxane) POSS, $C_{56}H_{88}O_{28}Si_8$, with eight vinyl end groups (*f* = 8) were obtained from Surface Specialties Inc. and Hybrid Plastics Inc., respectively. The molecular structure of these cross-linkers is shown in Figure 1. Sodium-exchanged montmorillonite (PGW, Nanocor), which has a cation exchange capacity (CEC) = 110 mequiv/100 g clay (MEQV)) was used in aerogel preparations; this clay was treated with XTA-250, a purified monoaminated triethylene glycol (MATEG), received from Huntsman Chemical Corp. 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 rotating lyophilization shell freezer (Virtis Freeze Mobile S2EL, 188−203 K temperature range) with (Virtis Freeze Mobile 35EL) freeze-dryer was used for synthesizing OMCAs.

Characterization. A Phillips XL-SEM scanning electron microscope was used to examine the morphology of aerogel and aerogel−hydrogel composites. The aerogel−hydrogel composites cross-linked with EGDMA were kept under water for 1 week, and then stability of the composite was examined using SEM in wet mode, where the humidity was varied by varying vapor pressure of water. A Rigaku (RINT 2000 series) X-ray diffractometer was used to examine the change in structure of aerogel in the composite. Water absorption was determined by measuring the weight gain of the gels, which were immersed in water for 24 h.

Clay Aerogel Preparation. The procedure of Kojima[31] was modified in the following manner to produce clay aerogel used in this study.[23] A single speed Waring laboratory blender fitted with 1.25 L glass vessel contained 250 mL of deionized water and 3.57 g (4.3 mmol exchange sites) of Nanocor (PGW) clay, which was sheared using a stainless steel rotor blade assembly and lid and was used for introducing clays, water, and surfactant. 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 to 1 surfactant:exchange site ratio. Blending was continued for an additional 5 min. 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. Half-filled shells were rotated at 30 rpm at a temperature of −80 °C until frozen. The ice from frozen shells was then evacuated for 36 h using the freeze-dryer.

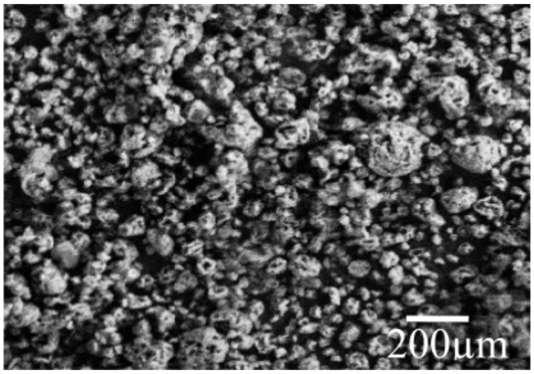


Figure 2. Starting clay.

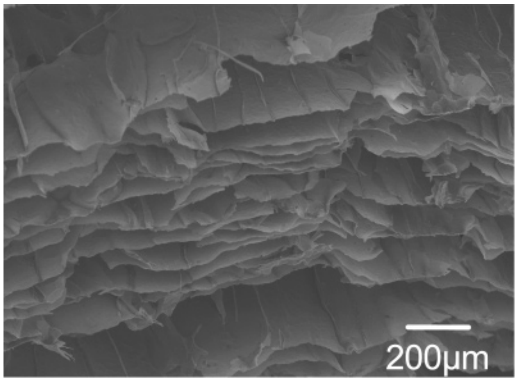


Figure 3. Clay aerogel.

Clay Aerogel Composite Formation. 1.00 g of NIPAM was dissolved in 5 mL of toluene with 0.01 g of AIBN initiator and then was in-situ polymerized with XTA-250-treated sodium-exchanged montmorillonite (MMT) clay aerogel (0.0224 g). This process was repeated with 0.1 g (10 wt %) of three different cross-linkers based on functionality: EGDMA (*f* = 2), Ebecryl 860 (*f* = 3), and POSS (*f* = 8). The control for these samples did not contain any clay aerogel. The reaction was flushed under nitrogen for 30 min, and then reaction temperature was raised to 60 °C, which was maintained for 24 h. Free toluene solution was decanted from the reaction flask, and then the toluene was removed under vacuum to leave the PNIPAM/clay aerogel composite. The polymer weight fractions were determined to be ∼88% of total for each of the clay aerogel composites—this was determined by comparing the starting aerogel weight with that of the final dried composite. These samples are then kept in water for 24 h to study water absorption of the composites. The swollen samples were manually measured for change in volume transition when temperature is varied.[28]

Results and Discussion

Montmorillonite, during its conversion into an aerogel via freeze-drying, undergoes volume expansion (accompanied by the change in density from 2.35 to 0.05 g/cm^3) which converts random microscale clay particles (Figure 2) to mesoscale (1−100 μm), well-arranged layered structures such as is shown in Figure 3.[23] The potential of clay aerogels as building blocks for polymer

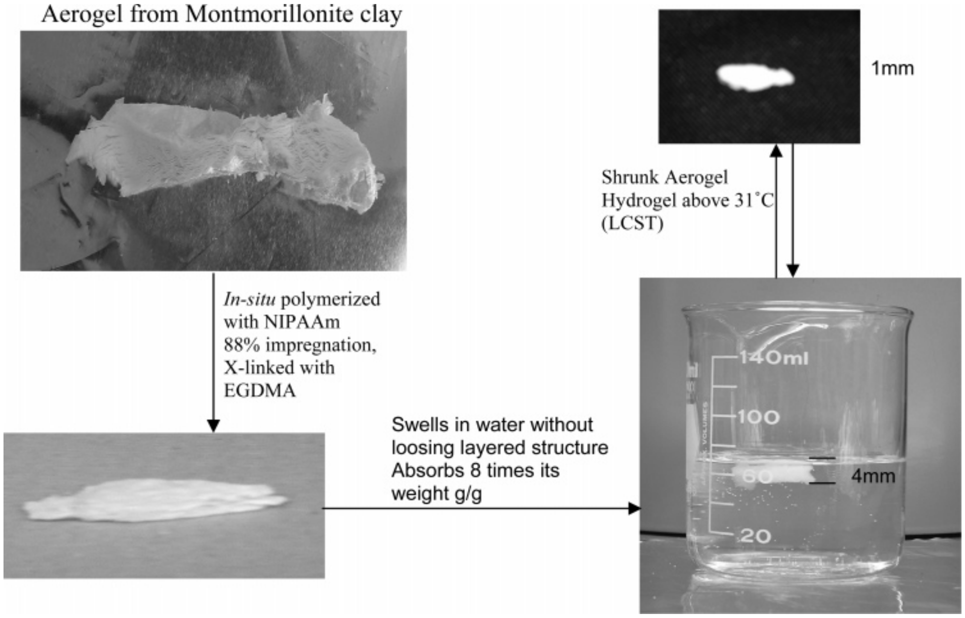


Figure 4. In-situ polymerized aerogel–hydrogel composite.

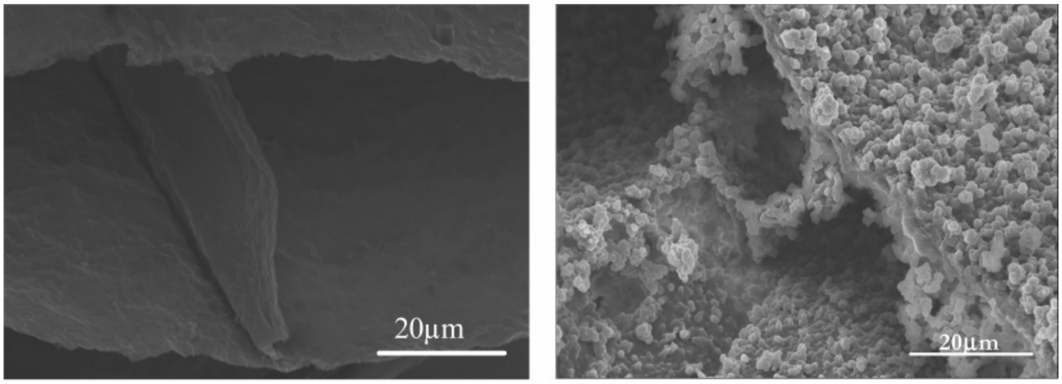


Figure 5. (a, left) Aerogel layered structure. (b, right) Aerogel–hydrogel composite.

composites was explored in a series of preliminary experiments, utilizing PNIPAM as the polymeric matrix.[29] This polymer was chosen because it is known to exhibit a thermoresponsive, lower critical solution temperature (LCST) behavior at which inverse solubility upon heating and a critical transition from hydrophilic (extended chain conformation) to hydrophobic (compacted conformation) takes place at a specific temperature.[25] Not only could the potential for clay aerogel/polymer composites be studied, but potential effects on its LCST behavior could be investigated as well. In-situ free radical polymerization of *N*-isopropylacrylamide monomer in the clay aerogel monolith was carried out in the presence of different cross-linking agents to produce materials which form water stable aerogel–hydrogel composites after hydration. In the absence of cross-linking, the PNIPAM polymer and composites lack significant structural integrity. The temperature-dependent swelling behavior of the aerogel/PNIPAM system in water is illustrated in Figure 4. The clay aerogel/cross-linked PNIPAM composites (containing 88% PNIPAM, as measured by starting aerogel weight gain) absorb 8 times their own weights in water, floating just below the meniscus when saturated. Between 30 and 32 °C the aerogel hydrogels undergo the LCST transition, shrinking to approximately one-fourth of their starting size. Upon cooling to 30 °C, rehydration and growth to the composites' original dimensions occurs. The composite LCST behavior is described as reversible through numerous cycles—no breakdown in structure or performance was observed. The presence of a cocontinuous aerogel scaffold within the PNIPAM structure was observed to have no effect upon that polymer's LCST behavior. This is perhaps surprising, as although the PNIPAM LCST is largely insensitive to the polymer molecular weight, other structural changes to PNIPAM, such as modification of molecular weight distribution, profoundly modify the transition temperature.[33] The open structure of the clay aerogel scaffold, shown in Figure 5a, is well encapsulated with the cross-linked NIPAM polymer (Figure 5b), resulting in low-density composites (0.05–0.07 g/cm^3 are typical bulk density values for the dry composites). X-ray diffraction patterns for the aerogel and the aerogel–hydrogel composite are shown in Figure 6. As the starting clay aerogel was converted to PNIPAM/aerogel composites, the relative *d* spacing of clay sheets undergoes a very minor change from 13.9 to 14.3 Å, which confirms the absence of extensive intercalation or exfoliation within the composites.

Wet Mode SEM Imaging. In-situ examination of specimen dehydration using SEM wet mode imaging was performed on a heating/cooling stage allowing imaging at a range of relative humidities. The morphology of an aerogel–hydrogel composite kept under ambient temperature water for 1 week is shown in Figure 7.

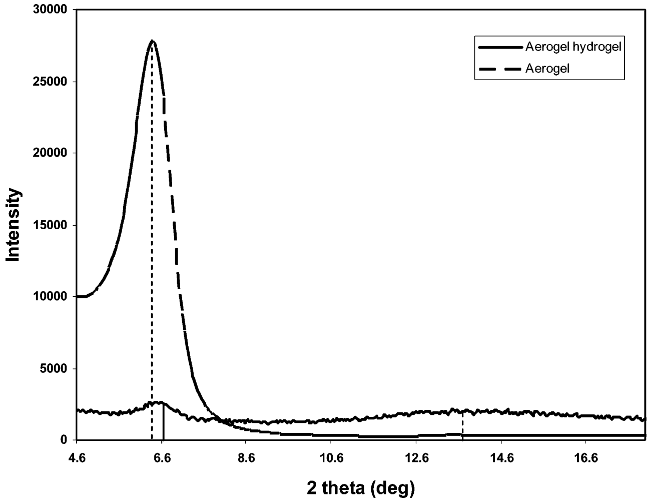


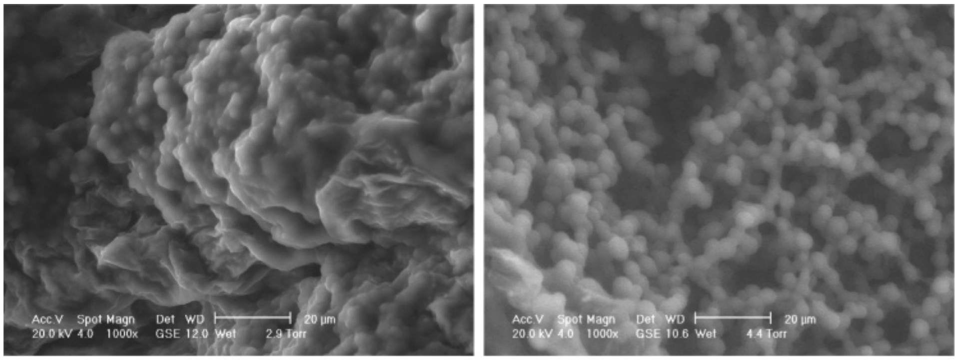
Figure 6. Wide-angle X-ray diffractograms of aerogel and aerogel−hydrogel composite.

A fully hydrated sample of aerogel−hydrogel was imaged under 100% relative humidity and was found to be composed of expanded polymer beads (Figure 7b). The relative humidity surrounding this sample was varied by decreasing the chamber pressure and increasing its temperature. The swollen composite loses water as temperature is increased and was observed to exhibit a high degree of mechanical shrinkage at the polymer LCST transition of ~31 °C. Compaction of the polymer hydrophobic groups at low relative humidity is shown in Figure 7a; the changes in morphology observed at 20% RH, in which individual spherelike structures coalesce into larger assemblies, was shown to be reversible through several cycles, with these structural changes occurring within 1 min of the humidity change.

Water Absorption. The water absorption weight gains in aerogel composites at room temperature (ca. 23 °C) were calculated using eq 1. The amount of cross-linking agents used was 10 wt % in each case; similar numbers of cross-linking equivalents were present in each of these materials. It was observed that the nature of cross-linking agents in these systems had little effect on the overall system water absorption, nor did the presence of the clay aerogels affect absorption properties (Figure 8). The one counterexample to this trend was when multifunctional POSS was used as the cross-linking agent. We propose that in the absence of aerogel the POSS is highly efficient at cross-linking the polymer, thereby reducing water absorbency. Upon addition of clay, the POSS could be expected to interact with that silicate filler, decreasing its cross-linking efficiency and enhancing water uptake. As limited chemical interactions are expected between this polymer and the clay surface, the consistency of LCST behavior with or without aerogel is not a major surprise. On the basis of their chemical structures, supported by SEM images taken it is reasonable to assume that the polymer is only physically attached to the clay aerogel substrate, and the composite transition temperature remains equal to that of the polymer.[28] It should be noted that when clay aerogels are combined with hydrophilic polymers, such as poly(vinyl alcohol), significant changes in polymer transitions can be observed.[32]

$$\text{water absorption (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

The mesoscale organization of the starting clay filler was completed prior to composite formation. Impregnation of the clay aerogel structure with monomers followed by in situ polymerization has been shown to produce novel materials. In this application, a temperature-responsive composite was produced, which behaves in some ways similar to that of the matrix polymer. Unlike the unmodified polymer, the complex retains it shape and is mechanically more robust than this gel-forming polymer. Perhaps most remarkable about the PNIPAM−clay aerogel composite material is the synergistic effect of interpenetrating organic and inorganic phases. As was stated above, PNIPAM polymer itself exhibits little structural integrity in its hydrogel form. The clay aerogels used in this study are reconverted over several hours to structureless gels when hydrated in water (this undoing the freeze-drying process). The hydrated PNIPAM/clay aerogel−hydrogel composite material has been shown to maintain its structure even when submerged under water for a week or longer, and under different relative humidity environments, its structure changes slightly and reversibly when cycled above and below critical temperature. Hence, physical encapsulation of inorganic aerogel with cross-linked organic polymer phase serves to bolster the mechanical properties while preserving the inherent properties of its constituent components. Such new materials could find use in applications ranging from temperature-responsive switches and controlled delivery devices to chemical sensors. The broad concept of supporting and microconfining polymers within these easily produced inorganic aerogels is currently being



(7a) 20% RH Reversible (7b) 100%

Figure 7. Variation of humidity in-situ SEM showing reversible morphology of X-linked PNIPAAm in (a) low and (b) high humidity states.

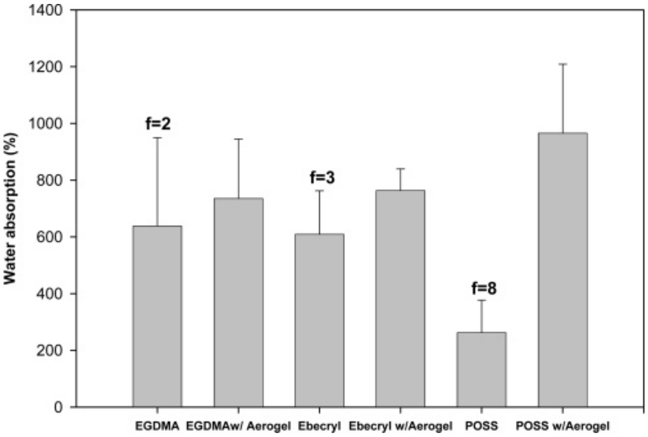


Figure 8. Room temperature water absorption with varying functionality with and without aerogels (error bars denote standard deviations, $n = 3$).

explored for use in high gas/liquid barrier structures, high impact structural components, and thermal/acoustical insulation.

Conclusions

Prior work in the field of polymer−clay composites has focused on the simultaneous polymerization of monomers and exfoliation of clays; such a process probably requires a significant enthalpic driving force for polymer−clay interactions. A new family of polymer/clay composites has been described in the present work—these new composites offer the promise of low bulk densities and readily modified structures. In-situ polymerization of *N*-isopropylacrylamide within a low-density montmorillonite aerogel lattice was shown to produce a low-density thermoresponsive composite which retains the LCST behavior of the polymer, while enhancing its mechanical robustness in its hydrogel form. Physically interpenetrating, cocontinuous organic/inorganic structure of this mesoscale composite has provided a synergistic improvement in moisture stability over each of the individual constituents.

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