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Polyacrylamide-montmorillonite composite with improved properties

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The high water absorption rates and poor long-term stability in high salinity of polymer-montmorillonite composites are ameliorated by introducing a polymerizable cationic hydrophobic monomer.

Polyacrylamide-montmorillonite—poly(AM/MMT)—composites generally have much better strength and thermal stability than most polymers.[1,2] Poly(AM/MMT) composites can thus be used as an appropriate replacement for polymer gels in controlling excessive water production during mining of oil fields. Such replacements, however, need to be improved because of specific problems, e.g., their excessive water absorption rates and poor long-term stability in high-salinity conditions. These deficiencies can be remedied by introducing a polymerizable cationic hydrophobic group into the hybrid materials.

In our work,[3] we have developed a method for the preparation of polymer-montmorillonite hybrid materials. In this approach, we first use an ion exchange process to introduce a long alkyl chain ammonium salt—synthesized by 2-(dimethylamino) ethyl methacrylate with 1-bromohexadecane (DMB)—into the crystal layer of montmorillonite (MMT). In this way, we obtain an intermediate (O-MMT) substance that we can then polymerize with acrylamide (AM) and N,N-methylene bisacrylamide. We conduct this polymerization reaction in an aqueous solution with the use of ammonium persulfate as the initiator. The full preparation process for the polymer-montmorillonite hybrid—poly(AM/O-MMT)—materials is illustrated in Figure 1.

In the first part of our study we investigated how the amount of DMB and MMT within our hybrids affects the water absorption of poly(AM/O-MMT). The results of this investigation (see Figure 2) show that the water absorption of the composites increased at first, and then decreased with increasing DMB and MMT contents. We found that the optimum concentration of these two components within the poly(AM/O-MMT) was about 2 and 30wt%, respectively. In contrast, we also studied the re-swelling ability of our samples by immersing the poly(AM/O-MMT) and poly(AM/MMT) in distilled water at 95°C.

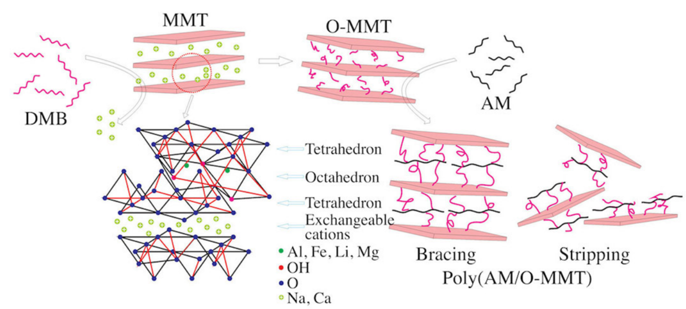

Figure 1. *Schematic illustration of the synthesis process for polymer-montmorillonite hybrid—poly(AM/O-MMT)—materials. DMB: 2-(dimethylamino) ethyl methacrylate with 1-bromohexadecane (a long alkyl chain ammonium salt). MMT: Montmorillonite. O-MMT: Intermediate-MMT. AM: Acrylamide. Al: Aluminum. Fe: Iron. Li: Lithium. Mg: Magnesium. OH: Hydroxyl. O: Oxygen. Na: Sodium. Ca: Calcium.*

The result of this test (see Figure 3) indicates that the saturated water absorbencies for both samples decreased with increased re-swelling times. The downward trend for the poly(AM/O-MMT) sample, however, was more gentle. After five re-swelling cycles, the poly(AM/O-MMT) sample still retained about 84% of the water, thus illustrating its stronger re-swelling ability.

To realize the stability of poly(AM/O-MMT) under high salinity conditions, we have also investigated its swelling behavior within various salt solutions at 95°C. The results (see Figure 4) indicate that the water absorption of poly(AM/O-MMT) decreased with increasing sodium chloride (NaCl) content, exhibiting the same behavior as our poly(AM/MMT) samples. The poly(AM/O-MMT), however, had a lower water absorption speed and better stability than the equivalent poly(AM/MMT) samples under the same conditions. For the poly(AM/O-MMT) samples, it took nearly 3.3, 1.3, and 3.0 times longer to reach maximum water absorption than for the

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poly(AM/MMT) composites when the NaCl content was 0, 1×10^5, and 2×10^5mg/L, respectively. Moreover, the water absorption was nearly constant during the whole test period (i.e., for 90 days from saturation).

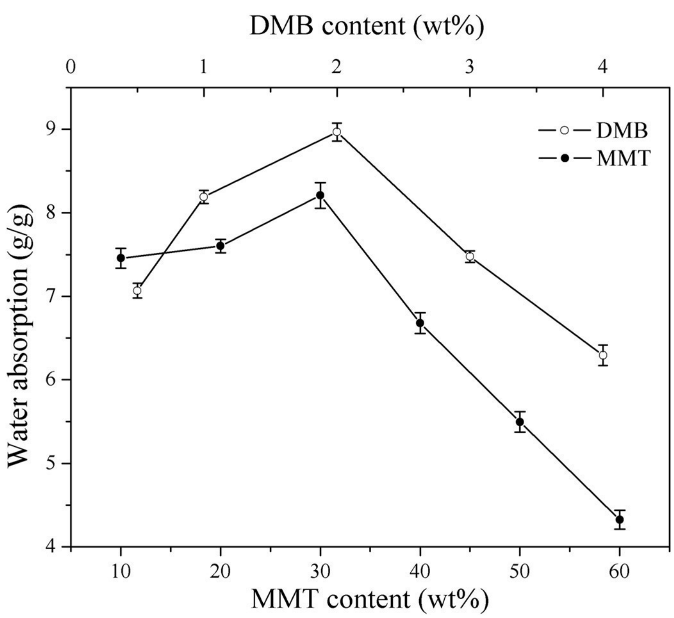

Figure 2. *The effect of changing DMB and MMT content on the water absorption of poly(AM/O-MMT).*

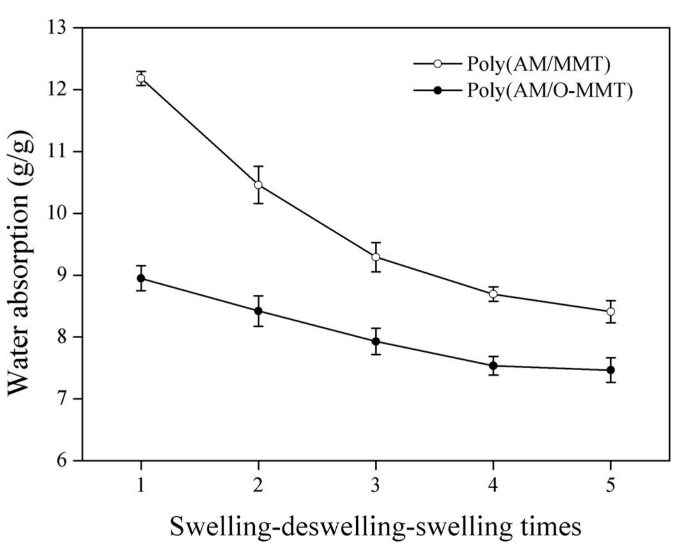

Figure 3. *The re-swelling ability (for 1–5 cycles) of polyacrylamide-montmorillonite—poly(AM/MMT) and poly(AM/O-MMT) composites in distilled water at 95°C.*

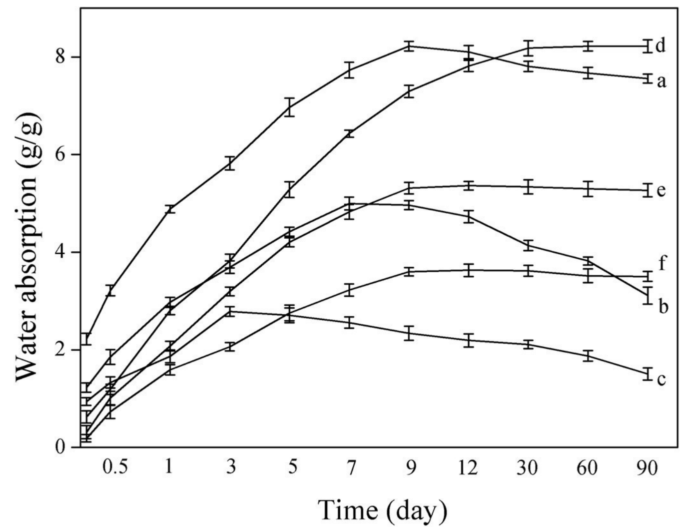

Figure 4. *The time and salinity dependence of water absorbency for (a–c) poly(AM/MMT) and for (d–f) poly(AM/O-MMT) composites. Results are given for salinities of (a) and (d) 0mg/L, (b) and (e) 1×10^5mg/L, and (c) and (f) 2×10^5mg/L.*

In addition, we measured the toughness index of the poly(AM/O-MMT) composites after swelling had occurred in different salinity solutions. From our results—indices of 0.95, 0.93, 0.88, and 0.85 for salinities of 5000, 5×10^4, 10×10^4, and 20×10^4mg/L, respectively—we see that the toughness index decreased only slightly with increasing salinity and thus indicates good stability. Furthermore, the measured toughness index of 0.85 at a salinity of 20×10^4mg/L demonstrated the consistently good level of deformability at high salinity of the poly(AM/O-MMT) particles.

In the final part of our study, we conducted core physical simulation experiments at high temperature (95°C) and high salinity (20wt% NaCl) to investigate the water blocking and profile control ability of poly(AM/O-MMT). We found that the blocking rate and the reserve amount of water plugging were 91.3 and 97.1%, respectively, after 20 days from particle injection. In addition, our results showed that the profile control efficiencies reached 99.7, 98.8, and 72.4% when the permeability ratio was 86.04, 42.81, and 26.28, respectively. Our measurements thus demonstrate that poly(AM/O-MMT) has good plugging and profile control abilities.

In summary, we have successfully synthesized a poly(AM/O-MMT) composite with optimum DMB and MMT contents. By introducing the polymerizable long alkyl chain ammonium salt, we were able to achieve poly(AM/O-MMT) with greater toughness, better re-swelling

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ability, lower water absorption rates, and stronger long-term stability under high salinity than the poly(AM/MMT) equivalent. Furthermore, our poly(AM/O-MMT) has a good plugging and profile control ability in high-temperature and high-salinity environments. In our future work we plan to investigate the effects of different alkyl carbon chain lengths and different polymerizable cationic monomer structures on the properties of the polyacrylamide-montmorillonite composites.

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