Semidry Synthesis of the Poly(acrylic acid)/Palygorskite Superabsorbent with High-Percentage Clay via a Freeze-Thaw–Extrusion Process

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ABSTRACT: A problem with the synthesis of polymer/clay composites is the poor compatibility between clay and polymers; this is particularly bad for those with a high percentage of clay. In response, we introduced a freeze–thaw–extrusion process before polymerization to make the best use of the high activation ability of acrylic acid (the monomer) and the exceptional hydration of palygorskite (clay). This processing was powerful for facilitating clay dispersed into the nanoscale and for obtaining good compatibility with the polymer, even for those polymers with high clay contents. The experiment showed that the quality of the consequent superabsorbent was improved significantly. As the dispersion was worked out perfectly by the freeze–thaw–extrusion process, we further explored the effect of the system water content on the water absorptivity of the consequent composite. With synthesis by the improved system, the water absorbency still amounted to 98.2 g/g in a 0.9 wt % NaCl solution for the composite with 35 wt % clay, whereas the water content (55 wt %) was much less than that of general synthesis (ca. 95 wt %). Scanning electron microscopy showed that the composite had a rich pore structure in the range of several hundred nanometers, and the palygorskite was distributed perfectly in the composite on the nanoscale. Fourier transform infrared spectroscopy gave further direct evidence for the reaction between the clay and polymer. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Superabsorbents, loosely crosslinked polymeric three-dimensional networks, are capable of absorbing and retaining large amounts of aqueous solution. There are a variety of valuable applications for superabsorbents, including in horticulture, disposable diapers, feminine napkins, drug-delivery systems, immobilization of enzymes, and other newly developed fields.[1–4] Compared with pure polymeric superabsorbents, the introduction of clays into polymers can upgrade their performance (e.g., giving them better resistance to hard water and a higher mechanical strength) and reduce costs remarkably.[5–10] Consequently, research on polymer/clay superabsorbents has attracted much attention. Research has been done on the modification and choice of clay[11–14] and on the selection of monomer.[15–18] However, little attention has been paid to the synthesis process. A higher performance/cost ratio usually means a higher percentage of clay in the polymer/clay composite, which means a rapidly increasing viscosity and consequent dispersion difficulty during synthesis.[19]

In this study, palygorskite was used as a target sample because of its nanorod structure and higher attractiveness in inorganic–organic polymer composites to demonstrate an improved synthesis process. Palygorskite is a kind of hydrated magnesium aluminum silicate; its formula is $Si_8O_{20}(Mg, Al, Fe)_5(OH)_2(OH_2)_4 \cdot 4H_2O$. Its structure (Figure 1) results in zeolite-like channels about 0.64×0.37 nm in size.[20] Thus, palygorskite can be characterized as a hydrous and porous structure with abundant reactive —OH groups on its surface.

As an inexpensive mineral, 30–40 wt % palygorskite is added to certain polymer/clay composites to obtain a high performance/cost ratio. The main process in a semidry synthesis is the freeze–thaw–extrusion cycle, which is the key to obtaining uniform polymer/clay composites with a high percentage of clay. Palygorskite ore is directly soaked into acrylic acid at first; then, after two or three freeze–thaw–extrusion cycles, other reagents are dispersed well into the reaction system via high-speed stirring. There are at least three main reasons for the improvements:
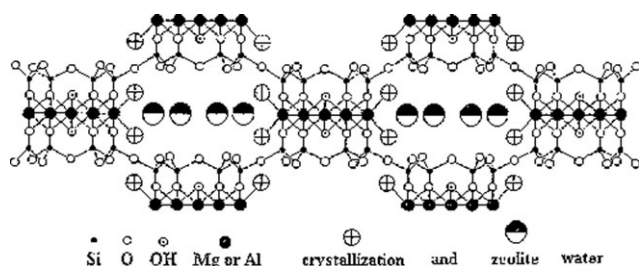
Figure 1. Crystal structure of palygorskite.

1. Acrylic acid, a monomer of a superabsorbent, possesses activating and dispersing functions for palygorskite because of its acidity,[21] and pure acrylic acid with very little water makes the activation and dispersion more efficient.
2. Palygorskite ore is hydrophilic and porous; its powerful hydration is able to drive water into every pore and interstitial space of palygorskite ore. The volume change in the transition from water to ice will disperse palygorskite agglomerates and crystal bundles into numerous small crystal bundles, even single crystals.
3. The freeze–thaw–extrusion cycle and vigorous stirring (ca. 6000 rpm) are key steps for dispersing palygorskite ore on the nanoscale and fully mixing every reagent.

It was found that appropriate freeze–thaw–extrusion cycles can disperse clay into single crystals with very small amounts of damage to the long, fine fibers of palygorskite.[22] Here, we further extended the freeze–thaw–extrusion cycles to synthesize a polymer/clay superabsorbent with a high percentage of palygorskite.

EXPERIMENTAL

Materials
The samples of palygorskite ore were obtained from Jiangsu Zhongyuan Minerals Co., Ltd. (Huaian, China). X-ray diffraction analysis suggested that palygorskite was the predominant constituent (∼ 70% pure) with montmorillonite and quartz as the major impurities. Acrylic acid (chemically pure, Shanghai Linfeng Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. The other reagents were all analytically pure and were used without further purification. All of the aqueous solutions were prepared with ultra-high-purity water, purified by a Milli-Q purification system.

Preparation of the Superabsorbent Composites
The palygorskite ore (4.2 g) was mixed with acrylic acid (7.2 g) and then extruded by a twin-screw extruder with the space of the two rolls in the range of 0.5–1 mm. The extruded samples were spread and frozen at −18°C for 2 h and then thawed for 30 min at 30°C. The extrusion–freeze–thaw process was repeated twice before synthesis if not specially mentioned otherwise. The number of repetitions was two, unless mentioned otherwise. A 25% sodium hydroxide solution (9.6 mL) was used to neutralized the sample to a 60% neutralization degree [calculated according to eq. (1)]. Then, 1 mL of 0.012 g/mL crosslinker (N,N-methylenebisacrylamide) and 1 mL of 0.4 g/mL initiator (ammonium persulfate) were consequently mixed into the sample:

$$\text{Neutralization degree} = \frac{m_{\text{NaOH}} \times M_{\text{AA}}}{m_{\text{AA}} \times M_{\text{NaOH}}} \quad (1)$$

where m_{NaOH} and m_{AA} are the weights of sodium hydroxide and acrylic acid (g), respectively. M_{NaOH} and M_{AA} are the molecular weights of sodium hydroxide and acrylic acid (g/mol).

The mixtures were stirred for 15 min at a certain speed and were then reacted for 3 h at 70°C. The stirring speed was 6000 rpm unless otherwise specified. The product was washed three times with distilled water and then dried at 65°C to a constant weight. All samples were milled and collected (60–100 meshes) before analysis. The process of preparation is shown in Scheme 1.

Water Absorbency Measurements
A 0.050-g sample was immersed in an excess 0.9 wt % NaCl (200 mL) aqueous solution at room temperature for 4 h to reach swelling equilibrium. The swollen sample was then separated from unabsorbed water by filtration through a 100-mesh screen. The water absorbency of the superabsorbent composite (Q_{eq}) was calculated as follows:

$$Q_{\text{eq}} = \frac{m_1 - m_2}{m_3} \quad (2)$$

where m_1 and m_2 are the weights of the swollen sample and the dry sample, respectively. Q_{eq} was calculated as the grams of water per gram of sample (g/g).

Characterization
The specific surface area (S_{BET}) and pore volume were recorded and calculated by an adsorption analyzer (Tristar 3020, Micromeritics Instrument Co., USA). IR spectra of the samples were recorded by a Fourier transform infrared (FTIR) spectrometer (Nicolet 5700, Thermo Electron Co., USA). X-ray diffraction patterns were recorded on an X-ray powder diffractometer (X'Pert Pro, PANalytical Co., The Netherlands). Scanning electron microscopy (SEM; S-3000N, Hitachi, Japan) was used to observe the microstructures of the palygorskite ore and the polymer/clay composite.

RESULTS AND DISCUSSION

Effect of the Freeze–Thaw–Extrusion Cycle
The effect of the freeze–thaw–extrusion treatment on palygorskite ore was investigated through analysis of the changes in the pore volume and S_{BET} values with processing times (Figure 2).
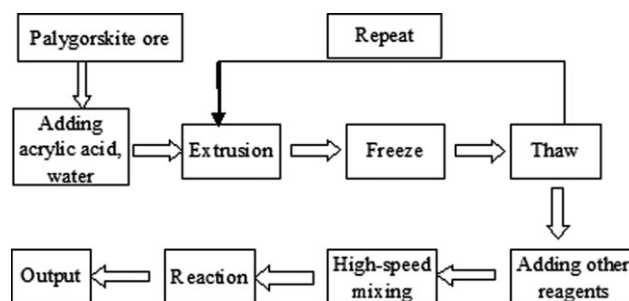
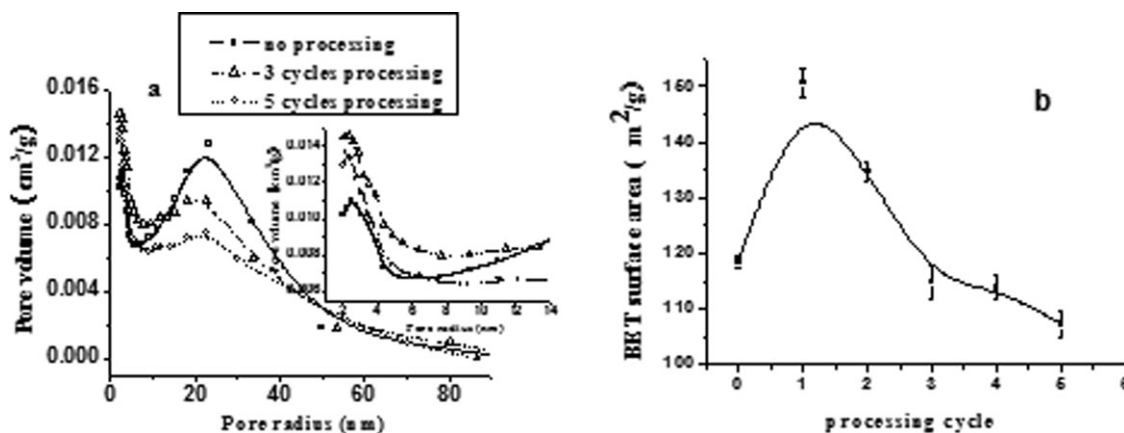

Scheme 1. Illustration of the reactive process.

Figure 2. Effect of the freeze–thaw–extrusion treatment on palygorskite ore: (a) the pore volume–pore radius curves of palygorskite ores with different processing cycles and (b) the S_{BET}–processing cycle curves of palygorskite ore. The processing cycles are the number the samples went through in the freeze–thaw–extrusion process.

The relationships among the pore radius, pore volume, and processing times of the sample are shown in Figure 2(a). Proper treatment can increase the total pore volume of a nanopore (<10 nm), but it decreases when the pore is overprocessed. The maximum value in our samples appeared with three treatments. The pore volume for the pore radius in the range 15–50 nm kept decreasing with increasing number of treatments, and the treatments made little difference to the pore radius past 50 nm. As shown in Figure 2(b), S_{BET} first increased and then decreased when the sample was overprocessed, with the maximum appearing after the first processing. The previous experiments proved that temperate treatment through the extrusion–freeze process was able to raise S_{BET} and the number of nanoholes with pore radius values below 15 nm. This indicated that a larger contact surface resulted in the palygorskite and polymer during the treatment.

Palygorskite ore is a kind of hydrophilic and porous clay. Water can be driven into its every pore and interstitial space easily through blunging. Proper treatment (freezing and extrusion) can further disperse large palygorskite particles into small crystal bundles, even single crystals, with negligible destruction to the crystalline forms of palygorskite. However, overextrusion can badly decrease the interstitial spacing of palygorskite ore and can even result in the breakage of the fine palygorskite fibers.

Effect of the Processing Mode

The van der Waals forces and hydrogen bonds are the main interaction between palygorskite single crystals. So, it is feasible to disperse palygorskite particles into single crystals by physical methods. The volume change in the transition from water to ice during the freeze–thaw process can facilitate ore dispersal appropriately. The dry process (with a Raymond pulverizer or roller mill) is a powerful dispersing technique, and roll extrusion is widely applied in the grinding mills of the palygorskite ore industry. However, excessive extrusion will cause serious damage to the long, fine fibers of palygorskite. In this article, traditional extrusion was combined with freeze–thaw treatments to achieve different complementarity and the perfect cooperation of agglomerations.

Figure 3 illustrates the variations in water absorbency as a function of treatment (e.g., freeze or extrusion) times. Figure 3(a) shows the

effect of the treatment times on the water absorbency of the sample via the extrusion process. Figure 3(c) presents the sample that underwent freeze processing, and Figure 3(b) represents the sample that underwent a joint freeze–thaw–extrusion cycle.

The water absorbency of the sample that underwent only the freezing treatment increased with the treatment times to a maximum (83.8 g/g) after two treatments; then, the value reversed. The samples treated by simple extrusion showed a peak value (88.7 g/g) after four treatments; however, the sample prepared through the freeze–thaw–extrusion cycle was able to produce a peak water absorbency of 95.2 g/g after two treatments. Therefore, we deduced that both freezing and extrusion played important roles in the water absorbency of the resulting composite. However, the maximum value appeared only when the synthesis system experienced two joint freeze–thaw–extrusion cycles; this also indicated extrusion and freeze possess mutual cooperation and complementarity with each other.
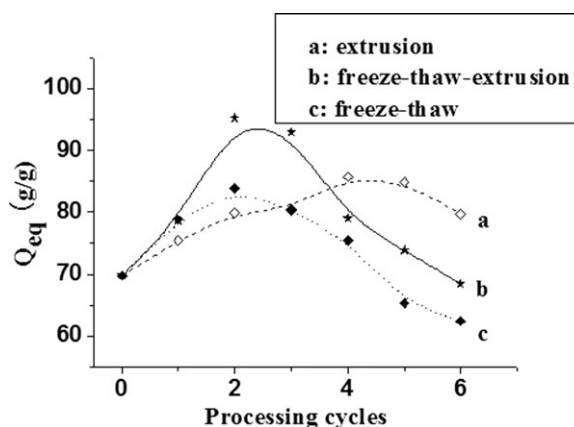

Figure 3. Effect of the processing cycles on the water absorbency of the superabsorbent composites treated (a) only through the extrusion process, (b) jointly through the freeze–thaw–extrusion process, and (c) only through the freeze–thaw process. The palygorskite ore content was 35 wt % in the superabsorbent composite, the stirring speed was 6000 rpm, and the water content in the synthesis system was about 58.5 wt %.

Effect of the Stirring Speed

Stirring is undertaken to ensure that all of the reagents disperse perfectly; this is especially important in synthesis systems with a high clay concentration and low water content. Hydration plays a major role in the disintegration of clay particles in water solutions. Most clays have this special property, and the hydration of palygorskite is exceptionally powerful and can be greatly improved by stirring. Upon stirring, the viscosity of the synthesis system became very high because of palygorskite dispersion; in turn, we needed a higher stirring speed. Figure 4 shows how vigorous a stirring speed was needed for the synthesis. With increasing stirring speed, the water absorbency of the superabsorbent composite increased to a peak at 6000 rpm, and then, the value reversed. It is important to point out that 6000 rpm is about three times the routine speed used in this type of synthesis.

The clay and monomer were coworkers in the formation of the polymeric network of the superabsorbent composite. With increasing stirring speed, palygorskite was dispersed more efficiently; this indicated that more crosslinking points were generated for the polymeric network. Under the experimental conditions, the suitable crosslinking density of the composite appeared to be 6000 rpm. Then, the shrinkage of the polymeric network occurred with a constant increase in the crosslink density.

Effect of the Water Content in the Synthesis System

Water was the solvent for the monomer, crosslinker, and initiator and was also important for the efficient dispersal of palygorskite. The water amount needed to be high enough to ensure that every reagent was well dissolved and perfectly dispersed. However, more water meant a greater energy consumption during the dewatering of the resulting product. Thus, there needed to be an optimal water content for this synthesis. Figure 5 shows the effect of the water content in the synthesis system on the water absorbency of the superabsorbent composite under constant concentrations of initiator and crosslinker.
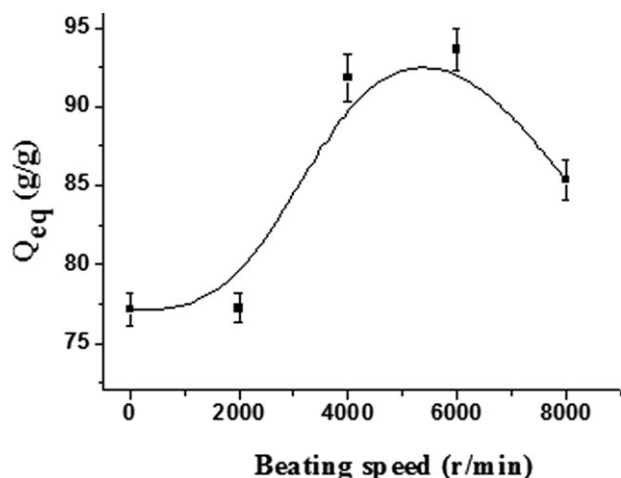

Figure 4. Effect of the stirring speed on the water absorbency of the superabsorbent composite prepared through two freeze–thaw–extrusion cycles. The other experimental conditions were the same as in Figure 3.
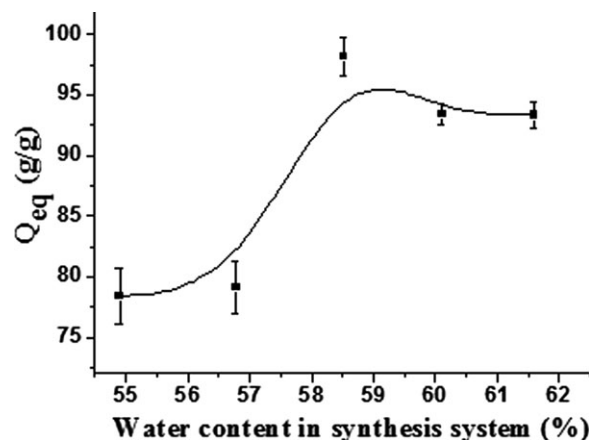

Figure 5. Effect of the water content on the water absorbency of the superabsorbent composite. The stirring speed was 6000 rpm. The other experimental conditions were the same as in Figure 4.

It can be seen from Figure 5 that the water absorbency of the resulting composite increased with the water content and amounted to a maximum volume of 98.2 g/g when the water content was about 58.5% in the synthesis system. After that, the water absorbency remained approximately constant with increasing water content under the experimental conditions. So, the water content of the semidry synthesis was much lower than that needed in the general synthesis system of a polymer/clay superabsorbent composite ($\sim$ 90%).

A perfect three-dimensional network structure is the determinant for a composite to have high water absorbency. Figure 5 clearly shows that enough water was necessary to form a perfect three-dimensional network structure. The formation of a three-dimensional network was not only dependent on the monomer, initiator, and crosslinker but also on the number of bonding sites of the unit palygorskite particles. With increasing water and dispersion processing, the particle concentration of palygorskite increased first and then remained constant over a considerable concentration extent (similar to a saturated concentration), although the mass concentration continued to drop. The number of bonding sites of unit palygorskite particles increased to a plateau; this explained why the water absorbency of the composite increased to a plateau.

SEM of Palygorskite Ore and the Resulting Superabsorbent

Figure 6(a) shows that the palygorskite ore existed as a massive solid with some fibers reaching out. The ore after two freeze–thaw–extrusion cycle treatments [Figure 6(b)] exhibited a free and easy alignment compared with the raw ore [Figure 6(a)]; this also further proved that most of the ore was needlelike palygorskite mixed with a little lamellar montmorillonite and granular quartz. Figure 6(c) represents the cross section of the superabsorbent composite treated with two freeze–thaw–extrusion cycles. Both palygorskite (most fibers were no more than 60 nm in width) and the impurities (ca. 100–200 nm granules) were dispersed very well in the composite.

In contrast to normal polymer/clay superabsorbents, the composite from this semidry synthesis showed well-connected open
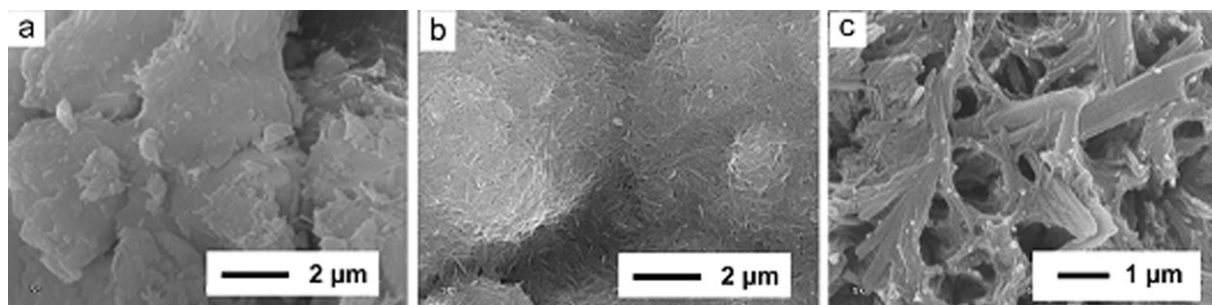
Figure 6. SEM micrographs of the (a) palygorskite ore, (b) palygorskite ore through two freeze–thaw–extrusion cycles, and (c) superabsorbent composite prepared through two freeze–thaw–extrusion cycles. The stirring speed was 6000 rpm, and the water content in the synthesis system was about 58.5 wt %. The palygorskite ore content was 35 wt %.

channels or pores in the structure, and the size of pores was generally in the range of several hundred nanometers [Figure 6(c)]. A low water content and great stirring speed should have been the main factors that brought this synthesis system high viscosity and resulted in abundant, delicate, and lasting bubbles. Those bubbles were also important for the improvement of the absorption ability of the polymer/clay composite.[23–25] SEM further proved that the semidry synthesis was quite efficient for the preparation of a high uniform polymer/clay composite with a high clay content, even though that water content was much lower than that in a general synthesis.

FTIR Spectra of Palygorskite Ore and the Resulting Superabsorbent

Powerful dispersive processing always brings significant mechanochemical effects, which promote the reaction of palygorskite and acrylic acid; this can be proven by FTIR spectral analysis. The FTIR spectra of palygorskite and the resulting superabsorbent composites are presented in Figure 7 and were consistent with those reported.[26,27] In the high-wave-number region, bands at 3548 cm^{-1} observed for palygorskite ore were attributed to the symmetric and antisymmetric stretching modes of molecular water coordinated to the magnesium at the edges of the channels. The band in the 1630–1640-cm^{-1} region for palygorskite

was assigned to the zeolitic water in the channels of the samples. The maximum absorbance of palygorskite was observed at 1035 and 986 cm^{-1}; this was ascribed to Si—O—Si and Si—O bonds on the layers of clay. Compared with the spectra of palygorskite, a new band around 1100 cm^{-1} was characteristic of esters and gave direct evidence for the participation of Si—OH in the reaction with acrylic acid. The new band around 1556 cm^{-1} was observed in the resulting superabsorbent composites and was ascribed to —COO of the resulting composite.

CONCLUSIONS

The effects of the processing mode, water content, and stirring speed on the synthesis of the poly(acrylic acid)/palygorskite superabsorbent composites were investigated in this study. Two to three freeze–thaw–extrusion cycles raised the ratio of nanoholes below 10 nm for the clay, which provided more contact surfaces for palygorskite to take part in the reaction. Both freezing and extrusion improved the water absorbency of the composite, and their mutual cooperation was very clear. The water absorbency of the resulting composite reached a maximum of 98.2 g/g in a 0.9 wt % NaCl solution, whereas the water content of the synthesis system was about 55 wt %; this was much lower than that of a general synthesis system (ca. 95 wt %). Under the experimental conditions, the optimal stirring speed was 6000 rpm. SEM showed that both palygorskite and the impurities were dispersed very well in the semidry synthesis. In contrast to general polymer/clay superabsorbents, the composite based on the semidry synthesis showed well-connected open nanoscale channels and pores in its structure; this resulted in a low water volume and great stirring speed. The FTIR spectra gave direct evidence for the participation of palygorskite in the preparation of poly(acrylic acid)/palygorskite networks.

As a kind of hydrous and porous clay mineral, palygorskite has a powerful hydration ability. All of the processing modes, including extrusion, freezing, and high-speed stirring, were very useful for improving the hydration and dispersion; this gave a more efficient dispersion of palygorskite in the synthesis system. So, despite a much lower water content, the semidry synthesis was still powerful for the preparation of good polymer/clay superabsorbent composites, especially for a high-clay-content synthesis system.
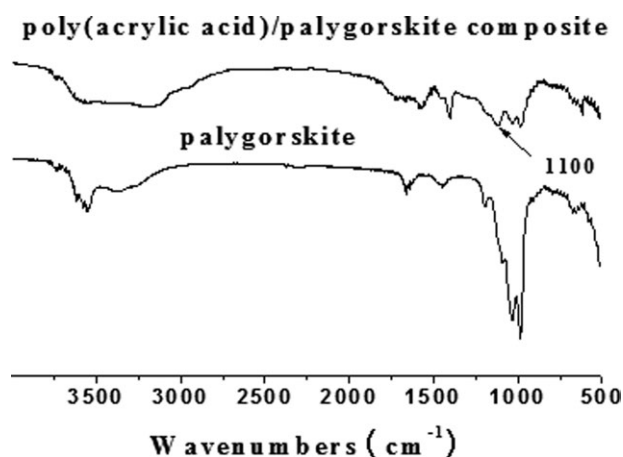

Figure 7. IR spectra of the palygorskite ore and poly(acrylic acid)/palygorskite composite. The preparation conditions of the polymer/clay composite were the same as in Figure 6.

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