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Synthesis of P(AA-AM)/Attapulgite Clay SAR Under Microwave Irradiation

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The aqueous solution polymerization of acrylic acid, acrylamide and attapulgite clay under microwave irradiation was studied, and a super absorbent resin was synthesized. The factors that influence the liquid absorbency rate of the super absorbent resin were discussed, including microwave irradiation time, neutralization degree of acrylic acid (AA), the dosage of initiator, crosslinking agent and attapulgite clay. The super absorbent resin was characterized by IR and scanning electron microscopy (SEM). It just needs 30 s to preparation the super absorbent resin. Its liquid absorbency rate is about 1620 $g.g^{-1}$ and 170 $g.g^{-1}$ in distilled water and 0.9 wt% NaCl solution, respectively.

Keywords: Microwave irradiation, super absorbent resin, acrylic acid, acrylamide, attapulgite clay

1 Introduction

Super-absorbent resin (SAR), as a new kind of functional macromolecule materials, is lightly crosslinked networks of hydrophilic polymer chains, has the characteristics of high water/or salt absorption and retention, so it has been widely used in personal hygiene products, sewage treatment, industry and agriculture(1, 2). Attapulgite clay is a natural clay mineral of nanoscaled fibrous hydrous magnesium silicates. It was used as a raw material for preparing SAR because of the reactive groups –OH on the surface. Microwaves are a portion of the electromagnetic spectrum with frequencies in the range of 300 MHz to 300 GHz. Microwave irradiation was shown to have a significant effect on reaction rates in various organic synthesis. This increase in reaction rates can be very high, for instance, a 1240-fold increase in reaction rate upon irradiation was reported (3). Compared to conventional heating, the main advantages of microwave dielectric heating are the speed and easy control of the heating of the feed (4, 5). In our experiments, P(AA-AM)/attapulgite clay has been synthesized under microwave irradiation and the reaction time been decreased greatly.

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2 Experimental

2.1 Preparation of SAR

Unless otherwise noted, all of the raw materials were of analytical purity and used as received without further purification. A series of the samples with different amounts of attapulgite clay (chemical composition: SiO_2, 57.06%; Al_2O_3, 16.59%; Fe_2O_3, 6.11%; MgO, 8.63%; CaO, 4.55%; TiO_2, 0.71%; MnO, 0.08%; K_2O, 3.51%; Na_2O, 1.35%; SO_3, 0.42%; P_2O_5, 0.22%), crosslinking agent (the weight ratio of crosslinking agent in the feed is 0.01%, 0.02%, 0.03%, 0.04%, 0.05%, respectively), initiator (the weight ratio of initiator in the feed is 0.8%, 0.9%, 1.0%, 1.1%, 1.2%, respectively), acrylamide and acrylic acid with different degrees of neutralization (65%, 70%, 75%, 80%, 85%, respectively) were prepared by the following procedure: Typically, acrylic acid (15.0 g) was neutralized with 40 mL of NaOH solution (11.9 wt%, 12.7 wt%, 13.5 wt%, 14.3 wt%, 15.0 wt%, respectively) in a glass beaker. A certain amount of attapulgite clay and acrylamide (3.5 g) were added to the above partial neutralized monomer solution. The crosslinking agent N,N-methylenebisacrylamide (MBA) and initiator [n ($K_2S_2O_8$) :n($NaHSO_3$) =1:1] were dissolved in 10 mL distilled water and then added to the AA-AM-attapulgite clay mixture solution and the mixed solution was stirred at room temperature. The prepared precursor solution was put into an open ceramic pot, and then initiated by microwave irradiation (1000 W) for a certain seconds to synthesize SAR. The SAR was dried at 90°C for 24 h, then

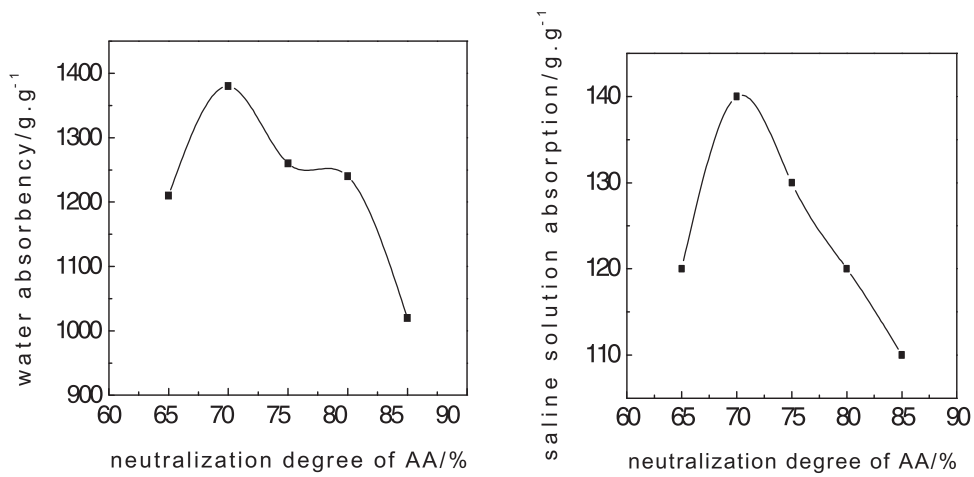

Fig. 1. Effect of neutralization degree on liquid absorbency rate.

cooled to room temperature and crushed into 60–100 mesh particles to evaluate its behavior.

2.2 Liquid Absorbency Measurement

A weighted quantity of the SAR was immersed in distilled water or 0.9 wt% NaCl solution at room temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by being filtered over a 100-mesh screen. The liquid absorbency of SAR was determined by weighing the swelled samples, and the Q of the samples was calculated using the following equation: $Q=(M_2\text{-}M_1)/M_1$, where M_1 and M_2 are the weights of the dry sample and the water-swollen sample, respectively. Q was calculated as grams of liquid per gram of sample.

2.3 Swelling Rate Measurement

A sample 1.0 g was poured into distilled water or 0.9 wt% NaCl solution at room temperature. The swelling rate of SAR was determined by weighing the swelled samples at 5 min intervals, and the measurement condition was the same as that for equilibrium water absorbency.

2.4 Water Retention Measurement

A swollen sample was dried at 60°C. The water retention performance of SAR was determined by weighing its weight at 1 h intervals.

2.5 Characterization

The IR spectra of the SAR was recorded on a FTIR (Spectrum 100, Perkin-Elmer, USA) using KBr pellets. The morphology of the dried sample was examined from a JSM-6700F Field Emission Scanning Electron Microscope equipped with an energy-dispersive spectrometer (JEOL, Japan) after coating the sample with gold film.

3 Results and Discussion

3.1 Effect of Neutralization Degree on Liquid Absorbency Rate

In order to investigate the effect of neutralization degree on liquid absorbency rate, we changed the neutralization degree of AA, while the radiation time was 30 s, *m*(AA):*m*(AM):*m*(attapulgite clay) = 15.0:3.5:1.0, weight ratio of initiator and MBA in the feed was 1.0% and 0.03%, respectively. According to Flory's network theory, the fixed charges on polymeric network of SAR play an important part in the swelling of the SAR. They are related to electrostatic repulsion between charges on the polymeric backbone and to osmotic pressure difference between polymeric network and external solutions. Therefore, the amount and type of hydrophilic groups on polymeric network play important parts in influencing water-absorbing properties of SAR. The effect of the neutralization degree of AA on equilibrium water absorbency of the SAR in distilled water and in 0.9 wt% NaCl solution is shown in Figure 1. With the neutralization degree increasing, the electrostatic repulsion, ionic hydrophilic property and osmotic pressure difference increases, which results in an increase of equilibrium water absorbency. However, further increasing the neutralization degree to a certain extent results in the generation of more sodium ions in the polymeric network, which reduces the electrostatic repulsion by screening the negative charges of –COO– groups, thus resulting in the decrease of equilibrium water absorbency. The optimal reaction condition is obtained as follow: Its liquid absorbency rate is about 1380 g.g^{-1} and 140 g.g^{-1} in distilled water and 0.9 wt%

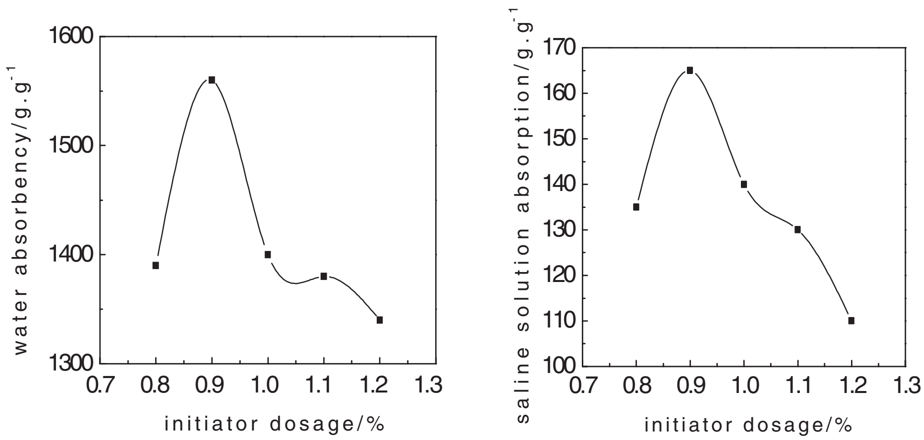

Fig. 2. Effect of initiator dosage on liquid absorbency rate.

NaCl solution, respectively, while the neutralization degree of AA is 70%.

3.2 Effect of Initiator Dosage on Liquid Absorbency Rate

In order to investigate the effect of initiator dosage on liquid absorbency rate, the radiation time and the dosage of AA, AM, attapulgite clay and MBA were the same as above, we changed the dosage of initiator, while the neutralization degree of AA is 70%. Figure 2 shows the effect of the initiator content on the water absorbency of SAR. When the content of the initiator is below the optimum values, the swelling capacity of SAR is decreased. This may due to a decrease in the number of radicals produced as the content of initiator decreases. The network cannot be formed efficiently with a few number of radicals in free-radical polymerization reaction, which results in the decrease of the water absorbency. The optimal reaction conditions are obtained as follows: Its liquid absorbency rate is about 1560 g.g^{-1} and 165 g.g^{-1} in distilled water and 0.9 wt% NaCl solution, respectively, while the neutralization degree of AA is 70%, the weight ratio of initiator in the feed is 0.9%.

3.3 Effect of MBA Dosage on Liquid Absorbency Rate

In order to investigate the effect of MBA dosage on liquid absorbency rate, the radiation time and the dosage of AA, AM and attapulgite clay were the same as above, we changed the dosage of MBA, while the neutralization degree of AA is 70%, the weight ratio of initiator in the feed is 0.9%. The effect of MBA content on water absorbency is shown in Figure 3, the swelling ratio of the hydrogel has a relation to the ionic osmotic pressure, crosslinked density, and affinity of the hydrogel with water. When the content of MBA is above the optimum values, as the content of MBA content increases, the crosslinking density of the SAR also increased. This would result in a decrease in the space between the copolymer chains and lead to a decrease in water absorbency. The results conform with Flory's network theory. The optimal reaction conditions are obtained as follows: Its liquid absorbency rate is about 1550 g.g^{-1} and 160 g.g^{-1} in distilled water and 0.9 wt% NaCl solution, respectively, while the neutralization degree of AA is 70%, the weight ratio of initiator and MBA in the feed is 0.9% and 0.03%, respectively.

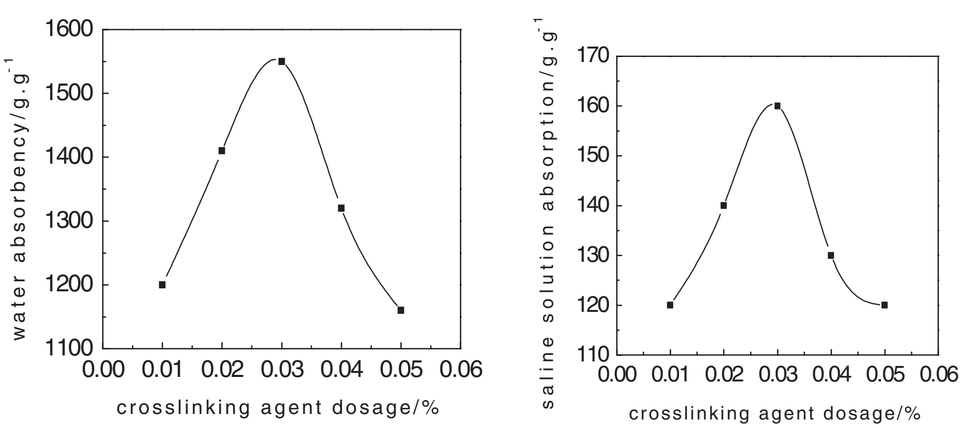

Fig. 3. Effect of MBA dosage on liquid absorbency rate.

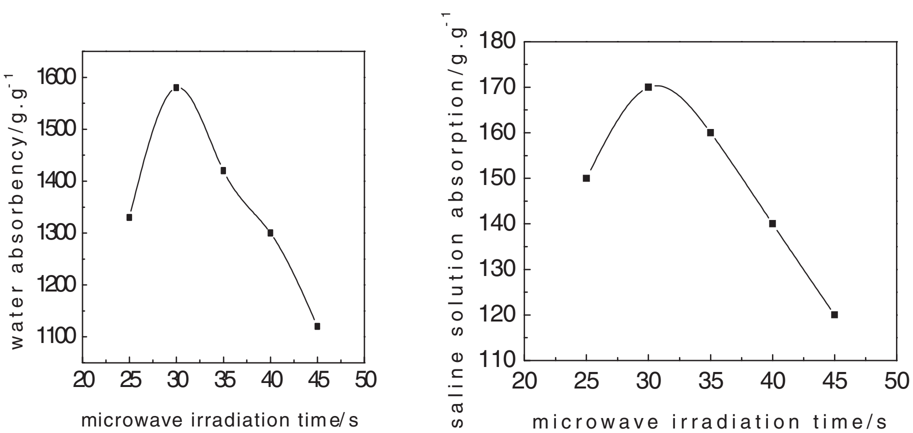

Fig. 4. Effect of microwave irradiation time on liquid absorbency rate.

3.4 Effect of Microwave Irradiation Time on Liquid Absorbency Rate

In order to investigate the effect of microwave irradiation time on the liquid absorbency rate, the dosage of AA, AM and attapulgite clay were the same as above, we changed the microwave irradiation time, while the neutralization degree of AA is 70%, the weight ratio of initiator and MBA in the feed is 0.9% and 0.03%, respectively. As shown in Figure 4, the network structure is destroyed when the radiation time is too long, this would result in a decrease in water absorbency. The optimal reaction conditions are obtained as follows: Its liquid absorbency rate is about 1580 g.g^{-1} and 170 g.g^{-1} in distilled water and 0.9 wt% NaCl solution, respectively, while the neutralization degree of AA is 70%, the microwave irradiation time is 30 s, the weight ratio of initiator and MBA in the feed is 0.9% and 0.03%, respectively.

3.5 Effect of Attapulgite Clay Dosage on Liquid Absorbency Rate

In order to investigate the effect of attapulgite clay dosage on liquid absorbency rate, the dosage of AA and AM were the same as above, we changed the dosage of attapulgite clay, while the neutralization degree of AA is 70%, the microwave irradiation time is 30 s, the weight ratio of initiator and MBA in the feed is 0.9% and 0.03%, respectively. Figure 5 shows the effect of attapulgite clay content on the water absorbency. The water absorbency decreases with the increase of attapulgite clay content when the content of attapulgite clay is above the optimum values. The inorganic clay mineral particle in network acts as an additional network point. The crosslinking density of SAR increases with the increase of attapulgite clay content, which results in a decrease in water absorbency. The optimal reaction conditions are obtained as follows: Its liquid absorbency rate is about 1620 g.g^{-1} and 170 g.g^{-1} in distilled water and 0.9 wt% NaCl solution, respectively, while the neutralization degree of AA is 70%, the microwave irradiation time is 30 s, the dosage of attapulgite clay is 1.0 g, the weight ratio of initiator and MBA in the feed is 0.9% and 0.03%, respectively.

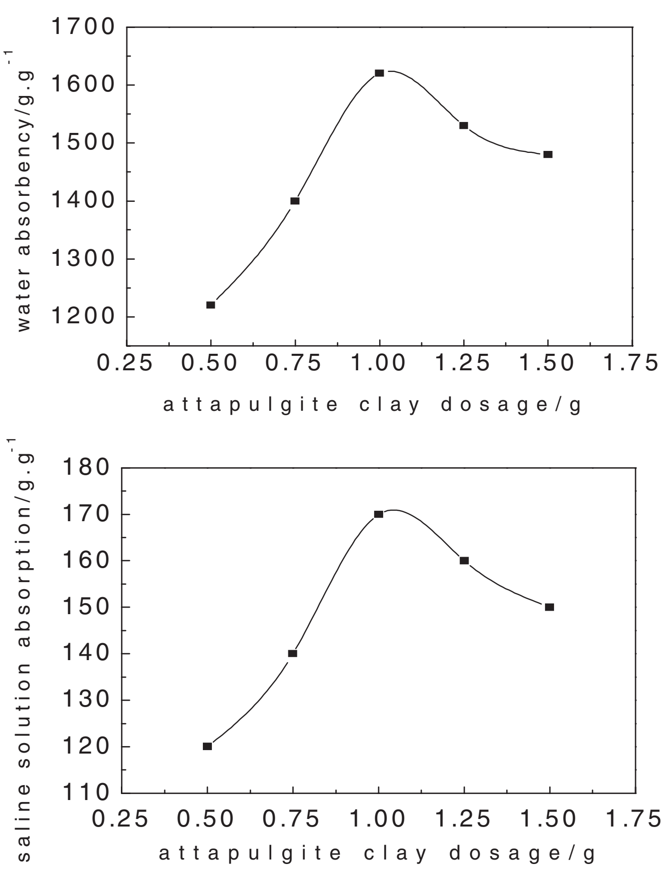

Fig. 5. Effect of attapulgite clay dosage on liquid absorbency rate.

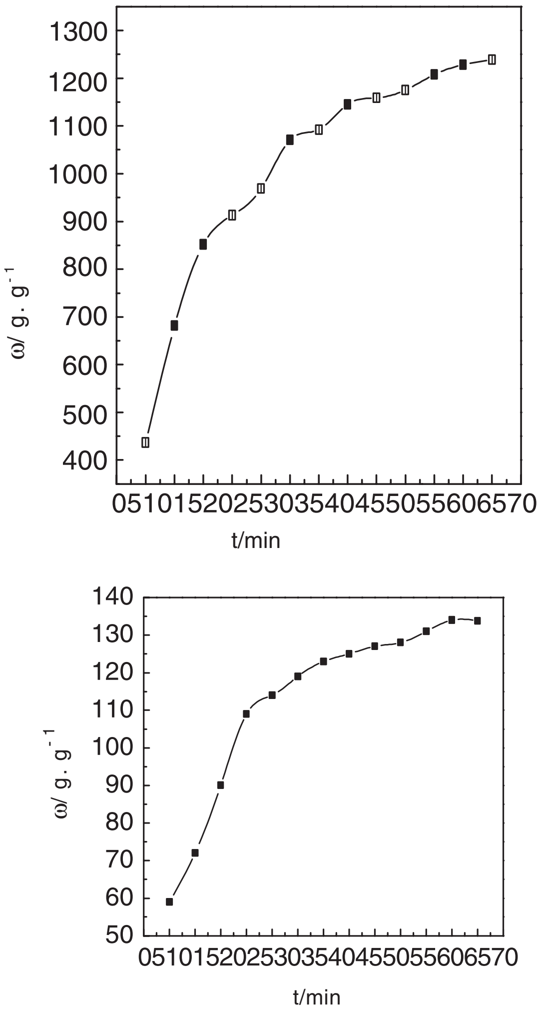

Fig. 6. Swelling rate.

3.6 Swelling Rate

The swelling rate of SAR is shown in Figure 6. It is indicated that the swelling rate of SAR is high in 0–30 min and the water absorbency of SAR reaches more than 80% of equilibrium water absorbency within 30 min. After 30 min, the swelling rate becomes low. It needs about 1 h to reach equilibrium water absorbency.

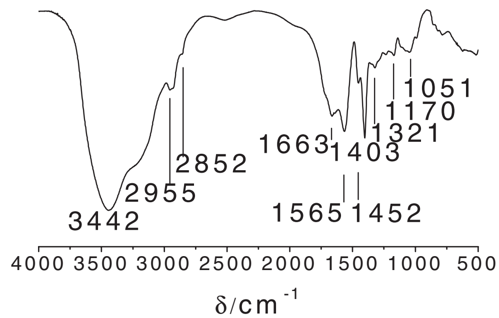

Fig. 8. FT-IR spectra of super absorbent resin.

3.7 Water Retention Test

It can be seen from Figure 7 that the swollen SAR samples show water retention capability and approximately 30% initial water absorbency can be kept after 10 h of a heating oven test at 60°C.

3.8 Spectroscopic Characterization

The infrared spectra of P(AA-AM)/attapulgite clay SAR are shown in Figure 8. According to the IR spectra, the band observed was at 3442 cm^{-1}, corresponding to the N–H stretching of acrylamide unit, the absorption bands at 2955 cm^{-1} and 2852 cm^{-1} attributed to the asymmetric stretching of C–H and symmetric stretching of C–H, respectively, 1663 cm^{-1}, corresponding to the carbonyl moiety of the acrylamide unit, 1170 cm^{-1}, corresponding to the –CO–O– stretching of acrylate unit, 1051 cm^{-1}, corresponding to the Si–O stretching of attapulgite clay. It is suggested that the graft copolymerization between OH

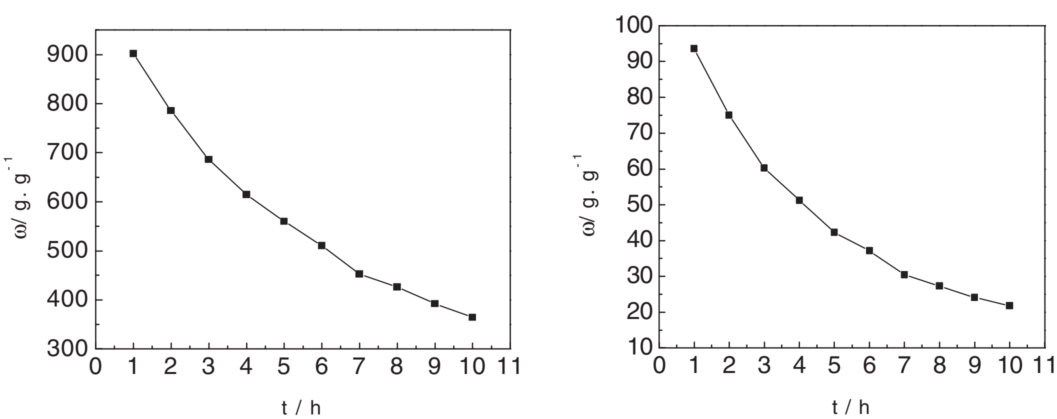

Fig. 7. Water retention.

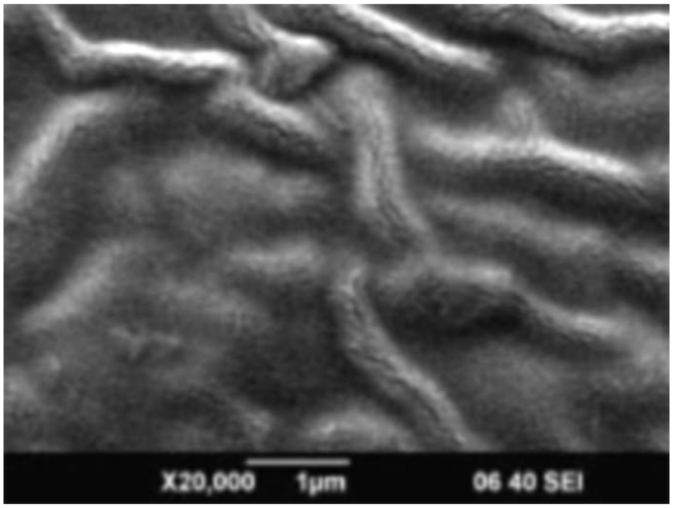

Fig. 9. Scanning electron micrograph of SAR.

groups on attapulgite clay and monomers take place during the reaction.

3.9 Surface Morphology of SAR

The micrograph of SAR is shown in Figure 9. It can be seen from this figure that it shows an undulant surface and a broad network structure. This undulant surface is convenient for the penetration of water into the polymeric network. It is believed that this coarse surface is related to equilibrium water absorbency and swelling behaviors of the corresponding the SAR and makes the SAR a high water absorption material.

4 Conclusions

The P(AA-AM)/attapulgite clay SAR with a water absorbency of higher than 1620 $g.g^{-1}$ and 170 $g.g^{-1}$ in distilled water and 0.9 wt% NaCl solution was synthesized under our experimental conditions: microwave irradiation power, 1000 W; radiation time, 30 s; 70% neutralization degree; m(AA):m(AM):m (attapulgite clay) = 15.0:3.5:1.0; weight ratio of MBA and initiator in the feed is 0.03% and 0.9%, respectively.

Acknowledgements

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