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Synthesis and Properties of Sepiolite/poly (acrylic acid-co-acrylamide) Nanocomposites

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Summary

Novel hydrogel nanocomposites, based on sepiolite, acrylic acid (AA), acrylamide (AM), and N,N'-methylenebisacrylamide (MBA), were synthesized by solution copolymerization. The structure, morphology and liquid absorbency of these composites were investigated through FTIR, SEM and the like. The influences of sepiolite, crosslinker content, initiator dosage, neutralization degree of AA and molar ratio of AA/AM on the distilled water absorbency (Q_w), physiological saline solution absorbency (Q_p) were discussed in detail. Results showed that needleshaped sepiolite dispersed in nanoscale, and the grafting of AA and/or AM on the sepiolite surface occurred. Compared with the sepiolite-free hydrogel, sepiolite contributed to liquid absorbency, and at its weight content of 15.0%, Q_w and Q_p were enhanced as high as 11.6% and 14.5%, respectively.

Introduction

Proper crosslinked polyacrylic acid (PAA) or its copolymers, usually called superabsorbent, is a special hydrogel which can absorb, swell and retain aqueous solutions up to hundreds or thousands times their own weight even under some pressure. Therefore, superabsorbents have great advantages over traditional water-absorbing materials such as cotton, pulp or sponge, and are widely used in agriculture [1], horticulture, sanitary goods, sealing[2,3], controlled drug delivery systems[4,5], concrete[6], drilling and so on. Nano- and micro-particles of inorganic materials such as montmorillonite[7,8], kaolin[9,10], mica[11], bentonite and Hydrotalcite [12] have recently received numerous attention for synthesizing superabsorbents. The main goals of using these particles are reducing cost, increasing swollen gel strength and achieving new materials for special applications such as moisture sensors[8]. But there are some disadvantages of using these inorganic particles in applications. They reduce swelling capacity and swelling rate of the hydrogels.

Sepiolite is an abundant fibrous talc-like mineral of $Si_{12}Mg_8(OH)_4O_{30}(OH_2)_4{\cdot}8H_2O$ formula, which has typically a surface area around $200m^2/g$ and a cation exchange capacity ranging from 20 to 40 meq/100g. On the other hand, silanol (Si–OH) groups are present on the external surface of the silica particles, and these groups are directly accessible to various organic and inorganic reagents[13]. Therefore, sepiolite is a reactive mineral exhibiting strong absorbing ability to water and other substances, and it's also candidate to prepare organic/inorganic absorbing composites.

In this article, a series of novel hydrogel composites, based on sepiolite, AA and AM were prepared by solution copolymerization. Morphological, structural, absorbing properties, and relating factors were investigated in detail.

Experimental

Materials

Acrylic acid (AA, chemically pure, Nankai Special Chemical Factory, Tianjin, China) was distilled twice by vacuum distillation at $63^{\circ}C/25$ mmHg and stored in a refrigerator. Potassium persulfate (KPS, analytical grade, Tianjin 3rd Chemical Reagent Factory, Tianjin, China) was recrystallized from water. N,N' -Methylenebisacrylamide (MBA, chemically pure) and acrylamide (AM, chemically pure), used as received , were purchased from Tianjin Chemical Reagent Institute(Tianjin, China). Sepiolite micropowder (Dingxing Fuli Saponite Factory, Hebei, China) was first screened through a 320 mesh sieve, then cooked at $120^{\circ}C$ in water for 6 h and dried at $110^{\circ}C$ for 8 h.

Preparation of sepiolite/poly (AA-co-AM)

A series of samples with different amounts of cooked sepiolite, MBA (crosslinker), KPS (initiator), AM, and partially neutralized AA were prepared by the following procedure. The partially neutralized AA was characterized with neutralization degree (ND), the ratio of moles of NaOH to that of AA. Typically, 0.050mol AA was preneutralized at $5^{\circ}C$ with 5.0 mL 25% aqueous sodium hydroxide (ca 7.96M) in a beaker, and then 0.010mol AM was dissolved completely. In a four-neck flask equipped with a stirrer, a condenser, a thermometer and a nitrogen line, 1.00g sepiolite, 0.0013g MBA and the preneutralized AA solution were added. After the mixed solution was stirred under nitrogen atmosphere at room temperature for 30 min, the flask was placed on a water bath at $65^{\circ}C$, and 10 min later 0.0255g KPS in 2.00mL water was dropped into the system during 30 to 40 min. After that, the system was heated stepwise to $70^{\circ}C$ for 1.0h, $75^{\circ}C$ for 0.5h, and $85^{\circ}C$ for 1.0h. At last, the resulting product was cooled to room, cut to small pieces, and dried in an oven at $120^{\circ}C$ to a constant weight. Thus, the dried composite was ground into powder, and milled through 40–80 mesh screen. The yield, calculated through the percentage of dry matrix obtained versus total grams of vinyl monomers, KPS and sepillite used, reached 98.5wt%.

Characterization

The IR spectra of the composites were recorded on an infrared spectrophotometer (Bruker, VECTOR-22 FTIR spectrophotometer) using KBr pellets. The IR spectrum of the composite shows absorption bands corresponding to the functional groups attached to the main chain of copolymer and on the surface of sepiolite.

Scanning electron microscopy (SEM) was used for visual observation of the morphology and the needle-like sepiolite dispersed in the composites. The SEM investigation was performed on a Philips XL30 apparatus operated after coating the sample with gold film.

Measurement of properties

Distilled water absorbency: An accurately weighted composite was immersed in distilled water at atmosphere pressure and allowed to swell at room temperature for 60 min The swollen sample was then filtrated through an 80 mesh sieve to remove non-absorbed water for about 60 min and weighted to obtain the amount of the water absorbed thereby. The water absorbency Q_w was calculated by using the following equation:

$$Q_w=(m_2-m_1)/m_1 \qquad (\mathbf{1})$$

where m_2 and m_1 denote the weight of the swollen hydrogel and the dried sample, respectively.

Physiological saline solution absorbency (Q_p): This property can be evaluated by repeating the measurement method of Q_w except 0.9 wt % NaCl solution instead of distilled water.

Results and Discussion

Effect of sepiolite

Sepiolite is formed by an array of parallel channels, consisting of a double layer of SiO_4 tetrahedral sandwiching an internal octahedral MgO_6 layer. These ribbons are arranged in such a way that tetrahedral sheet of SiO_4 is continuous but inverts in apical directions in adjacent ribbons, generating uniform size parallel intracrystalline tunnels (10.8 × 4.0Å) along the fiber. Under normal conditions, water fills the internal voids of the channels, solvating magnesium ions located at the edges of the fibers (Figure 1 [14]). Its excellent absorbing properties result in synergistic effect in sepiolite/poly (AA-co-AM) composites, as shown in Figure 2.

When a composite contained a small amount of sepiolite (less than 5%), the water absorbency of the resulting product significantly improves. When the content of sepiolite in composites from 5% to 15%, the water absorbency is nearly invariable with the increase of the amount of sepiolite. When the sepiolite content is more than 15%, the water absorbency decreases gradually. This may be attributed to the fact that a greater amount of sepiolite results in the generation of more crosslink points, which increases the crosslinking density of the hydrogel composites and reduces the absorbency of the composites. The crosslinkage may be physical type, such as $-CO_2^-\ldots Mg^{2+}\ldots {}^-O_2C-$, and chemical type, like easterization of SiOH on the surface of sepiolite, as described in the following sections.

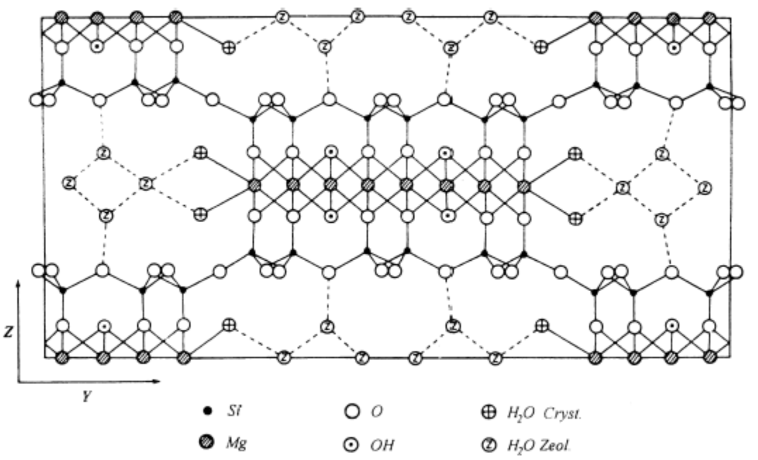


Figure 1. Schematic representation of the sepiolite structure projected onto the (001) plane.

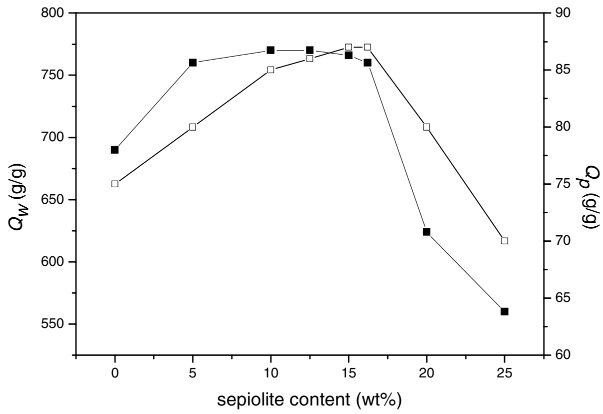


Figure 2. Dependence Q_w (■) and Q_p (□) of as function of sepiolate content in the sepiolite/poly (AA-co-AM) composite prepared at ND of 80%, AA/AM of 3:1 (mol); weight of MBA and KPS in the feed is 0.0013g and 0.0255g, respectively.

For the physiological saline solution absorbency in Figure 2, the absorbency improves with the increased sepiolite content at the level of below16.2%. This may be attributed to the fact that sepiolite exhibits preferable salt-resistance, and the increased sepiolite conduces to absorb sodium chloride. When the filler content was higher than 16.2%, Q_p dropped in virtue of crosslinkage enhancement as described above. Overall, sepiolite conduces to improve both Q_w and Q_p evidently. Compared with pure copolymer hydrogel (free of filler), absorbency of Q_w and Q_p of the hydrogel composite containing 15.0wt% sepolite was enhanced as high as 11.6% and 14.5%, respectively. These improvements are attributed mainly to the special microstructure of internal channel voids of sepiolite, exhibiting the excellent absorbing ability to inorganic salts[15]. On the other hand, the absorbency of organic hydrogel powers from osmotic pressure, and therefore, the Q_w was even above 10 times of Q_p.

Effect of crosslinker

Figure 3 shows the relationship between the amount of MBA and liquid absorbency. At the MBA usage of 0.02wt%, Q_w and Q_p appeares the peak values of 830 and 100 gH_2O/g, respectively. The relationship between the absorbency and network structure parameters was investigated by Flory and given as the following equation [16]:

$$q_m^{5/3} \cong \frac{\left(\frac{1}{2}\frac{i}{v_u}\frac{1}{S^{*1/2}}\right)^2 + \left(\frac{1}{2} - \chi\right)/V_1}{v_e/V_0} \qquad (\mathbf{2})$$

where q_m is the equilibrium swelling ratio, ν_e/V_0 is the number of effectively crosslinked chains in unit volume, S^* is the ionic strength of the swollen liquid, i/ν_u is the concentration of fixed charge referred to the unswollen networks, χ is the polymer–solvent thermodynamic interaction parameter, and V_1 are the molar volume of water. This relationship may be applied to the present composites, because the crosslinked poly (AA-co-AM) may be considered as a part of the network. S^*, i/ν_u, χ and V_1 are constant when the absorbed liquid is fixed. Therefore, ν_e/V_0 is the only factor that can influence the absorbency. The factor (ν_e/V_0) in Eq. (2) expresses the crosslinking density. Therefore, at the MBA content of above 0.02% the higher concentration of crosslinker may result in a decrease in absorbency.

In the range of introduced crosslinking monomer minor than 0.02 %, Q_w decreases with a decrease in the concentration of MBA: the decrease in crosslinking points results in increased swelling capacity allowing higher water absorption in the filtration method. But the highly swollen hydrogel with lower crosslinking density may lose larger amounts of absorbed water and soluble material, such as linear homopolymer or copolymer of AA and AM. Physiological saline solution absorbency, Q_p, shows similar behavior to that of Q_w, as shown in Figure 3.

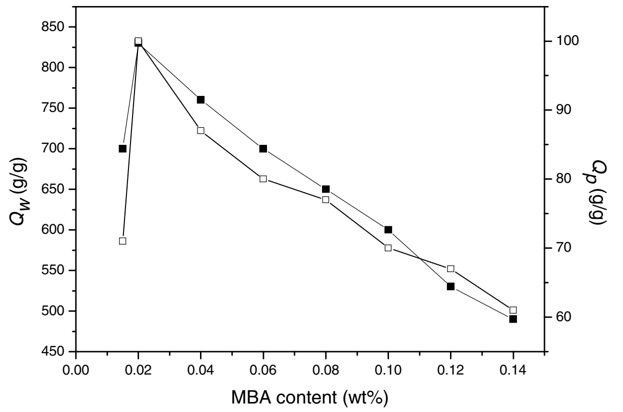


Figure 3. Relationship between Q_w (■), Q_p (□) and MBA content in the sepiolite/poly (AA-co-AM) composite prepared at ND of 85%, AA/AM of 5:1 (mol); weight ratio of sepiolite and initiator in the feed is 16.2% and 0.41%, respectively.

Effect of neutralization degree

The effect of neutralization degree (ND) on the liquid absorbency is shown in Figure 4. It is obvious that the water absorbency increases from 60% to 85% of ND and decreases with further increases in the neutralization degree of AA. According to Flory [16], ionic networks swell extensively due to the ionic charges of networks. The neutralized PAA network has negatively charged carboxyl groups which tend to expand the network due to the electrostatic repulsion. The electrostatic repulsion increases with the increase in ND, then decreases. This may be attributed to the screening effect of carboxyl groups with excess sodium ions: further increases in the neutralization degree of PAA result in the generation of more sodium ions, which reduce the electrostatic repulsion by screening the negative charges of carboxyl groups, thus resulting in the decrease of water absorbency. Sodium acrylate polymerizes less readily than acrylic acid, because ionized monomers react more slowly in the propagation step of polymerization. Higher percentages of soluble polymer and higher residual monomer concentrations on the final product can result. Therefore, there exists an optimum ND of PAA in the preparation of AA-based hydrogel composites. In our system, the ND of 85% was optimal according to the absorbency results.

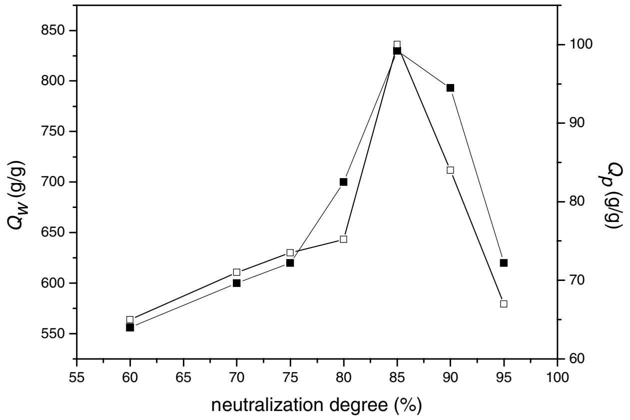


Figure 4. Absorbency Q_w (■), Q_p (□) of the sepiolite/poly (AA-co-AM) hydrogel composites vs. the neutralization degree of acrylic acid prepared at AA/AM of 5:1 (mol); weight of crosslinker, initiator and sepiolite in the feed is 0.0013g, 0.0255g, and 1.0g, respectively.

Effect of initiator

Chen [17] reported that the increase of chain ends in AA-based superabsorbent is the reason for the increased absorbency with increasing initiator concentration and polymerization temperature. It is well known that the degree of polymerization decreases with increase in initiator concentration and polymerization temperature, due to the increase in termination and chain transfer rate. The decrease in degree of polymerization brings about the increase in chain ends. The increase in chain ends may be the reason for the increase in absorbency to the maximum value in Figure 5. However, further increase in KPS concentration above the optimum values is accompanied by a decrease in absorbency. This may be attributed to the decrease in the swelling capacity resulting from the decrease in molecular weight, and the network cannot form efficiently and/or effectively with the chains of low molecular weight.

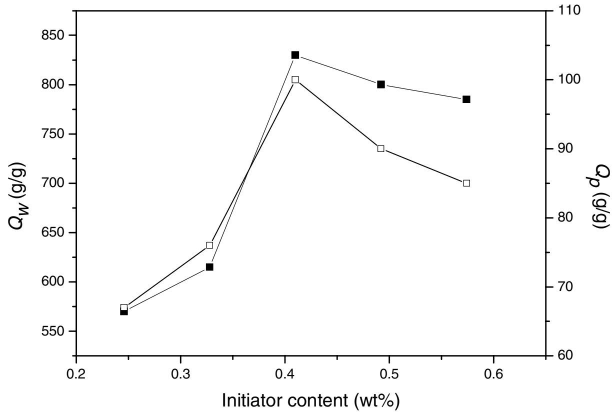


Figure 5. Influence of the initiator content on Q_w (■), Q_p (□) of sepiolite/poly (AA-co-AM) composite prepared at ND of 85%, AA/AM of 5:1 (mol); weight ratio of crosslinker and sepiolite in the feed is 0.02% and 16.2%, respectively.

Effect of AA/AM molar ratio

The results on liquid absorbency of the hydrogel composites synthesized by crosslinking polymerization of various molar ratios of AA/AM are shown in Figure 6. Water absorption capacity (Q_w) increases with decreasing AM contents or with increasing AA/AM ratio, because chain transfer to the polymer increases with monomer concentration. The chain transfer reaction, which results in increasing amounts of branching chains and self-crosslinking reactions of imidization by the amide moiety, affects the product's properties[18]. Another possible reason is the structure of the copolymer consists of more acrylamide units than acrylate units owing to the higher hydrophilicity of the carboxylate group, although the reactivity ratios of AM is lower than that of sodium acrylate, because the copolymerization reactivity of acrylamide and sodium acrylate are 0.355 and 2.852, respectively.

Physiological saline solution absorbency (Q_p) increases as AA/AM ratio increases from 1.0 to 3.0 and decreases with further increases in the AA/AM ratio. When AA/AM is less than 3, we anticipated that Q_p increase could contribute to sodium acrylate or AA due to its relatively hydrophilic nature compared with that of AM, and the association of the amide function groups may also take place. Contrast to AA or sodium acrylate, acrylamide is a nonionic group, being less susceptible to dissociation, and exhibits strong electrolyte-resistibility. Therefore, the hydrogel composites are impressible to sodium chliride, and Q_p decreases at the AA/AM ratios of more than 3. The flexibility of polymer chain is another important factor for the absorbency Q_p decrease with increasing concentration of acrylate units in the polymer chain, since the glass transition temperature (T_g) of sodium acrylate, 194°C (467K), is higher than that of acrylamide, 165°C (438K).

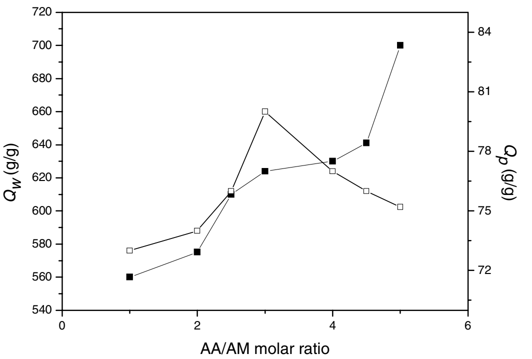


Figure 6. Effect of the mole ratio of AA/AM on the absorbency Q_w (■), Q_p (□) of the composite prepared at ND of 80%; weight ratio of crosslinker, initiator and sepiolite in the feed is 0.02%, 0.41% and 20.0%, respectively.

Composites microstrucure

FTIR spectra of sepiolite, sepiolite/poly (AA-co-AM) composite, and sepiolite-free poly (AA-co-AM) are shown in Figure 7. Strong absorption peaks, of asymmetric and symmetric R-COONa groups, appear at 1560 and 1410 cm^{-1}, respectively. The characteristic absorption peak of CONH$_2$ appears at the band of 1672 cm^{-1} in Figure 7 (b). The peak at 1675cm^{-1} is attributed to C=O stretching and the absorption band at 1020 cm^{-1} shows the existence of Si-O group. These peaks demonstrate that the product is the aimed composite. The disappearance of absorption bands at 877 and 3689 cm^{-1} in Figure 7(b), corresponding to the Si-O-H groups in Figure 7 (a), shows the esterization of carboxylic acid with silanol and the grafting of AA and/or AM on the sepiolite surface occurred. The grafting mechanism was presumed that the

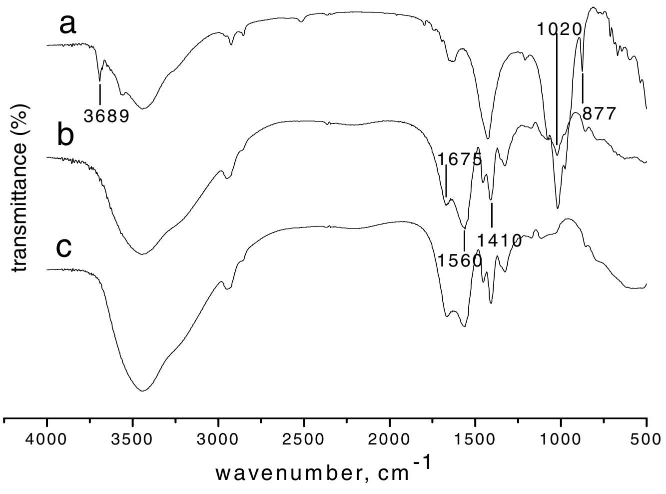
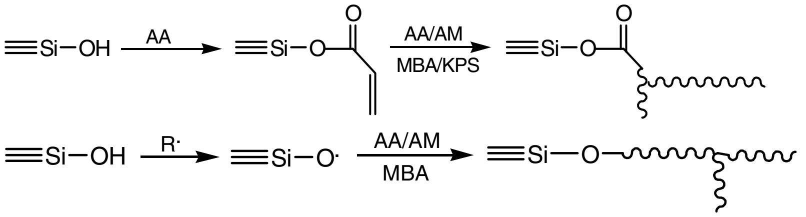
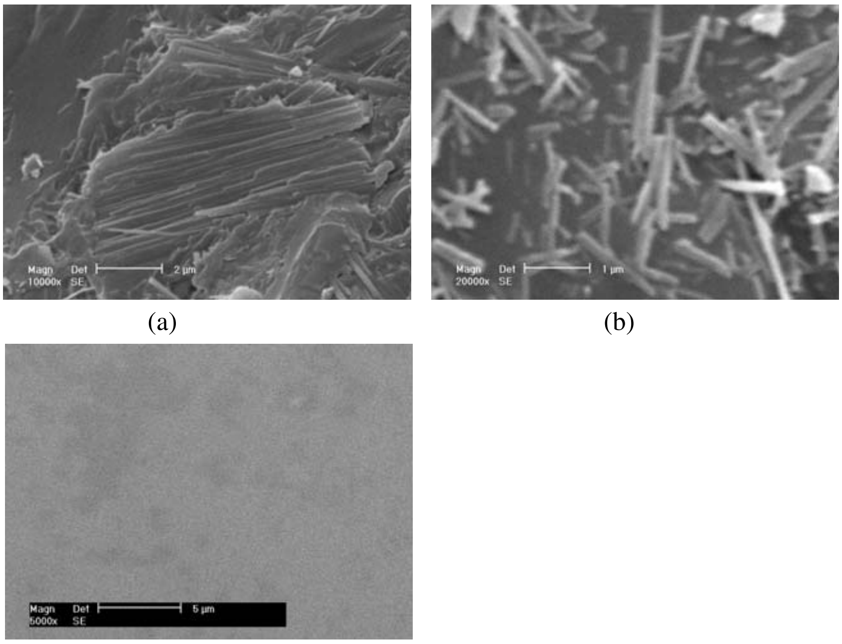


Figure 7. FTIR spectra of (a) sepiolite, (b) sepiolite/poly (AA-co-AM) prepared at ND of 85%, AA/AM of 5:1 (mol); weight ratio of crosslinker, initiator and sepiolite in the feed is 0.02%, 0.41% and 16.2%, respectively, and (c) poly (AA-co-AM): under the same conditions as sepiolite/poly (AA-co-AM) except that sepiolite dosage is zero.

hydroxyl groups in sepiolite may react with AA, and then radical polymerization take place. Another possible mechanism is that the hydroxyl groups may react with radical and liberate free radicals on the sepiolite structure and that the graft polymerization will take place on these free radicals, giving AA-AM branches on the sepiolite backbone as given in the following set of equations:



The samples discussed above were morphologically studied using SEM. The micrographs of sepioliate, sepiolite/hydrogel composite, and sepiolite-free hydrogel are shown in Figure 8 (a), (b) and (c), respectively. The SEM micrograph of sepiolite shows the needle-shaped sepiolite crystalline form agglomerates, while Figure 8 (c) shows that sepiolite-free sample is a homogeneous system and no sepioliate is observed in the micrograph. However, the sepiolite particles deagglomerate and evenly disperse in hydrogel composite, as shown in Figure (b). The SEM micrograph of the composite containing 16.2wt% sepiolite shows that the diameter of sepiolite fibers or needles is in the scale of 85nm, which confirms the sample of our synthesized hydrogel composite as real nanocoposite. This sample has a greater Q_w absorbency of 830 gH_2O/g and a Q_p absorbency of 98 gH_2O/g.



(a) (b)

(c)

Figure 8. Scanning electron micrographs of (a) sepiolite, (b) sepiolite/hydrogel composite, and (c) sepiolite-free hydrogel.

Conclusion

From the above results, some conclusions can be drawn as follows: synthesis of hydrogel nanocomposites is possible by using sepiolite in acrylic acid/acrylamide aqueous solution copolymerization. According to FTIR, grafting reaction occurs between silanol on sepiolite surface and acrylic network through ester formation. As a reactive additive, sepiolite may disaggregate and disperse at the scale of nanometer in the copolymer substrate. The effects of amount of crosslinker, neutralization degree, initiator dosage, and molar ratio of AA/AM on the water absorbency of hydrogel composites were investigated. Under our experimental conditions, a crosslinked sepiolite/poly(AA-co-AM) hydrogel composite with the water absorbency of 830 gH_2O/g and the physiological saline absorbency of 98 gH_2O/g was synthesized, which has a composition of 0.02 wt % of MBA, 0.41 wt % of KPS, 16.2 wt % of sepiolite, a neutralization degree of 85%, and a reaction temperature of 65-80°C. This excellent water absorbency and low coast may be considered as a good candidate for large scale production of superabsorbent hydrogel especially useful in agricultural and horticultural applications.

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References

1. Shimomura T, Namba T (1994) ACS Symp Ser 573: 121
2. Park J H, Kim D J (2001) J Appl Polym Sci 80: 115
3. Sun X, Zhang G, Shi G, Tang B, Wu Z (2002) J Appl Polym Sci 86: 3712
4. Dorkoosh F A, Brusee J, Verhoef J C, Borchard G, Tehrani M R, Junginger H E (2000) Polymer 41: 8213
5. Lee W-F, Chen Y-C (2004) J Appl Polym Sci 91: 2934
6. Jensen O M, Hansen P F (2002) Cement Concr Res 32: 973
7. Lee W-F, Yang L-G (2004) J Appl Polym Sci 92: 3422
8. Gao D, Heimann R B, Lerchner J, Seidel J, Wolf G (2001) J Mater Sci 36: 4567
9. Kabiri K, Zohuriaan-Mehr M-J (2003) Polym Adv Technol 14: 438
10. Zhang X H, Cui B J, Cui Y D (2003) Funct Maer (in Chinese) 20: 584
11. Lin J M, Wu J H, Yang Z F, Pu M L (2001). Macromol Rapid Commun 22: 422
12. Lee W-F, Chen Y-C (2004) J Appl Polym Sci 94: 2417
13. Akcay M J (2004) Mol Struct 694: 21
14. Esmer K, Yeniyol M (1999) Mater Lett 38: 445
15. Casal B, Merino J, Serratosa J M, Ruiz-Hitzky E(2001) Appl Clay Sci 18: 245
16. Flory PJ (1953). Principles of polymer chemistry. New York: Cornell University Press
17. Chen J, Zhao Y (1999) J Appl Polym Sci 74:119
18. Zhou W-J, Yao K-J, Kurt M J (1996) J Appl Polym Sci 62: 911