Grafted CMC/Silica Gel Superabsorbent Composite: Synthesis and Investigation of Swelling Behavior in Various Media

A. Pourjavadi, F. Seidi, H. Salimi, R. Soleyman

Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, Tehran, Iran

ABSTRACT: In the present study, we attempt to synthesize and characterize novel CMC-*g*-poly (acrylic acid-*co*-2-acrylamido-2-methylpropanesulfonic acid)/silica gel composite. Infrared spectroscopy and TGA thermal analysis were carried out to confirm the chemical structure of the hydrogel. Moreover, morphology of the samples was examined by scanning electron microscopy. The effect of reaction variables affecting on water absorbency of the composite and swelling behavior in various solvents, salt, and pH solutions was investigated. Maximum water absorbency of the optimized final product was found to be 4000 g/g in distilled water. The absorbency under load (AUL) of the hydrogel was also determined by using an AUL tester at various applied pressures. Finally, dynamic swelling kinetics of the hydrogel was studied. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3281–3290, 2008

Key words: hydrogel; superabsorbent; CMC; swelling behavior; graft copolymer

INTRODUCTION

Superabsorbent polymers (SAPs)[1] are loosely cross-linked hydrophilic polymers that have great potential for myriad of applications. The unique features of these promising materials such as capability to hold aqueous fluids up to thousands of times of their own weight and environmental sensitivity have been sufficient to attract considerable attention of scientists in many industries. Nowadays, the worldwide production of SAPs is more than one million tons in a year that have been widely used in many hygiene products, such as baby diapers or female hygiene absorbents. Diapers make up 83% of the worldwide market applications for SAPs, which represent a multibillion-dollar market, steadily growing around the globe. Technical applications outside of the hygiene sector, such as firefighting uses and food packaging are also growing. Moreover, to protect power and communication cables from damage through water penetration, SAPs can be used. Furthermore, they were introduced to agriculture about 30 years ago to improve the water-holding capacity of sandy soils to promote the germination of seeds and plant growth. Hydrogels also have potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract. As a consequence, they have become an important area of research and development in the field of medicine, pharmacy, and biotechnology.[2–8]

SAPs can be roughly divided into natural-based and full synthetic ones. Despite the advantages of hydrogels made from synthetic polymers, there are also severe limitations such as toxicity and nonbiodegradability to this type of material. Because of these shortcomings, natural-based SAPs have attracted much attention in recent years. Polysaccharides form the main part of the natural-based SAPs.[9–15] The higher production cost and low gel strength of these superabsorbents, however, restrict their application severely. To overcome these limitations, low-cost inorganic compounds can be used. Considerable interest has been focused on clay minerals such as montmorillonite,[16] bentonite,[17] and kaolin.[18] They are hydrated layered aluminosilicates with reactive hydroxyl groups on the surface. Because of their hydrophilic nature, these materials have been more suitable for use in water absorbents as additives. The introduction of inorganic fillers to a polymer matrix increases its strength and stiffness.

Cellulose is a polymeric raw material with fascinating structure and properties, which is available at low cost for preparation of various functional polymers.[19] Carboxymethyl cellulose sodium salt (CMC) is the first water-soluble ionic derivative of cellulose prepared in 1918 and produced commercially in the early 1920s in Germany. It has been the most important ionic cellulose ether with a worldwide annual production

WILEY
InterScience®
DISCOVER SOMETHING GREAT

of 300,000 tons.[20] Many studies have been reported in the case of cellulose-based SAPs.[10,21–23]

Building on our previous works on SAPs,[11,13,18,23] in this work, we attempt to synthesize and characterize novel CMC-*g*-poly (acrylic acid-*co*-2-acrylamido-2-methylpropanesulfonic acid)/silica gel composite. Silica gel has a hydrated surface; as a consequence, it has been suitable for use in water absorbents as additives. The preparation of the biopolymer-based superabsorbent composites can also give improved mechanical properties and can lower the cost of the finished product compared with all-synthetic counterparts as well as providing biodegradable characteristics. On the other hand, the water absorbency of the superabsorbent made from polyacrylates and polysaccharides-*g*-poly (acrylates) in salt solutions is low. In fact, the salt sensitivity of these hydrogels is high. According to our previous works, SAP hydrogels containing sulfonate groups comprises high swelling capacity in salt solutions. But, these hydrogels have a very low mechanical strength. As a consequence, in the present study, we used a binary mixture of two monomers (AMPS and AA) to achieve both aforementioned properties. The effect of reaction variables affecting on water absorbency of the composite and swelling behavior in various solvents, salt, and pH solutions was investigated. The AUL of optimized hydrogel was determined by using an AUL tester[24] in various applied pressures. This is a very important factor that is usually given in the patent literature and technical data sheets offered by industrial hydrogel manufacturers. Finally, dynamic swelling kinetics of the hydrogel was also determined. Therefore, this hydrogel may be considered as an excellent candidate for various applications.

EXPERIMENTAL

Materials

Sodium salt of CMC (DS = 0.52, M_w = 100,000) was obtained from Fluka Chemical (Fluka, Buchs, Switzerland). *N*,*N*′-methylene bisacrylamide (MBA, from Merck, Darmstadt, Germany), ammonium persulfate (APS, from Merck), 2-acrylamido-2-methylpropanesulfonic acid (AMPS, from Fluka), silica gel (230–400 mesh, from Merck), and acrylic acid (AA, from Merck) were of analytical grade and used without further purification. The solvents (all from Merck) were used as received. All other chemicals were also analytical grades. Double-distilled water was used for the hydrogel preparation and swelling measurements.

Instrumental analysis

Samples were characterized as KBr pellets using a Mattson-1000 FTIR spectrophotometer. Thermogravimetric analysis (TGA) of silica gel–free hydrogel and synthesized composite were performed using Polymer Laboratories systems at a heating rate of 20°C/min under nitrogen atmosphere. Morphology of the dried gel structures was studied by scanning electron microscopy (SEM). After Soxhlet extraction with methanol for 24 h and drying in an oven, superabsorbent powder was coated with a thin layer of gold and imaged in a SEM instrument (Philips, XL30).

Superabsorbent composite synthesis

Variable amounts of CMC (0.4–1.8 g) were dissolved in 40 mL distilled water at 80°C. The resultant solution was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three-blade propeller type, 300 rpm). The reactor was immersed in a thermostated water bath preset at 80°C. Then, appropriate amounts of silica gel powder (230–400 mesh, 0.4–1.8 g) were added to this solution with stirring. After 10 min, the stirrer was switched off. Again, after complete removal of air bubbles from the resultant viscose suspension, the stirrer is switched on (200 rpm), and certain amounts of AMPS (0.5 g), partially neutralized AA (3–6.5 g), and MBA (0.01–0.1 g) in 10 mL H_2O, and APS (0.03–0.1 g) in 5 mL H_2O were added simultaneously. After 30 min, the obtained gel was poured to excess nonsolvent ethanol (200 mL) and remained for 3 h to dewater. Then, ethanol was decanted and the product was cut into small pieces (diameter ∼ 5 mm). Again, 200 mL fresh ethanol was added, and the hydrogel remained for 48 h. Finally, the filtered gel was dried in an oven at 70°C for 72 h. After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat, and light.

Swelling measurements

An accurately weighed sample (0.1 ± 0.0001 g) of the powdered superabsorbent with average particle sizes between 40 and 60 mesh (250–400 μm) was immersed in 200 mL distilled water or other solvents for 2 h. The equilibrium swelling (ES) capacity was measured twice at room temperature by ''tea bag'' method and using the following formula:

$$ES(g/g) = \frac{W_2 - W_1}{W_1} \qquad (1)$$

where W_1 and W_2 are the weights of dry and swollen gels, respectively.

Absorbency under load

A macroporous sintered glass filter plate (porosity no. 0, d = 80 mm, h = 7 mm) was placed in a Petri

dish (d = 118 mm, h = 12 mm), and a weighed, dried hydrogel (0.5 ± 0.01g) was uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid weight (Teflon, d = 60 mm, variable height) which could slip freely in a glass cylinder (d = 60 mm, h = 50 mm) was used to apply the desired load [applied pressure 0.3, 0.6, and 0.9 psi (2068, 4137, and 6205 Pa)] to the dry hydrogel sample particles. Then, 0.9% saline solution was added so that the liquid level was equal to the height of the sintered glass filter. Whole of the set was covered to prevent surface evaporation with probable change in the saline concentration. After 2 h, the swollen particles were weighed again, and AUL was calculated according to eq. (1).[24]

Swelling in various salt solutions

Absorbency of the optimized sample was evaluated in different concentration of NaCl, CaCl$_2$, and AlCl$_3$ salt solutions.

Absorbency at various values of pH

Individual solutions with acidic and basic values of pH were prepared by dilution of NaOH (pH 13.0) and HCl (pH 1.0) solutions to achieve pH ≥ 6.0 and pH < 6.0, respectively. The pH values were precisely checked by a pH-meter (Metrohm/620, accuracy ± 0.1). Then, 0.5 (± 0.001) g of the dried hydrogel was used for the swelling measurements according to eq. (1).

Swelling kinetics

For studying the rate of absorbency of the composite, certain amount of sample (0.5 ± 0.001 g) with average particle sizes between 40 and 60 mesh (250–400 μm) was poured into a weighed tea bag and immersed in 200 mL distilled water. At consecutive time intervals, the water absorbency of the hydrogel was measured according to the earlier mentioned method.

RESULTS AND DISCUSSION

Synthesis, characterization, and mechanism aspects

The superabsorbent composite was prepared by simultaneous graft copolymerization of AA and AMPS onto CMC as a natural polymeric backbone in the presence of a crosslinking agent and powdery silica gel (Scheme 1). The reaction was conducted under normal atmospheric conditions. In fact, as previously described by Omidian et al,[25,26] because of the existence of an inhibition (retardation) period in such systems, which was followed by the onset of rapid, apparently normal polymerization, unrestricted access
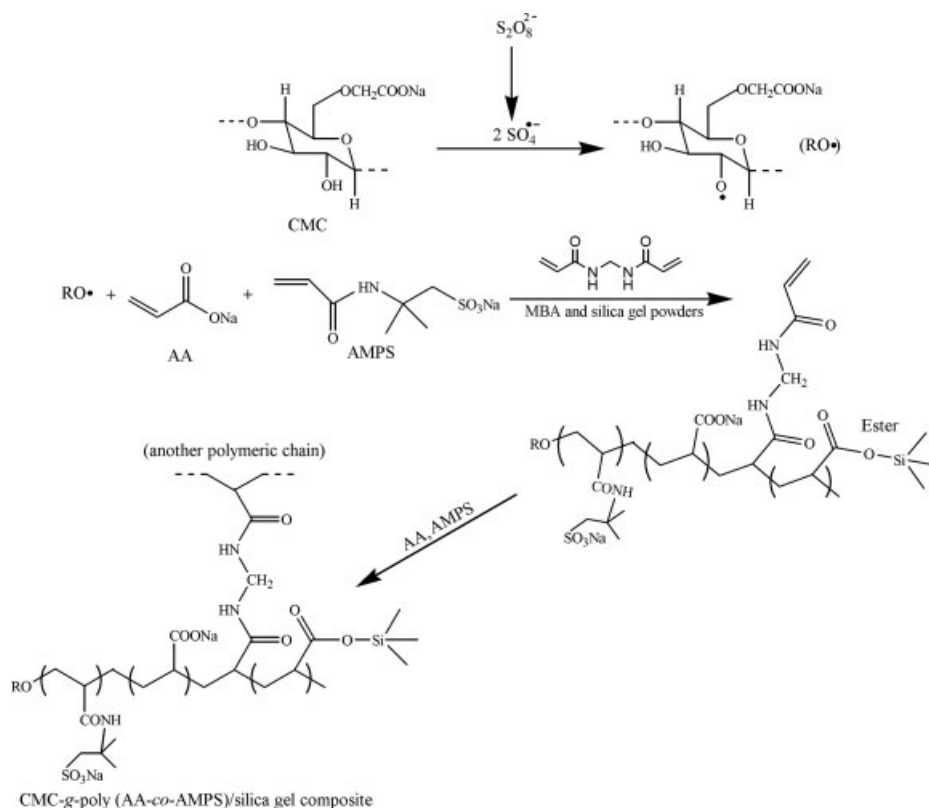
Scheme 1 Proposed mechanistic pathway for synthesis of the CMC-*g*-poly (AA-*co*-AMPS)/silica gel composite.
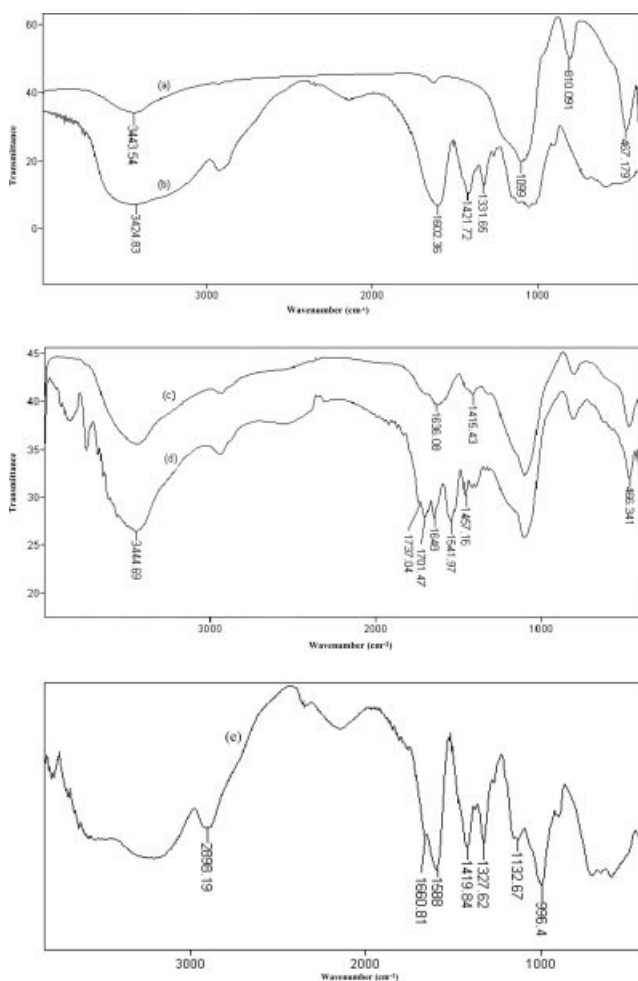
Figure 1 FTIR spectra of (a) silica gel, (b) CMC, (c) mixture of CMC/silica gel/poly (AA-*co*-AMPS), (d) synthesized composite, and (e) difference IR spectrum (CMC-synthesized composite).

Figure 2 TGA traces of (a) silica gel-free CMC-*g*-poly (NaAA-*co*-AMPS) hydrogel (CMC = 1 g, MBA = 0.03 g, APS = 0.05 g, AA = 5 g, AMPS = 0.5 g, NU% = 37%), and (b) CMC-*g*-poly (NaAA-*co*-AMPS)/silica gel composite (CMC = 1 g , silica gel = 0.8 g, MBA = 0.03 g, APS = 0.05 g, AA = 5 g, AMPS = 0.5 g, NU% = 37%). Heating rate 20°C/min, under N_2. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

of the reaction mixture to oxygen, and unrestricted evaporative loss of water complicates the polymerization of the acrylic monomers and the swelling characteristics of the products; however, because of industrial necessity for the process simplicity, this approach has been of interest from the industrial point of view. APS was used as an initiator. The sulfate anion radical that produces from thermal decomposition of APS abstracts hydrogen from the hydroxyl groups of the polysaccharide substrate to form corresponding alkoxy radicals on the substrate. This persulfate–saccharide redox system results in active centers capable to radically initiate polymerization of monomer led to a graft copolymer. Since a crosslinking agent, e.g., MBA, is presented in the system, the copolymer comprises a crosslinked structure. In these conditions, reaction of AA and hydroxyl groups on the silica surface is also a possibility.

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 1
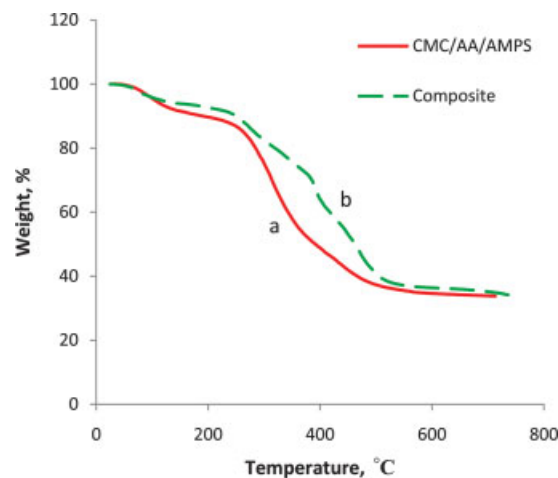
shows the FTIR spectra of the initial substrates, physical mixture of CMC/silica gel/poly (AA-*co*-AMPS), the synthesized composite, and difference FTIR spectrum (CMC-synthesized composite). As mentioned earlier, silica gel has a hydrated surface. The broad band at 3200–3500 cm^{-1} is due to stretching of these hydroxyl groups [Fig. 1(a)]. In the spectrum of CMC [Fig. 1(b)], two strong peaks were observed at 1602 and 1421 cm^{-1} due to the asymmetrical and symmetrical stretching of –COO^{-} groups. Characteristic absorption peak of CMC appeared at 3424 cm^{-1} for the hydroxyl group. FTIR spectrum of the composite [Fig. 1(d)] represents several new peaks. The absorption peak at 1737 cm^{-1} can be attributed to the ester groups formed during graft copolymerization. As already mentioned, the carboxylic groups of the grafted AA-*co*-AMPS can react with the —OH groups on the silica gel surface.

TGA traces of silica gel-free CMC-*g*-poly (NaAA-*co*-AMPS) hydrogel, and CMC-*g*-poly (NaAA-*co*-AMPS)/silica gel composite are presented in Figure 2. Improvement thermal stability of superabsorbent composite may be concluded from this Figure and the data summarized in Table I. According to this table, values related to the composite such as T_{10} (250.35°C) and char yield at 700°C (35.2%) are higher compared to that of the CMC-*g*-poly (NaAA-*co*-AMPS) hydrogel (T_{10} = 189.5°C, Y = 33.9%).

To achieve a better comparison between the polymers from the thermal stability point of view, integral procedural decomposition temperature, IPDT, as a means of summing up the whole shape of the

TABLE I
Thermal Properties of the Silica Gel-Free Superabsorbent Hydrogel
and Synthesized Composite

Polymer	Temperature (°C) at weight loss			Y^a (wt %)	IPDT (°C)
	5%	10%	30%		
CMC-g-p(NaAA-co-AMPS) hydrogel	104	189.5	313.9	33.9	308
CMC-g-p(NaAA-co-AMPS)/ silica gel composite	115.2	250.35	385.4	35.2	363

Heating rate 20°C/min, under N_2.
[a] Char yield at 700°C in nitrogen.

normalized data curve, was also calculated (Table I). This parameter that was first proposed by Doyle[27] gives more semiquantitative data regarding the relative thermal stabilities. Again, the synthesized composite was found to be the most thermally stable samples studied. The silica gel particles in the network may act as heat, barriers and as a consequence enhance the overall thermal stability of the synthesized composite.

Figure 3 shows the SEM pictures of superabsorbent composite. As it is obvious from this figure, the hydrogel has a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli, with the hydrophilic groups of the graft copolymers.

Optimization of the synthetic conditions

The relationship between the swelling ratio and network structure parameters given by Flory[28] is usually used as the following equation:

$$q_m^{5/3} \cong \frac{\left\{ \left[\frac{1}{2} \times \frac{i}{v_u} \times \left(\frac{1}{S^*}\right)^{1/2}\right]^2 + \frac{\left(\frac{1}{2}-\chi_1\right)}{v_1} \right\}}{\left(\frac{v_e}{V_0}\right)} \quad (2)$$

where q_m is the swelling ratio; S^*, the ionic strength of the swollen solution; χ_1 the polymer-solvent thermodynamic interaction parameter; v_1 the molar volume of the solvent; v_u the molar volume of a repeating unit; i the number of electronic charges per polymer unit in a polyelectrolyte; i/v_u, the concentration of the fixed charge of the unswollen networks; v_e the effective number (or number of moles) of chains in a real network; V_0 the volume of the undeformed (unswollen) polymer network; and v_e/V_0 is the crosslinking density that refers to the number of effectively crosslinked chains in unit volume. The sentence $(1/2 - \chi_1)/v_1$ stands for the network-medium affinity.

According to eq. (2), there are many variables affecting the ultimate swelling capacity. Some of these variables (i.e., concentration of AA, APS, and MBA, CMC/silica gel weight ratio, and neutraliza-

tion percent (NU %)) has been selected in this research. These parameters were systematically varied to achieve a superabsorbent with maximum water absorbency.

Effect of MBA concentration on swelling

The effect of crosslinker concentration on swelling capacity of the product was investigated. According
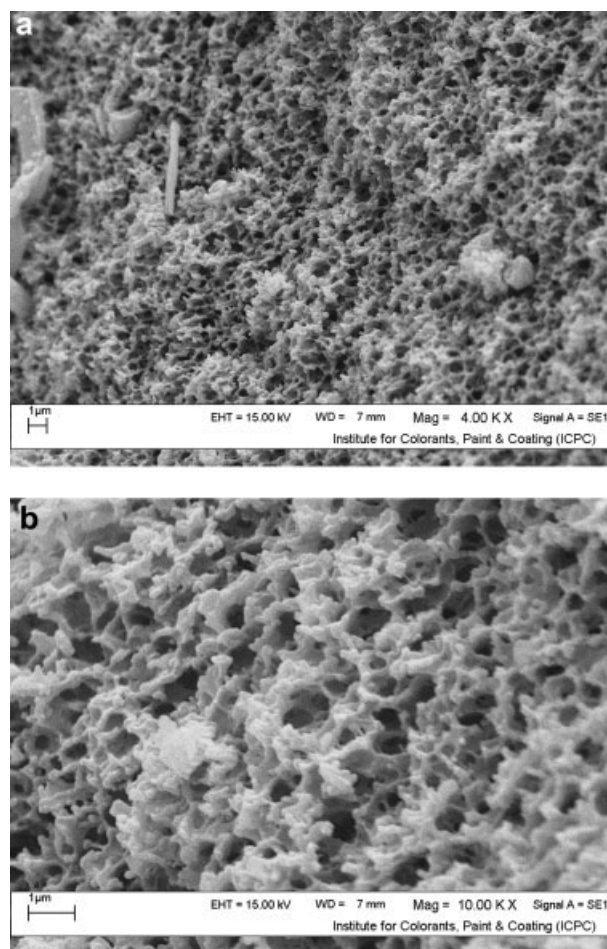

Figure 3 SEM photographs of optimized hydrogel. Surfaces were taken at a magnification of (a) ×4000 and (b) ×10000, and the scale bar is 1 μm.
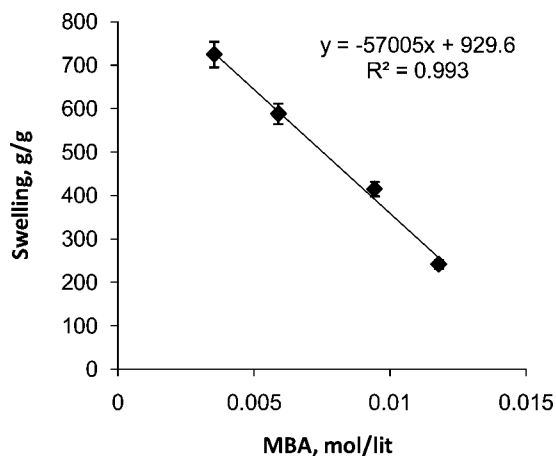
Figure 4 Dependency of swelling of the composite versus the crosslinker concentration employed in the polymerization process. Reaction conditions: CMC 1 g, silica gel 0.8 g, NU 41%, AMPS 0.044, AA 1.06, and APS 0.0064 mol/L, 80°C.
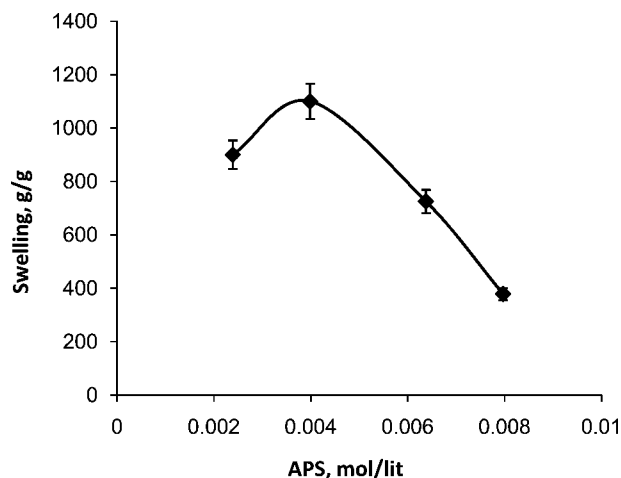

Figure 5 Dependency of swelling of the hydrogel versus the initiator concentration employed in the polymerization process. Reaction conditions: CMC 1 g, silica gel 0.8 g, NU 41%, AMPS 0.044, AA 1.06, and MBA 0.0035 mol/L, 80°C.

to the Figure 4, high values of absorbency are obtained by lower concentration of crosslinker as reported by other scientists earlier.[28] The maximum absorbency (725 g/g) is achieved at 0.0035 mol/L of MBA.

It is a well-known behavior and can be fully explained. As it is obvious from eq. (2), the swelling ratio (q_m) increases with decrease in the crosslinking density (v_e/V_0). In fact, more crosslinking concentration causes a higher crosslinking density and decreases the space between the copolymer chains, and consequently, the resulting highly crosslinked rigid structure cannot be expanded and holds a large quantity of water.

Effect of APS concentration on swelling

The effect of initiator concentration on swelling capacity of the hydrogels has been investigated by varying the APS concentration from 0.0024 to 0.008 mol/L. The maximum absorbency (1100 g/g) was obtained at 0.004 mol/L of the initiator. According to Figure 5, the absorbency is increased with increase in the APS concentration from 0.0024 up to 0.004 mol/L, and then, it is decreased considerably with a further increase in the amount of initiator. The initial increase in water absorbency may be ascribed to the increase in the active sites on the backbone of the CMC, arising from the attack of sulfate anion-radical. Subsequent decrease in swelling is originated from an increase in terminating step reaction via bimolecular collision, which in turn, causes to enhance crosslinking density. This possible phenomenon is referred to as *self-crosslinking* by Chen and Zhao.[29] Furthermore, the free radical degradation of CMC backbones by sulfate anion radicals

is another reason for swelling loss at higher initiator concentration. A similar observation is recently reported in the case of polysaccharides such as carrageenan[30] and chitosan.[31]

Effect of AA concentration on swelling

The swelling capacity of composite as a function of AA concentration is illustrated in Figure 6. As shown, with increasing the monomer concentration up to 1.32 mol/L, the swelling capacity is increased and then it is considerably decreased with further increase in monomer amount. The initial increment in swelling values can be attributed to increase in ionic groups existing in copolymer chains along with
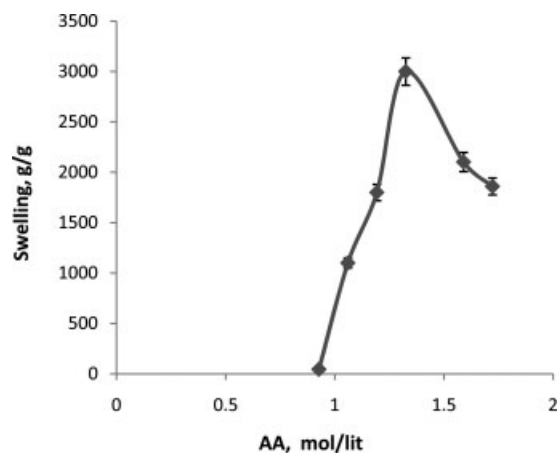

Figure 6 Dependency of swelling of the composite versus the monomer (AA) concentration employed in the polymerization process. Reaction conditions: CMC 1 g, silica gel 0.8 g, NU 41%, AMPS 0.044, APS 0.004, and MBA 0.0035 mol/L, 80°C.
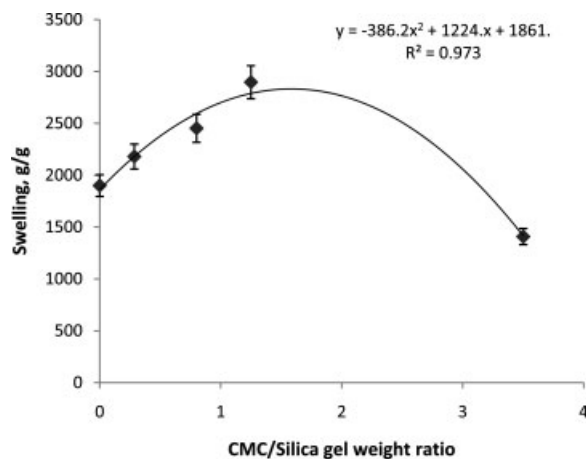
Figure 7 Dependency of swelling of the composite versus CMC/silica gel weight ratio employed in the polymerization process. Reaction conditions: NU 41%, AMPS 0.044, AA 1.32, APS 0.004, and MBA 0.0035 mol/L, 80°C.

an increase of AA in the gel, which allows polymer coils to expand more easily.

Above 1.32 mol/L, the water absorbency is considerably reduced. The swelling loss after the maximum (3000 g/g) can be attributed to (a) preferential homopolymerization over graft copolymerization, (b) an increase in the viscosity of the medium, which hinders the movement of free radicals and monomer molecules, and (c) an enhanced chance of chain transfer to monomer molecules.

Effect of CMC/silica gel weight ratio on swelling

The effect of the amount of silica gel on the swelling capacity of the composite was studied. The CMC/silica gel weight ratio was varied from 0.0 to 3.5, while other reaction variables were held constant. Figure 7 indicates that the water absorbency of the hydrogel was increased by increasing the silica gel content up to a weight ratio 1.25 and then decreased with any further increase.

Silica gel in this reaction may act in two ways: (a) the silica gel particles act as a crosslinking agent. This means that the carboxylate groups of the poly (AA-co-AMPS) chains react with silica gel, as obviously proved by FTIR spectra [Fig. 1(d)], and (b) silica gel prevents the growth of the polymer chains by a chain-transfer mechanism.

Effect of neutralization percentage on swelling

In this series of experiments, effect of neutralization percentage on swelling capacity was also studied. Without the neutralization stage, the carboxylate and sulfonate anions are protonated (i/v_u in eq. (2) is decreased), eliminating the main anion–anion repul-

sive forces and consequently decreasing the water absorbency (Fig. 8). According to Figure 8, the best neutralization percentage was found to be 37%. In high neutralization percent, reduced swelling is observed, which attributed to the "charge screening effect" of excess Na$^+$ ions in the swelling media.[28] The excess cations shield the carboxylate and sulfonate anions and prevent effective anion–anion repulsion (screening/shielding effect). Moreover, with increase in the NU% the ionic strength of the swollen solution [$S*$ in eq. (2)] is increased. As a result, the osmotic pressure between the aqueous and the gel phases is reduced and the water absorbency is consequently decreased.

The environmental sensitivity

pH

Water absorbency of the optimized composite was studied at various pH solutions ranged from 2.0 to 11.0. To prepare the pH media, the stock NaOH (pH 13.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. The results are illustrated in Figure 9. As shown, maximum swelling (5460 g/g) was obtained at pH 8.5. Under acidic pHs, most of the $—COO^-$ and $—SO_3^-$ groups are protonated; thus, the main anion–anion repulsive forces are eliminated, and as a result, swelling capacity values are considerably decreased. The swelling loss in the highly basic solutions can be attributed to the charge screening effect of excess Na in the swelling media, which in turn, shields the carboxylate and sulfonate anions and prevents effective anion–anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems.[13,32]
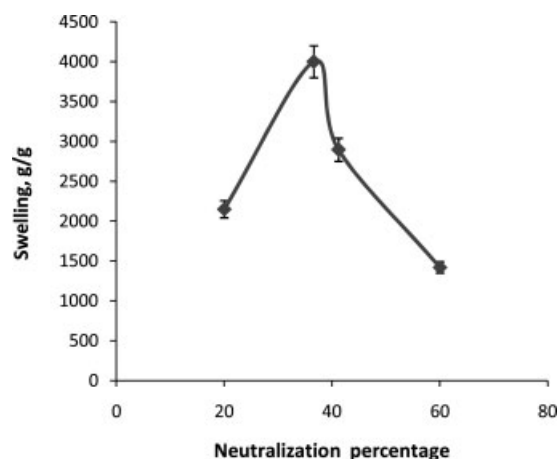

Figure 8 Effect of neutralization percentage on swelling. Reaction conditions: CMC/silica gel weight ratio 1.25, AMPS 0.044, AA 1.32, APS 0.004, and MBA 0.0035 mol/L, 80°C.
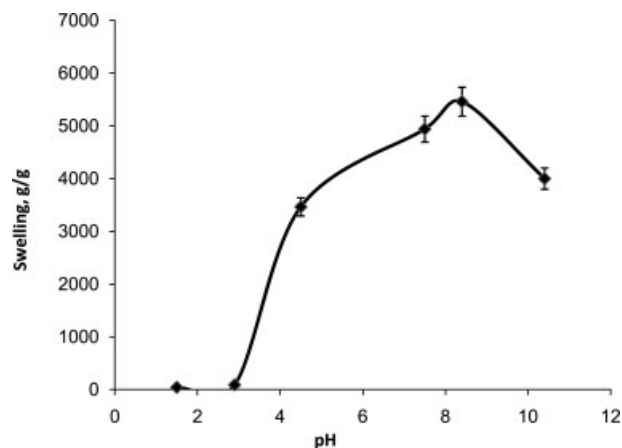
Figure 9 Effect of pH of solutions on swelling capacity of the hydrogel.

Salinity

Swelling capacity in salt solutions is of prime significance in many practical applications such as personal hygiene products and water release systems in agriculture. In the present study, swelling capacity was studied in various concentrations of NaCl solutions. The results are illustrated in Figure 10. A reverse and power law relationship between concentration of salt solution and swelling capacity of the hydrogel is obvious. It is a well-known relationship between swelling and concentration of salt solution that is stated as in the following equation in literature[28]:

$$\text{Swelling} = k[\text{salt}]^{-n} \quad (3)$$

where k and n are constant values for an individual superabsorbent. The k value is swelling at a high concentration of salt and n value is a measure of salt sensitivity. Figure 10 indicates that changing of the salt concentrations higher than $\sim 0.2M$ has no appreciable influence on superabsorbency of the superabsorbent.
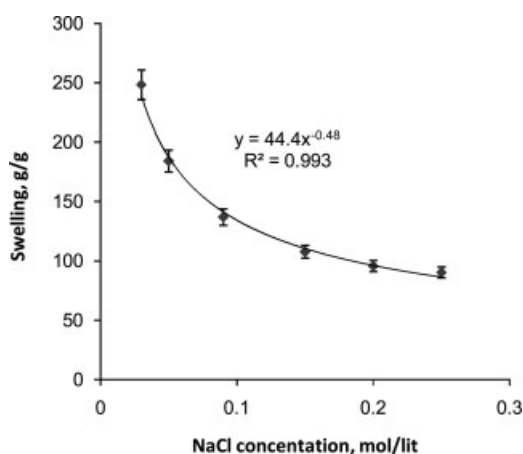

Figure 10 Swelling capacity variation of the optimized hydrogel in saline solutions with various concentrations.
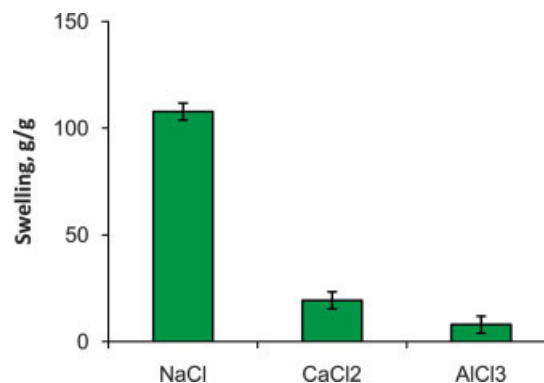
Figure 11 Swelling capacity of the optimized hydrogel in different chloride salt solutions (0.15M). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The effect of cation charge on swelling behavior is shown in Figure 11. Degree of crosslinking is increased with increase in the charge of cation, and the swelling is consequently decreased. Therefore, the absorbency for the hydrogel in the studied salt solutions is in the order of monovalent > divalent > trivalent cations. Similar results have been reported in similar previous studies.[13,15]

Solvent-induced phase transition

In the present study, the swelling changes of the optimized hydrogel were examined in various water-solvent systems. The swelling loss in these mixtures can be easily explained. Sodium carboxylate (NaAA) groups are easily solvated by water molecules. However, it is widely restricted in these organic solvent–water systems, because the organic solvent molecules (MeOH; $(CH_3)_2CHOH$; acetone) cannot solvate the ionic carboxylic groups. As a consequence, the swelling capacities are considerably decreased.

It can also be concluded from Figure 12 that in a fixed ratio of solvent–water (e.g., a 40 : 60 w/w solvent-water mixture), the swelling is increased in order of methanol > 2-propanol > acetone. This can be explained using the Hildebrand eq. (4)[33]:

$$\frac{\Delta H_m}{(V\Phi_1\Phi_2)} = (\delta_1 - \delta_2)^2 \quad (4)$$

where ΔH_m is the enthalpy change on mixing of a polymer and a solvent, Φ_1 and Φ_2 are the volume fractions for the solvent and the polymer, V is the whole volume of the solution, and δ_1 and δ_2 are the solubility parameters for the solvent and the polymer, respectively.

This equation clearly indicates that to dissolve a polymer in a solvent, the δ values must be close to each other. As a consequence, to predict the solubility
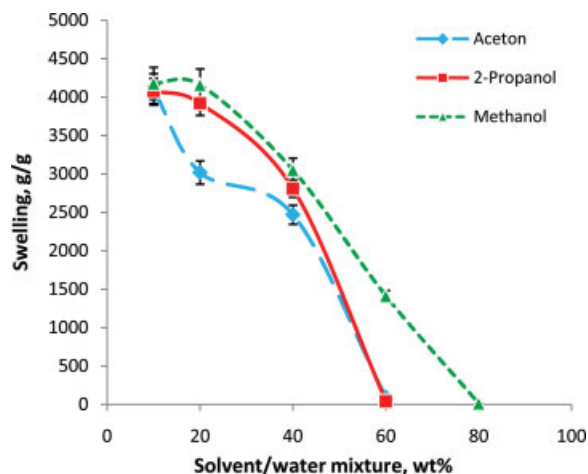
Figure 12 Sensitivity of the optimized hydrogel swelled in different solvent–water media with varied composition. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of a polymer, δ values should be calculated. As swelling capacity of the synthesized hydrogel in water is maximum, the δ value of water (23.4 $(cal/cm^3)^{1/2}$) can be regarded as the solubility parameter of it. The solubility parameter for solvent–water mixtures (δ_{mix}) can be calculated using following eq. (5)[34]:

$$\delta_{mix} = \delta_1\Phi_1 + \delta_2\Phi_2 \quad (5)$$

where Φ_1 and Φ_2 are the volume fractions, and δ_1 and δ_2 are the solubility parameters of the two solvents. According to data summarized in Table II, with increasing of δ_{mix} values toward 23.4, the hydrogel can be highly swollen as in pure water. In other words, the swelling capacity of the hydrogel in the solvent–water mixture will be close to that in pure water if δ_{mix} is close to δ_{water}. A similar observation is recently reported by Zohuriaan-Mehr et al.[15]

TABLE II
Solubility Parameters of Solvents and Solvent–Water Mixtures;[33] Swelling capacities of hydrogel in solvents and solvent–water mixtures

	δ (or δ_{mix})[a]	Swelling capacity (g/g)
Acetone	9.9	–
2-Propanol	11.5	–
Methanol	14.5	–
Water	23.4	4000
Methanol–water (40 : 60)	19.84	3050
2-Propanol–water (40 : 60)	18.64	2810
Acetone–water (40 : 60)	18	2470

[a] Symbols δ and δ_{mix} [$(cal/cm^3)^{1/2}$] are the solubility parameters for the solvent and the solvent–water mixture, respectively.

Swelling kinetics

In practical applications, not only a higher swelling capacity is required, but also a higher swelling rate is needed. Figure 13(a) represents the dynamic swelling behavior of the optimized superabsorbent sample with certain particle sizes (40–60 mesh) in water. Initially, the rate of water uptake sharply increases and then begins to level off. The time required to reach the ES capacity was achieved after ∼ 60 min. A power law behavior is obvious from Figure 13(a). The data may be well fitted with a Voigt-based equation [eq. (6)][35]:

$$S_t = S_e \left(1 - e^{-t/\tau}\right) \quad (6)$$

where S_t (g/g) is swelling at time t, S_e is ES (power parameter, g/g); t is time (min) for swelling S_t, and τ (min) stand for the ''rate parameter.'' To find the rate parameter for superabsorbent sample, $L_n[1 - S_t/S_e]$ versus time (t) was plotted [Fig. 13(b)]. The slope of the line passing the point zero and the point of 60% fractional swelling was determined (slope = $-1/\tau$ gives the rate parameter). Therefore, the rate
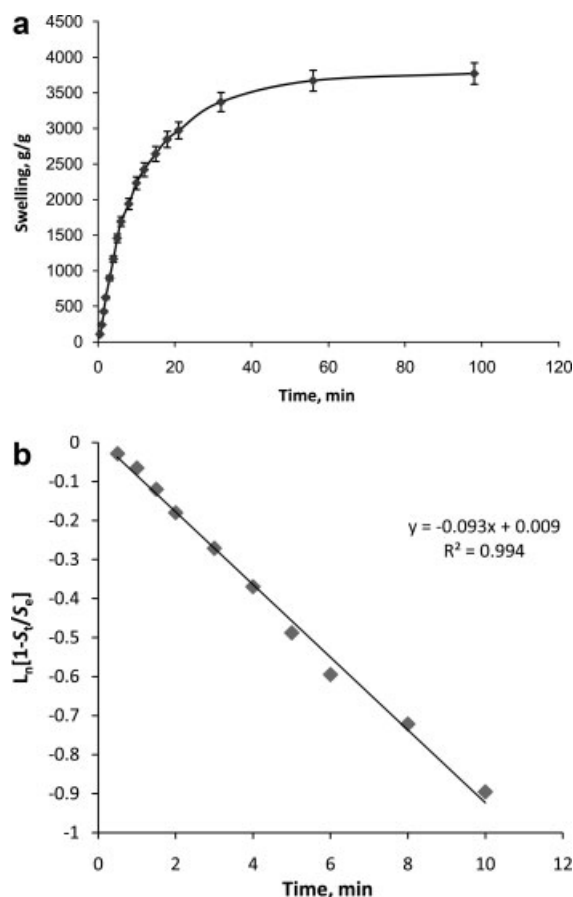

Figure 13 Representative swelling kinetics of the optimized hydrogel with certain particle sizes (40–60 mesh) (a), and the rate parameter (τ) calculating graph (b).

TABLE III
Absorbency Under Load (AUL) Values for Optimized Hydrogel Swollen in Saline Solution

Load (psi)	Swelling capacity (g/g)
0	4000[a]
0	108[b]
0.3	44[b]
0.6	40[b]
0.9	40[b]

[a] Swelling capacity in distilled water.
[b] Water absorbency in 0.9% saline solution under load.

parameter for the superabsorbent composite was found to be 10.7 min in distilled water.

Absorbency under load

The absorbency under load (AUL) is an important factor to determine the swollen gel strength in the practical applications. It is usually given in the patent literature and technical data sheets offered by industrial hydrogel manufacturers. To determine AUL, we used an AUL tester[24] at various applied pressures (0.3, 0.6, and 0.9 psi). This method is suitable for hydrogels with sugar-like particles. AUL was measured in 0.9% saline solution. The results are shown in Table III. The absorbencies considerably decrease under load in comparison with free state, as was expected. Furthermore, AUL slightly decreases in higher pressures, which confirm the low sensitivity of the hydrogel to different loads.

CONCLUSIONS

In the present study, we prepared a novel superabsorbent composite by simultaneous graft copolymerization of AA and AMPS onto CMC. The optimum reaction conditions to obtain maximum water absorbency (4000 g/g) were found to be CMC 1 g, silica gel 0.8 g, NU 37%, MBA 0.0035, AA 1.32, AMPS 0.044, and APS 0.004 mol/L. Swelling measurement of the optimized hydrogel in different salt solutions showed appreciable swelling capacity in comparison with our previous works. Moreover, the synthesized hydrogel exhibited high sensitivity to pH. Furthermore, the AUL of optimized hydrogel was investigated at various applied pressures. The composite shows high water absorbency (40 g/g) in 0.9 psi in 0.9% saline solution that makes it suitable for various applications. Finally, dynamic swelling kinetics of the hydrogel was also determined. Therefore, this composite may be considered as an excellent candidate for different applications in future.

References

1. Buchholz, F. L.; Graham, A. T. Modern Superabsorbent Polymer Technology; Wiley: New York, 1997.
2. Po, R. J Macromol Sci Rev Macromol Chem Phys 1994, C34, 607.
3. Peppas, N. A.; Mikos, A. G. In Hydrogels in Medicine and Pharmacy; Peppas, N. A., Ed.; CRC Press: Boca Raton, FL, 1986; Vol. 1.
4. DeRossi, D.; Kajiwara, K.; Osada, Y.; Yamauchi, A. Polymer Gels: Fundamentals and Biomedical Applications; Plenum: New York, 1991.
5. Hogari, K. In Advances in Superabsorbent Polymers; Ashiya, F., Ed.; American Chemical Society: Washington, DC, 1994.
6. Park, K. Controlled Drug Delivery: Challenges and Strategies; American Chemical Society: Washington, DC, 1997.
7. Brøndsted, H.; Kopeček, J. Biomaterials 1991, 12, 584.
8. Blanchfield, L. ICIS Chem Business Americas 2007, 271, 24.
9. Dutkiewicz, J. K. J Biomed Mater Res Appl Biomater 2002, 63, 373.
10. Kubota, H.; Kuwabara, S. J Appl Polym Sci 1997, 64, 2259.
11. Pourjavadi, A.; Mahdavinia, G. R.; Zohuriaan-Mehr, M. J. J Appl Polym Sci 2003, 90, 3115.
12. Kim, Y.-J.; Yoon, K.-J.; Ko, S.-W. J Appl Polym Sci 2000, 78, 1797.
13. Pourjavadi, A.; Barzegar, Sh.; Zeidabadi, F. React Funct Polym 2007, 67, 644.
14. Zohuriaan-Mehr, M. J.; Motazedi, Z.; Kabiri, K.; Ershad-Langroudi, A. J Macromol Sci Pure Appl Chem 2005, 42, 1655.
15. Zohuriaan-Mehr, M. J.; Motazedi, Z.; Kabiri, K.; Ershad-Langroudi, A.; Allahdadi, I. J Appl Polym Sci 2006, 102, 5667.
16. Wu, J.; Lin, J.; Li, G.; Wei, C. Polym Int 2001, 50, 1050.
17. Tao, W.; Xiaoqing, W.; Yi, Y.; Wenqiong, H. Polym Int 2006, 55, 1413.
18. Pourjavadi, A.; Mahdavinia, G. R. PolymPolym Compos 2006, 14, 203.
19. Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A. Angew Chem Int Ed 2005, 44, 3358.
20. Heinze, T.; Liebert, T. Prog Polym Sci 2001, 26, 1689.
21. Sannino, A.; Mensitieri, G.; Nicolas, L. J Appl Polym Sci 2004, 91, 3791.
22. Yoshimura, T.; Matsuo, K.; Fujioka, R. J Appl Polym Sci 2006, 99, 3251.
23. Pourjavadi, A.; Zohuriaan-Mehr, M. J.; Ghasempoori, S. N.; Hossienzadeh, H. J Appl Polym Sci 2007, 103, 877.
24. Ramazani-Harandi, M. J.; Zohuriaan-Mehr, M. J.; Yousefi, A. A.; Ershad-Langroudi, A.; Kabiri, K. Polym Test 2006, 25, 470.
25. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. G. Polymer 1998, 39, 3459.
26. Omidian, H.; Zohuriaan-Mehr, M. J Polym 2002, 43, 269.
27. Doyle, C. D. Anal Chem 1961, 33, 77.
28. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: New York, 1953.
29. Chen, J.; Zhao, Y. J Appl Polym Sci 2000, 75, 808.
30. Hosseinzadeh, H.; Pourjavadi, A.; Mahdavinia, G. R.; Zohuriaan-Mehr, M. J. J Bioact Compat Polym 2005, 20, 475.
31. Hsu, S.-C.; Don, T.-M.; Chiu, W.-Y. Polym Degrad Stab 2002, 75, 73.
32. Park, S.-E.; Nho, Y.-C.; Lim, Y.-M.; Kim, H. J Appl Polym Sci 2004, 91, 636.
33. Grulke, E. A. In Polymer Handbook, 4th ed.; Brandrup, J., Immergut, E. H.; Grulke, E. A., Eds.; Wiley: New York, 1999; p VII/675.
34. Chen, J.; Shen, J. J Appl Polym Sci 2000, 75, 1331.
35. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. Polymer 1998, 39, 6697.