

Synthesis and Properties of Carboxymethyl Cellulose-graft-Poly(acrylic acid-co-acrylamide) as a Novel Cellulose-Based Superabsorbent

Aili Suo,¹ Junmin Qian,² Yu Yao,¹ Wanggang Zhang³

¹Department of Oncology, First Hospital, Medical College, Xi'an Jiaotong University, Xi'an 710061, People's Republic of China

²State Key Laboratory for Mechanical Behaviors of Materials, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

³Second Hospital, Medical College, Xi'an Jiaotong University, Xi'an 710004, People's Republic of China

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ABSTRACT: A new cellulose-based superabsorbent polymer, carboxymethyl cellulose-graft-poly(acrylic acid-co-acrylamide), was prepared by the free-radical grafting solution polymerization of acrylic acid (AA) and acrylamide (AM) monomers onto carboxymethyl cellulose (CMC) in the presence of *N,N'*-methylenebisacrylamide as a crosslinker with a redox couple of potassium persulfate and sodium metabisulfite as an initiator. The influences of reaction variables such as the initiator content, crosslinker content, bath temperature, molar ratio of AA to AM, and weight ratio of the monomers to CMC on the water absorbency of the carboxymethylcellulose-graft-poly(acrylic acid-co-acrylamide) copolymer were investigated. The copolymer's structures were characterized

with Fourier transform infrared spectroscopy. The optimum reaction conditions were obtained as follows: the bath temperature was 50°C; the molar ratio of AA to AM was 3 : 1; the mass ratio of the monomers to CMC was 4 : 1; and the weight percentages of the crosslinker and initiator with respect to the monomers were 0.75 and 1%, respectively. The maximum water absorbency of the optimized product was 920 g/g for distilled water and 85 g/g for a 0.9 wt % aqueous NaCl solution. In addition, the superabsorbent possessed good water retention and salt resistance. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1382–1388, 2007

Key words: copolymerization; crosslinking; FT-IR

INTRODUCTION

A superabsorbent is a new kind of functional polymer that has a weakly crosslinked three-dimensional network structure and the ability to absorb considerable amounts of water or other liquids (tens to thousands of times its own weight) in a relatively short time. Superabsorbents can be applied to many industrial applications, such as baby diapers, personal hygiene products, controlled drug release, horticulture, and agriculture.^{1–4} Other advanced applications include moisture sensors,⁵ body water elimination systems for edemas occurring in many diseases,^{6,7} artificial muscles, and scaffolds for tissue engineering.⁸

Among the various superabsorbents, synthesized superabsorbent polymers from organic monomers have been paid particular attention because these materials possess good absorption capacity, desirable

swelling rates, and receivable resistance to metallic ions and water retention.^{9–15} However, in recent years, superabsorbent polymers prepared from natural polymers such as starch,^{16–18} chitosan,¹⁹ poly(amino acids),²⁰ and carrageenan^{21,22} have received increasing interest because they are environmentally friendly, biodegradable, and independent of oil resources and people are paying more and more attention to environmental preservation. Cellulose and its derivatives are also attracting a great deal of interest again for preparing superabsorbent polymers because of their biodegradable characteristics,^{23,24} their natural abundance, and potentially high absorption properties.^{7,25,26}

Cellulose is one of the main constituents of natural plant fibers such as cotton, wood, and jute.²⁷ Its derivatives are among the main raw materials used for synthesizing early superabsorbent polymers.^{28–30} To synthesize successful superabsorbent polymers based on cellulose, the techniques mostly used are (1) the crosslinking graft copolymerization of hydrophilic vinyl monomers such as acrylic acid (AA) and acrylamide (AM) onto cellulose or its derivatives and (2) the crosslinking of cellulose derivatives with difunctional molecules such as divinyl sulfone as crosslinkers because they themselves possess nonideal water absorption, strong hydrogen bonds among cellulose molecules,

Correspondence to: J. Qian (junminqian@hotmail.com).

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high crystallinity, and poor water-soluble and forming properties. Many efforts have been made to synthesize cellulose-based superabsorbents and to improve the swelling capacity. For example, Kuwabara and Kubota³¹ synthesized highly water-absorbing AA-grafted carboxymethylcellulose (CMC) by photografting in the presence of *N,N'*-methylenebisacrylamide (NMBA) as a crosslinker. Yoshinobu et al.³² reported partially hydrolyzed graft copolymers of crosslinked polyacrylamide on cellulose and its derivatives synthesized by a ceric salt initiation method. Kubota and Kuwabara³³ prepared AA-grafted and methacrylic acid grafted CMC superabsorbents by photoinitiation, ceric salt initiation, and radiation initiation, and the highest water absorbency obtained was less than 250 g/g. Lionetto et al.³⁴ prepared a superabsorbent cellulose-based hydrogel by crosslinking a sodium salt of CMC and hydroxyethyl cellulose with divinyl sulfone as a crosslinker.

In this study, we attempted to synthesize a new cellulose-based superabsorbent by simultaneously grafting two kinds of hydrophilic monomers, AA and AM, onto CMC in the presence of the crosslinker NMBA, combining the high absorption capacity of poly(acrylic acid) and the strong resistance to metallic ions and fast swelling rate of polyacrylamide. The effects of various reaction parameters, such as the bath temperature, AA/AM molar ratio, monomer/CMC mass ratio, and crosslinker and initiator contents, on the water absorbency of the products, as well as their water retention and resistance to aqueous NaCl solutions, were investigated.

EXPERIMENTAL

Chemicals and materials

AA (Zhengzhou Pains Chemical Agent Co., Henan, China), AM (Tianjin Damao Chemical Agent Co., Tianjin, China), NMBA (Tianjin Kemiou Chemical Agent Co., Tianjin, China), potassium persulfate (PPS; Tianjin Haijing Fine Chemical Agent Co., Tianjin, China), and sodium metabisulfite (SMB; Shanghai First Chemical Agent Factory, Shanghai, China) were all analytically pure and were used as received. CMC (Ningbo Haishu Cellulose Derivatives Co., Zhejiang, China; degree of substitution = 0.2–0.5) was used without further treatment. Other agents (analytically pure) were purchased from Xi'an Chemical Agent Co. (Xi'an, Shaanxi, China).

Preparation of the superabsorbent samples

AA was first dissolved in distilled water to obtain an aqueous AA solution, and the solution was neutralized to 85% by the dropwise addition of a 5 mol/L aqueous NaOH solution to form a mixture of AA and sodium acrylate. The whole process was performed in an ice-

water bath to avoid the possible polymerization of AA due to the increasing temperature caused by the neutralization reaction. An aqueous solution of CMC was placed in a 250-mL, four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a nitrogen line and purged with a stream of nitrogen at room temperature to remove the dissolved oxygen from the solution. After a redox couple of PPS and SMB was added to the solution and it was gently stirred for 15 min to facilitate free-radical formation on the CMC backbone, AM and the partially neutralized AA were added to the flask. The crosslinker NMBA was added just after the addition of the monomers. The reaction solution was heated by the water bath to desired temperatures to start the polymerization with constant stirring in an atmosphere of N₂ for a certain time and then transferred to a stainless steel reactor for further reaction at 80°C for 2 h. The obtained product was cut into small pieces and dried *in vacuo* at 70°C for 24 h. The dry product was milled and sieved through a 40-mesh sieve. To remove soluble CMC, monomers, homopolymers, and other uncrosslinked copolymers from the products, these small pieces of copolymer were then soaked in hot, distilled water, reaching equilibrium swelling under continuous stirring, and then were filtered. The process was repeated several times. The product was called carboxymethylcellulose-graft-poly(acrylic acid-co-acrylamide) [CMC-g-poly(AA-co-AM)]. Unless otherwise stated, the basic composition was as follows: the molar ratio of AA to AM was 3 : 1; the total weight of the two monomers with respect to the CMC weight was 4 : 1; the weight percentages of the crosslinker and initiator with respect to the monomers were 0.75 and 1%, respectively; the total weight percentage of AA, AM, and CMC with respect to distilled water was 11.6%; and the volume of the reaction system was 100 mL.

Measurement of the water absorbency

A sample of the polymer (ca. 1 g) was immersed in 2 L of distilled water or 500 g of an aqueous NaCl solution at room temperature and allowed to swell with mild agitation. The steady-state uptake of water or equilibrium swelling was determined by absorption being allowed to occur overnight (typically requiring 6 h). The swollen gels were then separated from unabsorbed water with a weighted 100-mesh nylon bag, kept in the bag to drain for 1 h, and then weighted. The water absorbency (*Q*) was calculated according to the following equation:

$$Q = (W_1 - W_2)/W_2 \quad (1)$$

where *W*₁ and *W*₂ are the weights of the swollen gel and the dry CMC-g-poly(AA-co-AM), respectively. The water absorbency denotes the grams of water

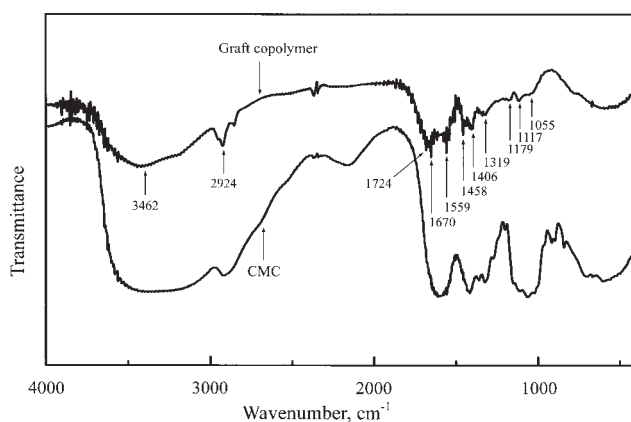


Figure 1 FTIR spectra of CMC and the graft copolymer.

retained per gram of the dry sample. All swelling data reported in the following are average values from three measurements.

Water retention at a constant temperature

A weighed quantity of the superabsorbent was immersed in distilled water at room temperature to reach the swelling equilibrium. The equilibrated gels were drained in 100-mesh nylon bags for 1 h, and then the bags containing the gels were placed in an oven heated by a current of hot, dry air at 60°C. The weights of the bags were measured every hour to reveal the relationship between their weights and heating time.

IR spectroscopy

The structure of the superabsorbent samples was characterized with Fourier transform infrared (FTIR) spectrometry with an IR Prestige-21 FTIR spectrophotometer. The samples were powdered and mixed with KBr to make pellets.

RESULTS AND DISCUSSION

FTIR spectra of the CMC and graft copolymer

The structural changes during the grafting copolymerization were studied by a comparison of the FTIR spectrum of the CMC substrate with that of the graft copolymer CMC-g-poly(AA-co-AM). Figure 1 shows their FTIR spectra.

The band at 3462 cm^{-1} observed in the IR spectrum of the graft copolymer is attributed to the NH stretching of the AM unit, which overlaps the —OH stretching band of the CMC portion of the copolymer. The peak at 2924 cm^{-1} is ascribed to the C—H stretching of the polymer backbone. The peak at 1724 cm^{-1} is attributed to the carbonyl stretching of the carboxylic acid groups. The peak at 1670 cm^{-1} is assigned to the characteristic absorption bands of the

carboxamide-functional groups of the amide moiety of the AM unit.^{19,35} The very intense characteristic band at 1559 cm^{-1} is due to the C=O asymmetric stretching in the carboxylate anion that is reconfirmed by another sharp peak at 1406 cm^{-1} , which is related to the symmetric stretching mode of the carboxylate anion.^{36,37} In addition, peaks at 1458 and 1179 cm^{-1} corresponding to the —CO—O— and OH coupling interactions of the carboxylic group and C—N stretching vibrations can also be observed.³⁸ The peak at 1055 cm^{-1} , ascribed to the C—O—C stretching interactions, can also be observed. A comparison of the two IR spectra shows that the characteristic absorption bands of AA and AM repeating units appear in the spectrum of the copolymer, and this confirms the grafting copolymerization of AA and AM monomers onto the CMC backbone.

Effect of the initiator content on the water absorbency

PPS/SMB is a redox initiator couple in free-radical chain polymerization. In free-radical polymerization, the initiator has a great effect on both the polymerization rate and the molecular weight of the polymer. During crosslinking polymerization, the initiator also affects the crosslinking degree and molecular weight between two crosslinking points.

The water absorbency values obtained by the alteration of the initiator content are shown in Figure 2. The water absorbency of the product increases, reaches a maximum of 910 g/g at 1 wt % initiator, and then decreases considerably with an increase in the initiator amount. The number of radicals produced is small before the initiator content increases up to the optimum value, and the network cannot form efficiently in the free-radical polymerization; this results in low water absorbency. At low contents, the initiator must be mostly used in producing a large number of free-

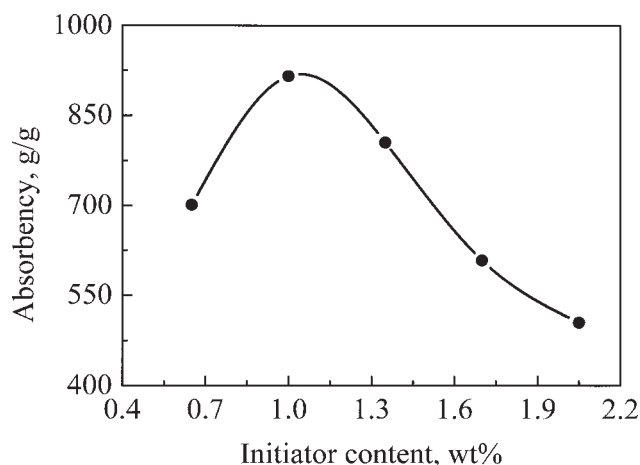


Figure 2 Effect of the initiator content on the water absorbency.

radical sites on the CMC backbone at which the monomers can be grafted. Therefore, the absorbency of the graft polymer increases with increasing initiator content. However, above a critical concentration of 1 wt %, a large number of active free radicals on the CMC backbone are produced, and this leads to more polymer chain ends in the network, termination of the step reaction via bimolecular collision, and a short average of the kinetic chain length; that is, it decreases the polymerization degree or the molecular weight of the graft copolymer, resulting in a shortening of the average macromolecular chains and reducing the available free volume within the superabsorbent. An excess of the initiator is used in the homopolymerization of the monomers. The free-radical degradation of CMC backbones by sulfate radical anions is an additional reason for a swelling loss at higher initiator contents. Therefore, the increase in the initiator content is responsible for the decline in the water absorbency.

Effect of the crosslinker content on the water absorbency

Crosslinkers have to be present in a hydrogel to prevent the dissolution of hydrophilic polymer chains in an aqueous environment. The crosslinking density is an extremely important swelling-control element. The efficiency of crosslinker incorporation controls the overall crosslink density in the final hydrogel. In general, the crosslinking structure of a hydrogel decides both its dissolution and swelling capacity in an aqueous solution, so a moderate crosslinking degree is suitable for the absorbency enhancement of the resulting hydrogel. It is a well-known rule for all hydrogels that a relatively small increase in the crosslinking degree can play a major role in modifying the properties of superabsorbent polymers. The influence of the crosslinker content on the water absorbency of CMC-g-poly(AA-co-AM) is shown in Figure 3.

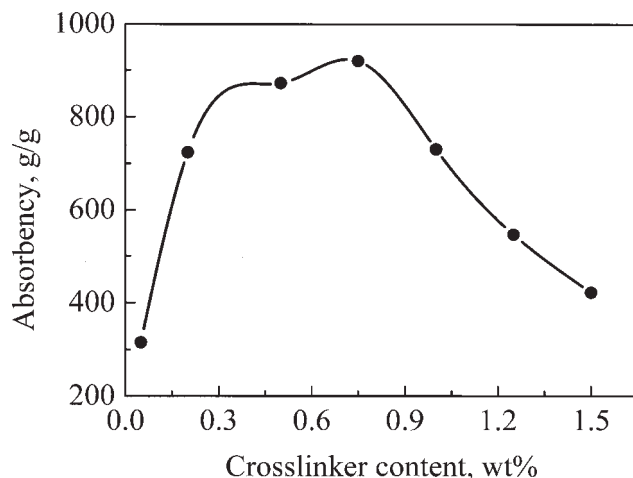


Figure 3 Effect of the crosslinker content on the water absorbency.

As the crosslinker content increases, the absorbency of the hydrogel for distilled water increases and reaches the maximum absorbency of 920 g/g when the concentration of the crosslinker is 0.75 wt % of that of the monomers, but the absorbency decreases as the concentration of the crosslinker is further increased.

The water absorbency increases as the crosslinker content increases up to 0.75 wt % because of the formation of (1) a moderately crosslinked graft copolymer with a continuous network, (2) crosslinked, insoluble homopolymers, and (3) insoluble carboxymethyl cellulose-graft-*N,N'*-methylenebisacrylamide copolymer. In general, the decrease in the crosslinker content is limited by a value at which gel formation is prevented, causing a poorly crosslinked network dissolving in water during the swelling experiments. The as-prepared hydrogels do not possess good dimensional stability when the crosslinker concentration is lower than 0.05 wt % because the crosslinked network structure in the copolymer cannot form effectively, and AA, AM, and CMC exist as monomers or linear low-molecular-weight polymers. The absorbency of the resultant hydrogel cannot be measured despite high absorbency for the AA, AM, and CMC monomers. Under our experimental conditions, the crosslinker concentration should be higher than 0.05 wt %.

The water absorbency decreases considerably with an increase in the crosslinker concentration from 0.75 to 1.5 wt %. A higher crosslinker concentration will produce more crosslinked points in polymeric chains, cause a higher crosslinking density, and decrease the space between the copolymer chains, leading the pendant AA and AM chains on the CMC backbone to form a tight network. Consequently, the resulting highly crosslinked, rigid structure cannot be expanded and hold a large quantity of water. Nevertheless, crosslinking also increases the mechanical strength of these hydrogels.

Effect of the bath temperature on the water absorbency

Figure 4 demonstrates the effect of the bath temperature on the water absorbency of the products. As the bath temperature increases, the water absorbency increases, reaches a maximum value at 50°C, and then decreases.

The increasing bath temperature before 50°C will result in a higher polymerization rate, which leads to the decline of the crosslinking efficiency. At the same crosslinker concentration, the water absorbency increases with the reduction of the crosslinking efficiency according to Flory's network theory. In addition, the diffusion rate of AA and AM onto CMC macroradicals and the kinetic energy of radical centers are increased at higher temperatures, and results in a higher graft polymerization degree and consequently a higher final water absorbency of the as-produced

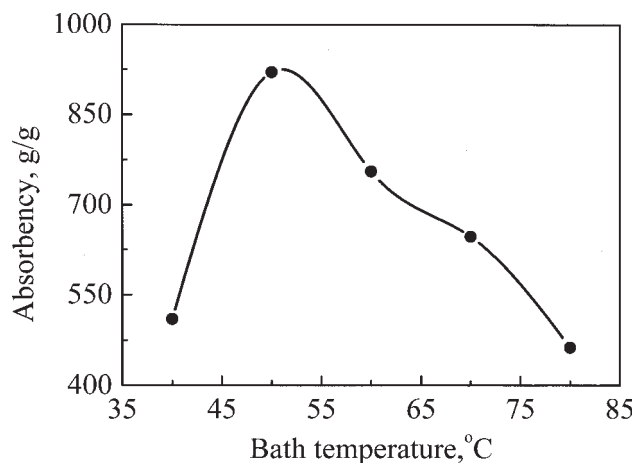


Figure 4 Effect of the bath temperature on the water absorbency.

hydrogel. However, when the bath temperature increases above 50°C, the polymerization rate further increases, the degree of polymerization decreases because of the increase in the chain-termination and chain-transfer-reaction rates, and the oxidative degradation of CMC chains caused by sulfate radical anions originating from the initiator may occur. The aforementioned factors shorten the molecular chains and reduce the molecular weight. The network structure does not encourage water absorption, so water absorbency decreases.

Effect of the AA/AM molar ratio on the water absorbency

The effects of various molar ratios of AA to AM on the water absorbency of the products have been investigated, as shown in Figure 5. The water absorbency increases with an increase in the molar ratio of AA to AM in the monomer feed.

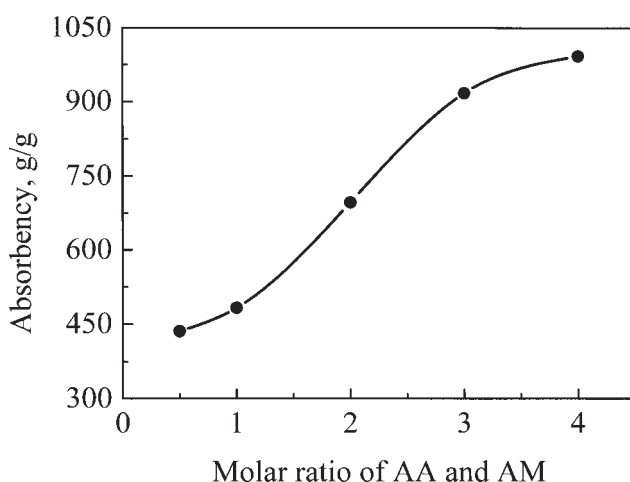


Figure 5 Effect of the molar ratio of AA to AM on the water absorbency.

The internal structural factors influencing the swelling characteristics of an absorbent polymer are the nature of the network charges, the crosslink density, the monomer composition, the gel modulus, and so forth. Because AM is a nonionic monomer, its dissociation degree in water is lower than that of ionic monomers such as AA and sodium acrylate. When a certain amount of AM together with AA is graft-copolymerized onto the CMC backbone, it not only weakens the hydrogen bond between water and carboxyl group, thereby reducing the water absorbency of the resultant hydrogel, but also exerts an influence on the water absorbency because of the synergistic effects of different hydrophilic groups. However, AM may enhance the salt resistance of the resultant hydrogel.

As the molar ratio of AA to AM increases, the number of osmotically active ionic carboxylate groups (from neutralized AA) in the CMC-g-poly(AA-co-AM) copolymer becomes much larger than that of nonionic carboxamide (from AM), which favors water absorbency because of the electrostatic repulsion from these carboxylate groups as main driving forces. As a result, the water absorption will increase. This result is consistent with previous work reported in the literature.^{16,39}

Effect of the monomer/CMC weight ratio on the water absorbency

Figure 6 shows the variation of the water absorbency with the weight ratio of the monomers and CMC. The water absorbency rapidly increases almost linearly with an increasing monomer/CMC weight ratio. The reason is that the water absorbency of CMC is much lower than that of poly(acrylic acid-co-acrylamide). Actually, the copolymer contains four kinds of hydrophilic groups, namely, $-\text{OH}$, $-\text{CONH}_2$, $-\text{COOH}$, and $-\text{COONa}$. Among them, the $-\text{COONa}$ group from

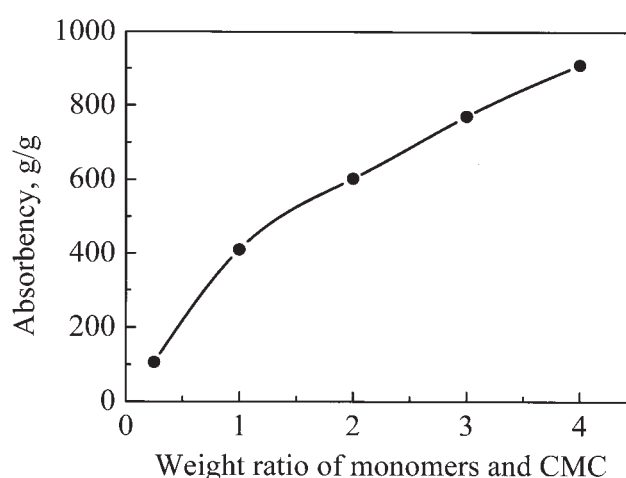


Figure 6 Effect of the weight ratio of the monomers to CMC on the water absorbency.

partially neutralized AA will ionize into Na^+ and $-\text{COO}^-$ ions in water and has much better absorbency capacity than the other three kinds of hydrophilic groups because of the ionic hydrophilic and osmotic effects of $-\text{COO}^-$ ions. CMC has good hydrophilicity and can easily dissolve in water because of its linear macromolecular structure and $-\text{OH}$ and $-\text{CH}_2\text{COOH}$ groups; this is not called swelling. In this study, the main purpose of introducing CMC into the superabsorbent is to make the products cheaper and easier to biodegrade.

Enhanced monomer content increases the diffusion rate of AA and AM molecules into the CMC backbone, and this improves the availability of monomer molecules in the vicinity of CMC macroradicals to produce a graft copolymer and subsequently improves its hydrophilicity and water absorbency.

Water retention at a constant temperature

From the point of view of practical applications, it is very important to know the water retention of a superabsorbent. Figure 7 shows the water retention of an absorbing-saturated superabsorbent (15 g) in open air at 60°C . As shown in Figure 7, the water retention of the samples decreases continuously with prolonged heating time, and the superabsorbent can retain 61.3 and 20.7% of the absorbency after heating for 4 and 10 h, respectively. This arises because a membrane is formed on the sample surface as the sample is dried, and this reduces the drying rate. In addition, water is bound to polymer chains via the hydrogen bonds formed between CMC-g-poly(AA-co-AM) and water molecules, leading to an increase in the vaporizing energy and a decrease in the drying rate. In other words, the result suggests that the synthesized copoly-

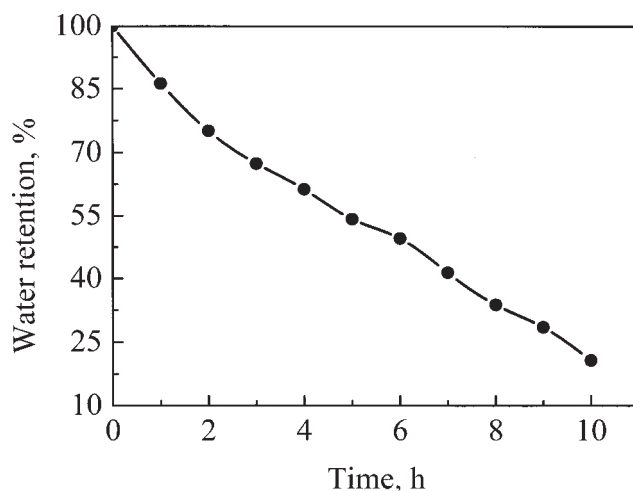


Figure 7 Relationship between the water retention and the heating time at 60°C .

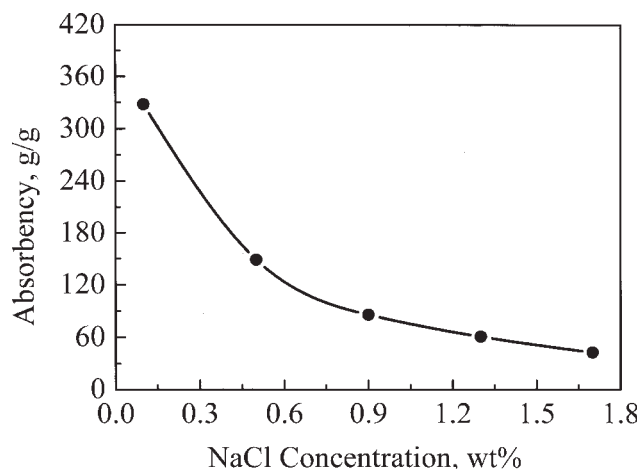


Figure 8 Effect of the concentration of the aqueous NaCl solution on the water absorbency.

mers have a good water-retaining capacity in air even at high temperatures.

Effect of the concentration of the aqueous NaCl solution on the water absorbency

Figure 8 shows the effect of the concentration of an aqueous NaCl solution on the water absorbency of the superabsorbents. The water absorbency decreases as the concentration of the aqueous NaCl solution increases. At the same time, the results from Figure 8 also indicate that the resistance of CMC-g-poly(AA-co-AM) to metallic ions is ideal, and its absorbency is larger than 85 g/g at a 0.9 wt % NaCl concentration.

It is known that the chemical potential of water in a superabsorbent is equal to that of the water surrounding the superabsorbent at the swelling equilibrium. Because the ionic strength in the aqueous salt solution outside the superabsorbent is larger than that in distilled water, the osmotic pressure is greatly reduced. Therefore, the superabsorbent polymers cannot absorb an aqueous NaCl solution as much as distilled water.

CONCLUSIONS

A new cellulose-based superabsorbent polymer, CMC-g-poly(AA-co-AM), has been prepared by the grafting polymerization of AA and AM onto CMC in an aqueous solution with NMBA as the crosslinker and PPS/SMB as a redox couple of the initiator. FTIR studies suggest that AA and AM monomers are graft-copolymerized onto CMC macromolecular chains. The initiator content, crosslinker content, and bath temperature mainly affect the molecular weight and crosslinking density of the copolymer and the polymerization rate, respectively. They have a collaborative effect on the water absorbency of the products, and each of them presents an optimum value. The greater the weight

percentage of the AA monomer in the starting stock is, the more numerous the ionic carboxylate groups are, and this greatly improves the water absorbency. The maximum absorbency of the products obtained under the optimum reaction conditions is 920 g/g for distilled water and 85 g/g for a 0.9 wt % aqueous NaCl solution. In addition, the superabsorbent has good water retention and salt resistance.

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