

PREPARATION OF MACROPOROUS CELLULOSE-BASED SUPERABSORBENT POLYMER THROUGH THE PRECIPITATION METHOD

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Superabsorbent polymer was prepared by graft polymerization of acrylic acid onto the chain of carboxymethyl cellulose. This superabsorbent polymer was further treated by the solvent precipitation method. We found that the water absorption rate of the treated polymer was greatly increased and the microstructure of the treated polymer was changed from close-grained structures to loose macropores. The swelling processes of the polymers before and after modification fit first-order dynamic processes. The amount of the residual acrylic acid was detected through high performance liquid chromatography (HPLC) with aqueous solution of MOPS of 0.02mol/L (pH=5.70) as the mobile phase. It was found that the amount of the residual acrylic acid decreased from $83.8 \times 10^{-4} \%$ to $6.7 \times 10^{-4} \%$ after treatments.

Keywords: Carboxymethyl cellulose; Superabsorbent polymer; Macropores; Precipitation method

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INTRODUCTION

Superabsorbent polymers can be described as having a network structure and a moderate degree of crosslinking (Omidian et al. 2005). They can absorb a large amount of water, considerably more than their dry mass. The amount of the absorbed water can range from hundreds of times to thousands of times that of the polymer. These polymers have been extensively used as absorbents in personal care products, such as infant diapers, feminine hygiene products, and incontinence products (Li et al. 2007; Suo et al. 2007; Zhang et al. 2006; Peng et al. 2008). They have also received considerable attention for a variety of more specialized applications, including matrices for enzyme immobilization, bioabsorbents in preparative chromatography, materials for agricultural mulches, and matrices for controlled release devices (Hany 2007; Marcos et al. 2005).

Some natural polymers, such as cellulose or starches, can be prepared as superabsorbent polymers through radical graft polymerization with vinyl monomers and proper crosslinking (Li et al. 2007; Suo et al. 2007; Zhang et al. 2006; Peng et al. 2008). Our research group also has reported the preparation of a superabsorbent polymer by graft copolymerization of sodium acrylate and acrylamide along the chain of carboxymethyl cellulose (Li and Tan 2003; Li et al. 2006). Because of their very good biocompatibility, superabsorbent polymers based on natural polymers are expected to be widely used in many applications such as medical materials, sanitary products, controlled release devices, and matrices for enzyme immobilization (Sannino et al. 2003; Lionetto et al. 2005).

For superabsorbent polymers used as medical and sanitation materials, they must have high absorption rates and low residual levels of toxic chemicals. Usually, the porous superabsorbent polymers are prepared by adding chemical reagents to produce bubbles in

the polymer. Although high water absorption rates have been observed (Chen et al. 1999; Park et al. 1998) in those superabsorbent polymers, toxic chemicals are introduced during this process. In this study, the superabsorbent polymer was modified through novel physical methods, based on the solvent precipitation method. The processes were simple and the results were dramatic. The absorption rate of the polymer was increased greatly, and the amount of residual monomer was decreased markedly. These modification methods have not been reported before. They are likely useful in the preparation of high quality superabsorbent polymers.

EXPERIMENTAL

Materials

Carboxymethyl cellulose (CMC) was supplied by Hebei Maoyuan Chemical Industry Co., Ltd (China). It has a viscosity at 25 °C of 140 ± 60 mPa·s as a 2% aqueous solution, and at a degree of substitution of 0.82. Acrylic acid (AA, Analytical Reagent) was purchased from Tianjin Chemical Reagent Institute (China) and purified by reduced pressure distillation before the polymerization. Ammonium persulfate (APS, Analytical Reagent) was used as the initiator and N, N'-methylene diacrylamide (MBAM, Analytical Reagent) was used as the crosslinking agent. Ethanol and sodium hydroxide are analytical reagents and used as received.

Preparation of the Superabsorbent Polymer

Carboxymethyl cellulose (1.2 g) was dissolved in a specified amount of water and then added into a three-necked flask, which was equipped with a stirring apparatus and a reflux condenser. The solution was stirred for 30 min under the protection of nitrogen and then heated by a water bath of 60 °C. A certain amount of APS (0.3 g) dissolved in a moderate amount of deionized water was slowly added into the flask to initiate the graft polymerization. 12 g acrylic acid neutralized to 50% and 0.45g MBAM were added 30 min later. The total volume of water in the system was controlled at a certain level, whereas the stirring speed was fixed. After reacting for 5h, air was introduced into the reactor to cool down the flask and stop the reaction. The product was precipitated by pouring alcohol into the reaction mixture. The precipitate was filtered, washed thoroughly with the ethanol/water mixture (4:1, v/v) for several times under high-speed stirring, and then soaked with the ethanol/water mixture (4:1, v/v) for 24 h. The product was collected by filtration and dried under vacuum. (Found: $v_{\max}(\text{KBr})$ 3430, 2931, 2560, 1720, 1589, 1450, 1421, 1170, 1040, and 819 cm^{-1})

Treatment of the Superabsorbent Polymer by the Precipitation Method

The superabsorbent polymer (1.0 g) of 80 mesh size was added into 150 ml distilled water. It was allowed to swell during agitation in a water bath at the constant temperature of 25 °C for 48 h. The polymer was recovered by precipitation with ethanol. The precipitate was filtered and dried under vacuum at 60 °C.

Characterization

Test of the water absorption capability

To test the water absorption capability, 0.100 g of the superabsorbent polymer was placed into a sieve pouch. The pouch was then immersed into the distilled water to swell. After a suitable period, the sample was taken out from the water. After removing

the excess water, the weight of the swollen polymer was measured. The swelling ratio (Q , g/g) is calculated by:

$$Q = (m_2 - m_1) / m_1 \quad (1)$$

where m_1 is the weight of the dry superabsorbent polymer, and m_2 is the weight of the swollen superabsorbent polymer.

Determination of the residual acrylic acid

Acrylic acid was detected by HPLC. The Agilent 1100 series HPLC instrument (Agilent Technologies, USA) equipped with a wavelength adjustable UV detector and the chemical workstation software was used. The column was the Diamonsil™ (Diamond)-C18 (5 μ , 250 \times 4.6mm). MOPS aqueous solution of 0.02 M with pH= 5.70 was used as the mobile phase, and the flow rate was 0.8 ml/min. The detection wavelength was 210 nm and the injection volume was 20 μ l.

Dried superabsorbent polymer (0.100 g) was accurately weighed and added to 10 ml 0.9% normal saline. The mixture was agitated on an oscillator at room temperature for 2 h. Then it was filtered with a filter paper. The filtrate liquid was collected and used for HPLC analysis.

Scanning electron microscopy (SEM) examination

The surface structure of the superabsorbent polymer before and after the processing was viewed with a scanning electron microscope (QUANTA200, Philips—FEI Co., Netherlands). The samples were coated with Au prior to SEM observation.

RESULTS AND DISCUSSION

Effect of the Treatments on the Water Absorption Rate of the Polymers

The water absorption rates of the polymers were increased greatly after further treatments by the solvent precipitation method. It can be seen from Fig. 1 that it took about 45 min to reach the steady state of absorption before treatments. For the polymer treated with solvent precipitation method, the water absorption rate reached steady state in just 10 min.

On the assumption that the swelling of the polymer fits a first-order process (Liu et al. 1996), the swelling rate at a given temperature is:

$$dQ_t / dt = k(Q_e - Q_t) \quad (2)$$

where t is the swelling time, Q_t is the swelling ratio at that time, and Q_e is the equilibrium swelling ratio. Eq. 1 can be integrated to:

$$\int_{Q_0}^{Q_t} dQ_t / (Q_e - Q_t) = \int_0^t k dt \quad (3)$$

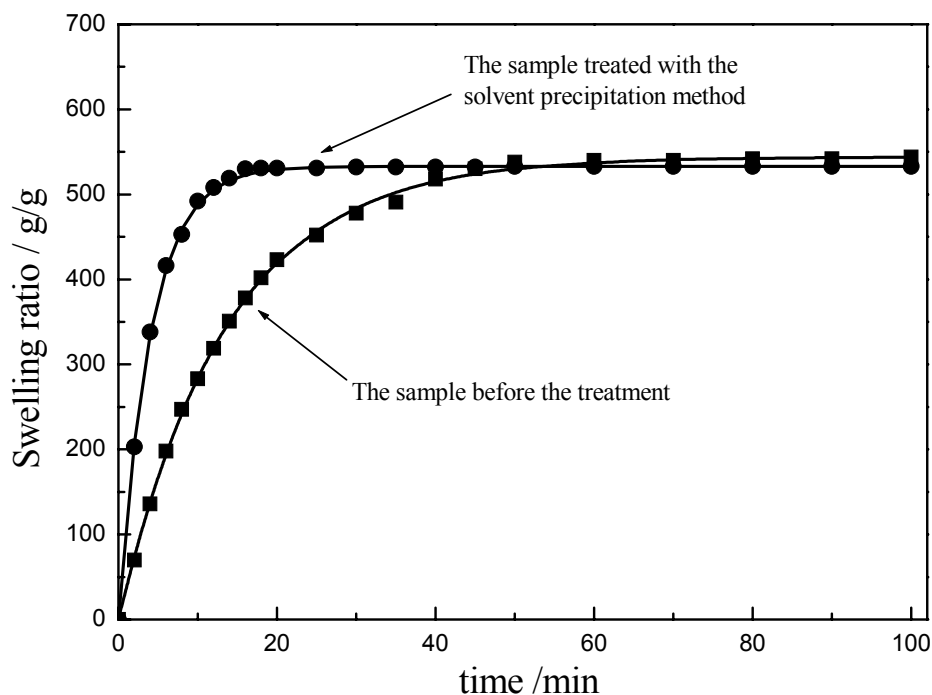


Fig. 1. Water absorption rates before and after treatments

The result is:

$$\ln[(Q_e - Q_0)/(Q_e - Q_t)] = kt \quad (4)$$

then the following equation is gained:

$$Q_t = Q_e - (Q_e - Q_0)/e^{kt} \quad (5)$$

The curve between $\ln[(Q_e - Q_0)/(Q_e - Q_t)]$ and t (the diagonal part of the water absorption curve) was drawn, and the slope was the swelling rate constant (k). The k value of the untreated sample was 0.074; the k values were 0.247 for the samples treated with the solvent precipitation method. The k values also indicated that the water absorption rates of the polymer were increased dramatically after treatments. The theoretical swelling curves of the polymer were obtained by introducing the k values into Equation 5 (the solid line in Fig. 1). The results of theoretical calculation and experiment data agreed well, indicating that the assumption of a first-order process was valid.

The microstructures of the polymers before and after treatments were examined by SEM (Fig. 2). The SEM photographs showed that the microstructures of the polymer were changed from the close-grained structure to loose macropores as the polymers underwent treatments. During the first step of the solvent precipitation method, the polymer was extensively swollen in water. When the organic solvent that is miscible with water was added, water was displaced from the network by the organic solvent. During this displacement process, the polymer retained its expanded porous structure. In

addition, the residual organic solvent left in the precipitated polymer was easily removed by vacuum drying, and the porous structure remained.

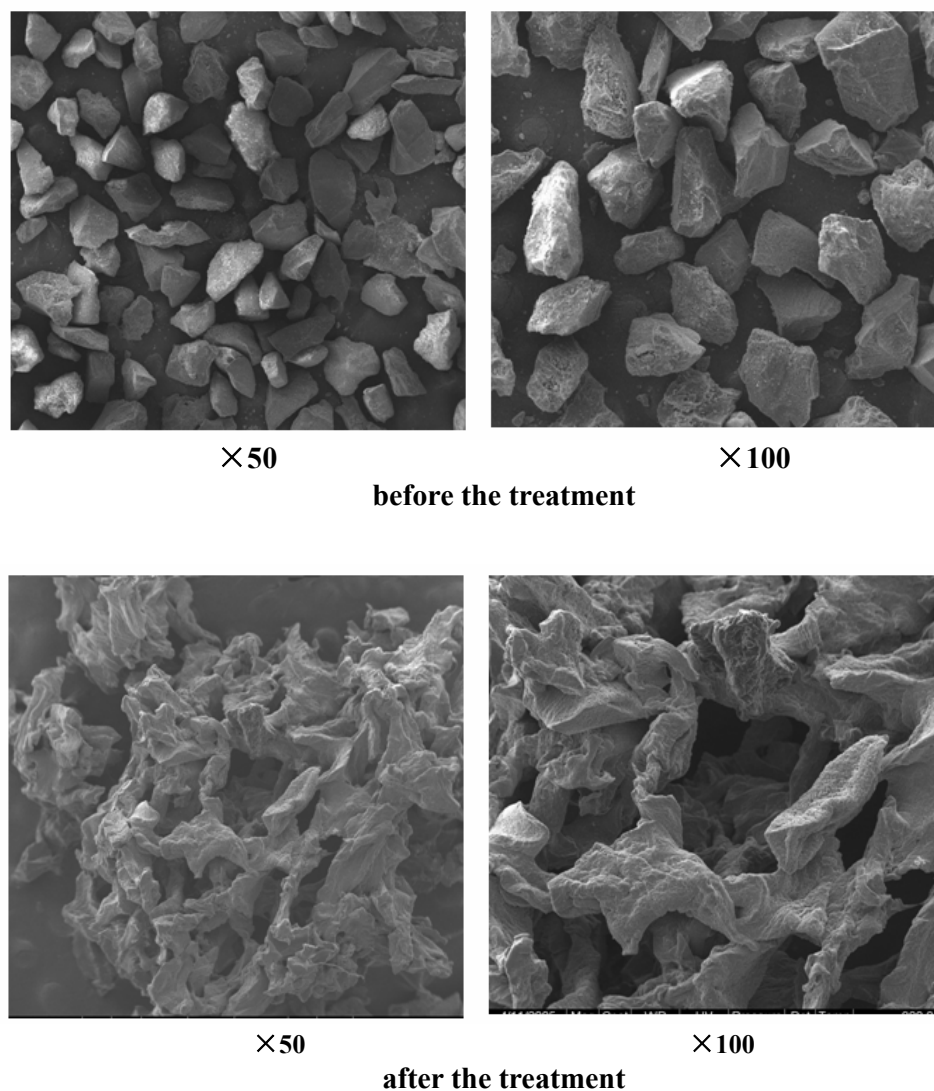


Fig. 2. SEM pictures of the polymer before and after treatments

With the increase of the mean pore size, The Na^+ ions move to the outside of the polymer more easily, and the hydrophilic $-\text{COO}^-$ groups attract more water molecules. Therefore, the water absorption rate of the polymer was enhanced greatly. Moreover, the distance between the polymer chains was increased, and the contractibility of the polymer was decreased, leading to an ultimate increase in the water absorption rate.

Effects of the Treatments on the Amount of the Residual Acrylic Acid Monomer

A standard calibration curve between the concentration of acrylic acid and the area of the chromatographic peak was generated by analyzing a series acrylic acid aqueous solutions at 20, 10, 5, 2, 1, 0.5, 0.2, 0.1, and 0.05 $\mu\text{g/ml}$ by HPLC (Fig. 3). The

relationship between them was expressed as,

$$y = 24.62057 + 152.87579 x \quad (6)$$

where y is the area of the chromatographic peak, x is the concentration ($\mu\text{g/ml}$) of the acrylic acid, and $R=0.99981$.

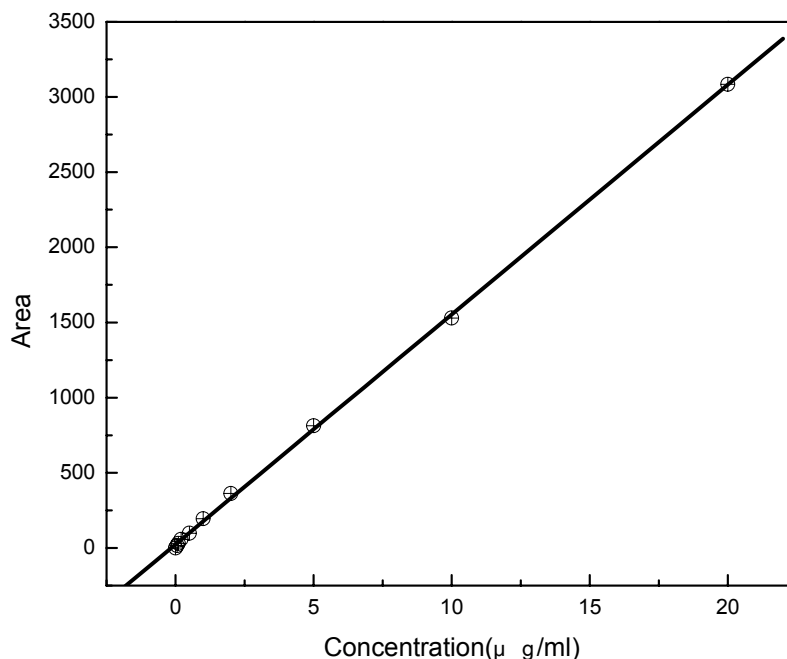


Fig. 3. The standard curve between concentrations of acrylic acid and areas of the chromatographic peak.

Because of the special network structure of the superabsorbent polymers, acrylic acid monomers are easily trapped inside the polymer. To be used as medical materials and sanitarian materials, the amount of the residual monomer must be kept as low as possible. We used solvent precipitation to remove the residual acrylic acid and HPLC to detect it.

It can be seen from the Fig. 4 that the amount of the residual acrylic acid was decreased markedly after treatments with the solvent precipitation method (the amount was decreased from $83.8 \times 10^{-4} \%$ to $6.7 \times 10^{-4} \%$). This dramatic decrease was because, during the process of treatment, the network of the polymer was swollen fully, and the residual hydrophilic acrylic acid monomer was diffused from the network to the water. Moreover, because a large excess of water was added to swell the polymer, even after organic solvent precipitation, few monomers were trapped in the polymer.

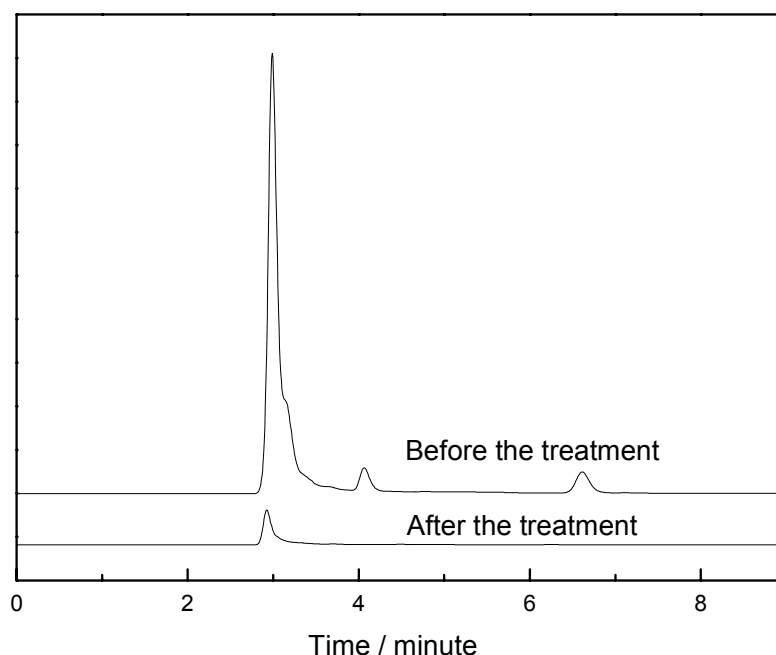


Fig. 4. HPLC diagrams of residual acrylic acid in polymers before and after treatments

CONCLUSIONS

1. A novel superabsorbent polymer was prepared by graft copolymerization of sodium acrylate onto the chain of carboxymethyl cellulose. The superabsorbent polymer was further treated with the solvent precipitation method.
2. The water absorption rate of the polymer was increased greatly as the microstructure of the polymer was changed from a close-grained structure to a loose macroporous structure after the treatments. The water absorption process of the polymers with and without treatments fit a first-order dynamic process.
3. The amount of the residual acrylic acid was detected through high performance liquid chromatography (HPLC) with the aqueous solution of MOPS of 0.02mol/L (pH=5.70) as the mobile phase. It was found that the amount of the residual acrylic acid decreased from $83.8 \times 10^{-4} \%$ to $6.7 \times 10^{-4} \%$ after treatments.
4. The process of this method is simple and the results are very obvious. Moreover, the procedure and results have not previously been reported. The superabsorbent polymers prepared through this method appear to be suitable for medical applications, in which high water absorption rate and low amount of harmful residual monomer are expected to be important.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Natural Science Foundation of China (No. 50773005) and the basic study program of Beijing Institute of Technology (20060442004).

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Article submitted: Jan. 8, 2008; Peer review completed: Feb. 1, 2008; Revised version received and accepted: Feb. 4, 2008; Published: Feb. 5, 2008.