

# Characterization and Biodegradability of Amphoteric Superabsorbent Polymers

Dan Wang,<sup>1,2</sup> Zhan-Qian Song,<sup>1,2</sup> Shi-Bin Shang<sup>1,2</sup>

<sup>1</sup>Institute of Chemical Industry of Forest Products, CAF, Nanjing, China

<sup>2</sup>Key and Open Laboratory on Forest Chemical Engineering, SFA, Nanjing 210042, China

Received 17 July 2007; accepted 15 October 2007

DOI 10.1002/app.27639

Published online 17 December 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Novel amphoteric superabsorbent polymers (SAPs) based on carboxymethyl cellulose, acrylic acid, acrylamide, and [2-(methylacryloyloxy)ethyl]trimethylammonium chloride were prepared by inverse suspension copolymerization. The SAPs were characterized by Fourier transforms infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. The absorbency or swelling behaviors in deionized water, saline solutions, and pH value solutions were investigated. Experimental results indi-

cate that the absorbency in various solutions decreases with an increase of the ion concentration, which was attributed to osmotic pressure of water and ions between the polymeric gel and the external solutions. Biodegradability of the amphoteric SAPs was also reported. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 4116–4120, 2008

**Key words:** amphoteric; swelling; biodegradable; FTIR; characterization

## INTRODUCTION

Superabsorbent polymers (SAPs) are lightly cross-linked functional polymeric materials with strong hydrophilic groups, which can absorb a large amount of water during a short time and the absorbed water is hardly removable even under pressure. Therefore, SAPs have great advantages over traditional water-absorbing materials such as cotton, pulp, and sponge, and have found a variety of valuable applications, such as disposable diapers, feminine napkins, soil for agriculture, water blocking tapes, and numerous biomedical and pharmaceutical applications.<sup>1–8</sup>

Recently, cellulose-based SAPs were finding increasing interest in the scientific and industrial field due to their biodegradable character and the high swelling capacity.<sup>9–14</sup> Most cellulose-based SAPs were obtained by cross-linking of cellulose derivatives using difunctional molecules as cross-linkers, which covalently bind different polymer molecules in a three-dimensional hydrophilic network, or by graft copolymerization of hydrophilic vinyl monomers onto cellulose or its derivatives. In this article, we reported the characterization and

biodegradability of novel amphoteric cellulose-based SAPs, which were obtained by free-radical inverse suspension graft copolymerization of sodium acrylate, acrylamide (AM), and [2-(methylacryloyloxy)ethyl]trimethylammonium chloride onto carboxymethyl cellulose (CMC). There are anionic, nonionic, and cationic hydrophilic groups on the backbone of the copolymer, which prove contribution to high absorption capacity and salt-tolerance. The graft copolymers were characterized by Fourier transforms infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The absorbency or swelling behaviors in deionized water, saline solutions, and pH value solutions were investigated, respectively. Biodegradability of the amphoteric SAPs was tested by soil burial method.

## EXPERIMENTAL

### Materials

Acrylic acid (AA) (chemically pure) was distilled under reduced pressure and stored at  $-8^{\circ}\text{C}$  until it was used. [2-(methylacryloyloxy)ethyl]trimethylammonium chloride (MAETAC) (76.12 wt %, aqueous solution) was purchased from Xinyu Chemical Industry, China and was used without purification. AM, NMBA, SBS, and APS were all chemically pure and used as purchased. Ethanol and cyclohexane were of analytical grade. Deionized water was used in the reaction system and water absorbency measurements.

Correspondence to: S.-B. Shang (shangsb@hotmail.com).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 30471362.

Contract grant sponsor: Ministry of Science and Technology of China; contract grant number: 2006BAD18B10.

*Journal of Applied Polymer Science*, Vol. 107, 4116–4120 (2008)  
© 2007 Wiley Periodicals, Inc.

### Inverse suspension copolymerization

Copolymerization was carried out in a 250-mL four-necked flask equipped with mechanical stirrer, thermometer, condenser, and nitrogen gas line. About 120-mL cyclohexane and the surfactant mixed with Span60 and Tween 80 (1 : 1 in weight) for stabilizing the suspension were added. It was used at a concentration of 6% (w/w) of the dispersed phase. The mixture was heated in a water bath, which was stirred until the complex surfactant was dissolved into continuous phase.

AA solution with 75% neutralization degree was prepared by gently dropping AA in a predetermined amount of aqueous sodium hydroxide solution under cold water bath to avoid polymerization in a beaker. Exact amounts of AM, and MAETAC were dissolved in the above-mentioned AA solution. The weight ratio of AA : AM : MAETAC is 1.86 : 1.00 : 0.31. CMC dosage was 5% of the total three monomers. The weight percentages of the crosslinking agent (NMBA) and initiator (SBS and APS) with respect to the monomers were 0.1 and 3.0%, which were added into the monomers solution and stirred until a homogeneous mixture was obtained. The weight ratio of CMC and monomers to distilled water was 1 : 4, and the volume of the reaction system was 40 mL.

The reaction system was added into the continuous phase, while being agitated at 200 rpm and purged with a stream of nitrogen at room temperature for a 20-min period. The mixture was heated to a desired reaction temperature using a water bath and the reaction was allowed to proceed for 3 h to ensure complete consumption of the monomers. After graft copolymerization, the suspension solution was cooled and then precipitated by 500-mL ethanol (95%) under stirring. The product was filtered and washed several times by ethanol. The product was then dried in a vacuum oven at 60°C for 24 h. The dried copolymers were ground and white powdered SAPs were obtained.

### Characterization

#### Infrared spectra

IR spectra of the superabsorbent samples were recorded with Nicolet 550 FTIR spectrophotometer (KBr disk).

#### Thermogravimetric analysis

TGA of the samples was carried out using a TA Instrument Q500. The temperature range in the experiment is 50–800°C at a heating rate of 20°C/min using nitrogen at a flow rate of 20 mL/min.

### Morphology

The dried samples were examined for morphological details by FEI quanta 200 SEM instrument with an acceleration voltage of 30 kV and magnification of 3000.

### Measurement of property

#### Absorbency in deionized water

The dried sample (0.1 g) was immersed in the excess of deionized water for at least 10 h to reach the swelling equilibrium at room temperature. The swollen gel was filtered on sieve to remove residual water for 5 min, then it was weighed and equilibrium absorbency,  $Q_{eq}$ , was calculated by the following equation:

$$Q_{eq} \text{ (g/g)} = \frac{\text{swollen gel (g)} - \text{dried sample (g)}}{\text{dried sample (g)}}$$

#### Absorbency in saline solutions

The dried sample (0.5 g) was immersed in an excess of NaCl saline solutions with different concentrations, retained there for at least 10 h and then filtered and weighed. The water absorbency in the above saline solutions was obtained.

#### Absorbency in solutions of various pH values

The method was the same as the water absorbency in saline solutions. The pH values of the external solution were adjusted by adding HCl or NaOH in water.

#### Soil burial degradation

Soil burial<sup>14,15</sup> is a traditional and standard method for degradation because of its similarity to actual conditions of waste disposal. Biodegradability of the amphoteric SAPs was studied by weight loss of the polymers over time in soil, which was collected from Zijin mountain forest in Nanjing, China. Samples were weighed (1 g) and then buried in the soil for up to 100 days. The soil was maintained at ~ 20% moisture by weight, and samples were buried at a depth of 15 cm. The buried samples were dug out at certain intervals, washed with deionized water, dried in a vacuum oven at 60 ± 1°C for 24 h before evaluation, and were equilibrated in a desiccator for at least a day. The samples were then weighed to determine the weight loss.

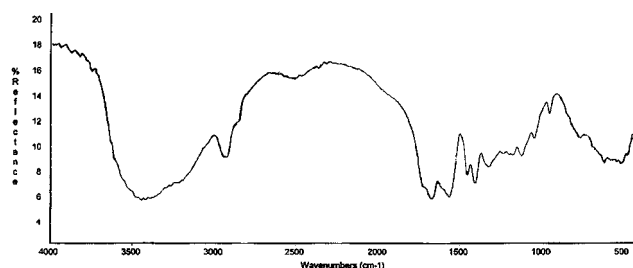


Figure 1 FTIR spectra of amphoteric SAPs.

## RESULT AND DISCUSSION

### IR analysis

IR spectroscopy is a valuable tool of identifying graft copolymerization reaction, which is used to establish the evidence of grafting, and to determine the functional group of the grafted samples.<sup>14</sup>

Grafting AA, AM, and MAETAC onto CMC was established by IR spectroscopy shown in Figure 1. The broad absorption band at  $3443\text{ cm}^{-1}$  was attributed to N—H stretching of the AM unit, which overlapped the O—H stretching band of the CMC portion of the copolymer. The peak at  $1731$  and  $1672\text{ cm}^{-1}$  was due to  $>\text{C}=\text{O}$  stretching vibration in amide moiety of the MAETAC and AM unit. The peaks at  $1562$  and  $1405\text{ cm}^{-1}$  were attributed to the carbonyl stretching of the carboxylic acid and acrylate groups, respectively. In addition, peak at  $1121\text{ cm}^{-1}$ , corresponding to C—O—C stretching vibration of CMC, were also observed. From the above IR data, it was observed that the monomeric units were incorporated into the copolymer chain.

### Thermal analysis

The thermal behavior of amphoteric SAPs modified by CMC was shown in Figure 2. The completely dried powder sample was taken for TGA. Because of

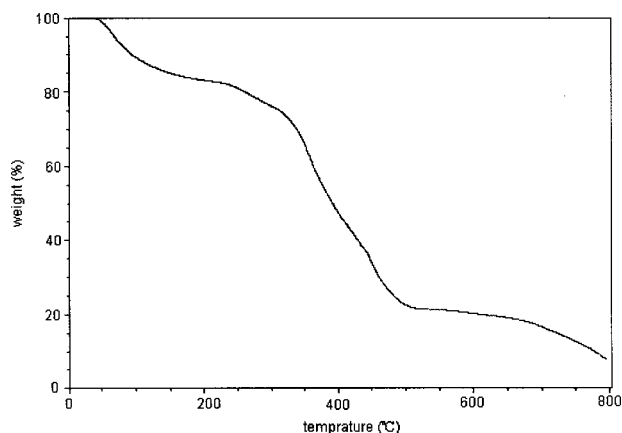


Figure 2 TGA thermogram of amphoteric SAPs.

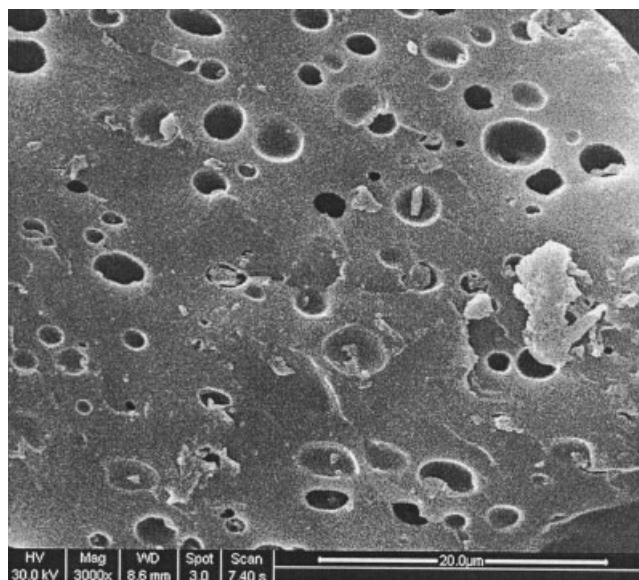


Figure 3 SEM micrograph of amphoteric SAPs.

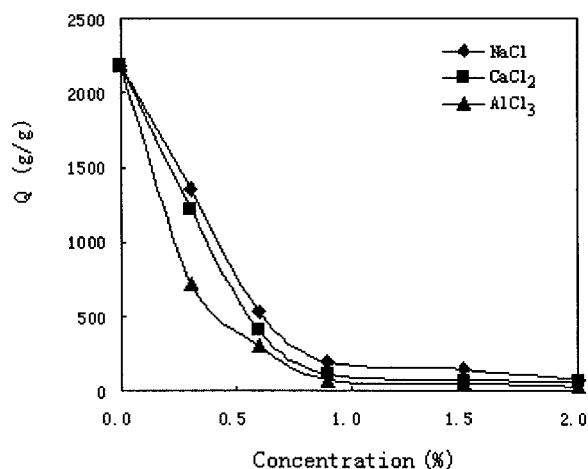
the high absorbency of water, weight loss below  $100^\circ\text{C}$  is due to the loss of the bound water molecules. From the curve, the temperature of decomposition ( $T_D$ ) was found to be  $353^\circ\text{C}$ . A sharp weight loss within the range of  $353\text{--}500^\circ\text{C}$  was suggested to be due to the thermal decomposition of the cross-linked graft polymer chain. The residual weight at  $524^\circ\text{C}$  was 37.18%. The result of thermal analysis indicated that the copolymer sample was thermally stable.

### Morphology

The surface morphologies of the amphoteric SAPs were shown in Figure 3. As shown in these pictures, surfaces of the samples were irregular, and microporous. These observations were in good agreement with high water absorbency of the copolymers.

### Effect of salt solution on water absorbency

The water absorbencies for amphoteric SAPs, as a function of different saline concentration for NaCl(aq), CaCl<sub>2</sub>(aq), and AlCl<sub>3</sub>(aq), were shown in Figure 4. The absorbency of amphoteric SAPs was 2184 g/g. The data in Figure 4 indicated that the absorbency decreased with increasing of the saline concentration. This is suggested to be due to the increase in the concentration of the mobile ions such as Na<sup>+</sup>, Ca<sup>2+</sup>, and Al<sup>3+</sup> outside the gel network in comparison with the osmotically-active ions inside the hydrogel, which leads to a decrease in the osmotic pressure and therefore a reduction in absorbency.<sup>16</sup> From data of these curves, decreased swelling capacity was also observed with an increase

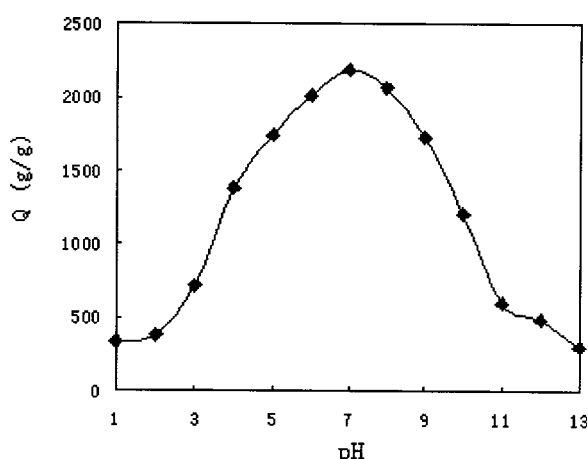


**Figure 4** Absorbency of amphoteric SAPs in different saline solution.

in the charge of the cationic ions. In case of same concentration, the absorbency sequence in different solutions was found to be  $\text{Na}^+ > \text{Ca}^{2+} > \text{Al}^{3+}$ . This could be attributed to the higher complexing ability arising from the complexation of the multivalent cations with anionic groups of grafted copolymers.

#### Absorbency in solutions of various pH values

The pH values of external solutions could affect the swelling capacity of SAPs. The tendency of absorbency in different pHs depended upon the network charge density and also the nature of the ionizable groups attached to the backbone of the polymeric chains for the hydrogel including nonionic, cationic and anionic groups. Swelling behavior of the amphoteric SAPs was investigated in pH values solutions ranged from 1 to 13. The pH values of the external solutions were adjusted by adding HCl or NaOH in



**Figure 5** Effect of pH values on swelling capacity of amphoteric SAPs.

**TABLE I**  
Soil Burial Degradation of Amphoteric SAPs  
Derived from CMC

Time period (days)	Weight loss in soil (%)
20	5.1
40	13.8
60	20.5
80	32.3
100	43.6

deionized water. As shown in Figure 5, the absorbency decreased in acidic and basic pHs. In acidic solutions, decrease in swelling was due to carboxylate groups on the polymeric chain having been reduced to the carboxylic acid group by  $\text{H}^+$ . In addition, the ionization of quaternary ammonium groups on the polymeric chain was inhibited by  $\text{Cl}^-$ . A decreased repulsion of ionic groups lead to a decreased swelling capacity. The decreased absorbency at higher basic pHs was related to "screening effect" of excess cations ( $\text{Na}^+$ ) in the external solutions.

#### Soil burial degradation

The biodegradability of amphoteric SAPs synthesized in this work was measured by soil-burial test. Degradations of samples for different time period were shown in Table I. After 100 days, the weight loss of the sample in soil was 43.6%. As a result, the superabsorbent copolymers prepared in this work proved to have biodegradability together with high swelling capacity.

#### CONCLUSIONS

Novel cellulose-based amphoteric SAPs were prepared by the grafting polymerization of AA, AM, and MAETAC onto CMC. The SAPs were characterized by FTIR and TGA. FTIR studies suggested that the three monomers were graft-copolymerized onto macromolecular chains of CMC. TGA data revealed that the amphoteric SAPs were moderately thermally stable. The maximum absorbency 2184 g/g was obtained in deionized water. The swelling behavior of the grafted copolymers was significantly influenced by the nature of the external solution. Experimental results indicated that swelling capacity exhibited high sensitivity to the pH and ionic concentration of solutions. In addition, the SAPs showed good biodegradability in soil.

#### References

- Samal, R. K.; Sahao, P. K.; Samantaray, H. S. *J Macromol Sci Macromol Chem Phys* 1986, 26, 81.
- Gross, J. R. In *Absorbent Polymer Technology*; Brannon-Peppas, L.; Harland, R. S., Eds.; Elsevier Science: New York, 1990; p 3-22.

3. Weaver, M. O.; Bagley, E. B.; Fanta, G. F.; Doane, W. M. U.S. Pat. 3,981,100 (1976).
4. Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. *J Appl Polym Sci* 1993, 47, 113.
5. Stannett, V. T.; Doane, W. M.; Fanta, G. F. In *Absorbency*; Chatterjee, P. K., Ed.; Elsevier: Amsterdam, 1984.
6. Sakiyama, T.; Chu, C. H.; Fujii, T.; Yano, T. *J Appl Polym Sci* 1993, 50, 2021.
7. Yoshida, M.; Asano, M.; Kumakura, M. *Eur Polym Mater* 1989, 25, 1197.
8. Ericksen, P. H.; Nguyen, H. V.; Oczkowski, B.; Olejnik, T. A. *Eur. Pat.* 40,087 (1981).
9. Buchholz, F. L.; Graham, A. T. *Modern Superabsorbent Polymer Technology*; Wiley-VCH: New York, 1998.
10. Yoshimura, T.; Matsuo, K.; Fujioka, R. *J Appl Polym Sci* 2006, 99, 3251.
11. Deo, H. T.; Gotmare, V. D. *J Appl Polym Sci* 1999, 72, 887.
12. Wang, D.; Shang, S. B.; Song, Z. Q. *Chem Ind Forest Prod* 2006, 26, 33.
13. Sahoo, P. K.; Sahu, G. C.; Rana, P. K.; Das, A. *Adv Polym Technol* 2005, 24, 208.
14. Sahoo, P. K.; Swain, S. K.; Debsarkar, N. L. *J Appl Polym Sci* 2002, 83, 1963.
15. Chandra, R.; Rustogi, R. *Polym Degrad Stab* 1997, 56, 185.
16. Pourjavadi, A.; Zohuriaan-Mehr, M. J.; Ghasempoori, S. N. *J Appl Polym Sci* 2007, 103, 877.