Using DSC Studying the Relationship between Water Absorbency of Superabsorbent Polymer and Its Structure

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Abstract. A series of superabsorbent ter-polymers (SAPs) with acrylic acid, acrylamide and 2-acrylamido-2-methylpropanesulfonic acid, crosslinked by polyethylene glycol diacrylate-600 were prepared. The SAPs were characterized by Fourier transform infrared spectra (FTIR) and the water absorbency was measured by the Tea-bag method. Differential scanning calorimetry (DSC) was used to determine the bound water content of the different samples with various water contents. It was found that the more hydrophilic groups the ter-polymer has, the larger the bound water content is, the stronger the ability of interacting with water is, and the larger the water absorbency the ter-polymer has.

1. Introduction
Superabsorbent polymer (SAP) is a kind of hydrophilic material which can absorb plenty of water [1, 2]. SAPs are usually slightly cross-linked poly(acrylic acid) based ter-polymers, and most of the studies have been devoted to the improvement of water absorbency or salt-resistance [3-7]. Only a few investigations on the relationship between the water absorbency mechanism of SAP and the molecular structure have been done.

The ability of interacting with water chiefly determined by the monomer functional groups is one of the most important factors that influence the water absorbency. According to the modes of interaction, the water existing in hydrogels can be divided into the following categories: free water, freezeable bound water and unfreezable bound water [8-10]. Differential scanning calorimetry (DSC) is an effective way to study the state of water in some hydrophilic materials [11-14].

In this study different kinds of and SAPs were prepared, and the state of water in these SAPs were investigated by DSC. Based on the content of bound water and bulk total water obtained from the DSC measurements, the abilities of interacting with water for various kinds of ter-polymers with different monomer ratios were investigated. Comparing the water absorbency of SAP with its corresponding abilities of interacting with water represented by the DSC measurements, the relationships of the mechanisms of water absorbency (water retention) and the molecular structures of the SAPs with different monomer ratios were obtained.

2. Experimental
The acrylic acid (AA) was supplied by Sigma (USA), with a purity of >99.5wt%, and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was purchased from Chang-tian Inc. (China) with a purity of >99.0wt%. The other reagents were supplied by Aladdin (USA). Acryl amide (AM) and AMPS were dissolved in 50 mL of distilled water in a 100-mL beaker. Before polymerization, N,N'-Methylenebisacrylamide is dissolved and then was added into the 100-mL beaker and the mixture poured into 250-mL flask with three necks. The reaction solution was heated to 60°C and the initiators...
added; at the end of the reaction, the flask needed to be heated to 70 °C for 4 h. The synthesis of the homopolymers was similar to the preparation of the ter-polymers, using the same initiator and crosslinking agent concentration as that of the ter-polymers.

3. Results and Discussion

3.1. Identification of SAPs

The FTIR spectra analyses of the AA-AM-AMPS ter-polymer are shown in figure 1. It showed the variation of the functional groups in the molecules, such as the carbonyl groups connecting with –OH and –NH2 with peak at about 1715 cm\(^{-1}\) and 1646 cm\(^{-1}\), respectively, and the –OH groups’ stretching vibrations at about 3443 cm\(^{-1}\). The vibrations of -C-N bonds appeared at 1210 cm\(^{-1}\). Symmetric stretching vibrations and asymmetric stretching vibrations of the -S=O bonds at 1043 and 1187 cm\(^{-1}\) and the absorption peak of 626 cm\(^{-1}\) was the sulfonate groups in the polymer matrix. The results showed that the AA-AM-AMPS ter-polymer was synthesized successfully.

3.2. DSC Analysis of Different Homopolymers Swollen in Distilled Water

Figures 2-4 show the DSC curves of the three homopolymer samples: PAA, PAM and PAMPS. The swelling ratios of the samples in figures 2-4 were 50%, 75% and 91%, respectively. There was no endothermal peak in the DSC curve when the water content was 50%, which means that there was no free water in the hydrogel, so the curves showed no differences. When water content reached 75%, endothermal peaks at 0°C appeared in the DSC curves. By calculation, the peak areas for the different homopolymers differed from each other; the endothermal peak of PAM homopolymer had the largest area, while the PAMPS homopolymer’s endothermal peak was the smallest. According to the results, the magnitude of free water content of the three homopolymer samples were in the order PAMPS<PAA<PAM, while the bound water content showed the reverse order. Considering the polymerization conditions and parameters, the crosslinking agent and reaction temperature were the same; the only difference was the monomer ratio. So the difference in the free water content must be due to the differences of the monomers. Generally speaking, the stronger the ability of interacting with water the monomer has, the more water its homopolymer can absorb, which means the more water that can attach onto the polymer framework. Considering the bound water content, the sequence of ability of interacting with water in the corresponding homopolymer was PAMPS>PAA>PAM. The ability of absorbing water of the structural units are primarily related to the functional groups on it, so the ability of interacting with water of the three functional groups is -SO\(_3\)H>-COOH>-NH\(_2\). From the structures of the three monomers, the reason can be explained as follows: AA has –COOH in it and is an excellent hydrophilic monomer, but the –COO– can easily be complexed by cations. AM is a nonionic molecule whose functional group can hardly be influenced by external cations, but the hydrophilicity of AM is not very good. AMPS is an extremely salt-resistant monomer: the two Π-bounds and electronegative oxygen atoms on AMPS share one negative charge and make it stable, the charge density is large and the hydrophilicity is very strong which make the AMPS insensitive to external cations, and the –NH– was also shielded by the large side group.

3.3. DSC Analysis of the SAP Samples Swollen in Saline Water

Figures 5 and 6 show the DSC curves of the three homopolymers swollen in NaCl solution (0.9 wt%). In figures 2-4, the water contents were 50%, 75% and 91%, respectively. Because the samples used in the DSC test was partial swollen hydrogels, the hydrogel can be regarded as containing NaCl solution (0.9 wt%) in the low water content. So it can be used to measure the bound water and free water content of the hydrogels swollen by NaCl solution (0.9 wt%). The results also showed there were no endothermal peaks in the DSC curves when the water content was 50%, which means that there was no free water in the hydrogel, so all of the curves were the same, with no peak. However, when water content was 75% and 91% the DSC curves had endothermal peaks at 0 °C. Compared with the hydrogels swollen by distilled water, the sequence of free water content was different:
PAMPS>PAM>PAA. The sequence of the bound water content in the NaCl solution (0.9 wt%) was PAA>PAM>PAMPS. It is obvious that PAM’s abilities of interacting with water was better than that of PAA in the NaCl solution (0.9 wt%), and the PAMPS also had the strongest abilities to interact with the water. From this result, it can be inferred that the salt resistance in NaCl solution (0.9 wt%) was: PAMPS>PAM>PAA.

![Figure 1. FTIR spectrum of AA-AM-AMPS ter-polymer.](image1)

![Figure 2. Heat flow-temperature curves of homopolymer containing distilled water with water content of 50%.](image2)

![Figure 3. Heat flow-temperature curves of homopolymer containing distilled water with water content of 75%.](image3)

![Figure 4. Heat flow-temperature curves of homopolymer containing distilled water with water content of 91%.](image4)

Figures 7 and 8 show the DSC curves of samples swollen in NaCl solution (0.9 wt%) with water contents of 75% and 91%, respectively. The area of the endothermal peaks at 0 ℃ increased with the increase of AA content and decrease of AM and AMPS content, which reflected the change trend of the free water content. Meanwhile, the bound water content of the samples rose with the increase of AM and AMPS content and decrease of AA content, so the change trend of bound water content of the ter-polymer samples swollen in 0.9% NaCl solution was in accord with the homopolymer samples.
Figure 5. Heat flow-temperature curves of homopolymer containing NaCl solution (0.9 wt%) with water content of 75%.

Figure 6. Heat flow-temperature curves of homopolymer containing NaCl solution (0.9 wt%) with water content of 91%.

Figure 7. Heat flow-temperature curves of different SAPs containing NaCl solution (0.9 wt%) with water content of 75%.

Figure 8. Heat flow-temperature curves of different SAPs containing NaCl solution (0.9 wt%) with water content of 91%.

4. Conclusions
A new superabsorbent polymer was successfully synthetized by aqueous solution polymerization using acrylic acid, acrylamide and 2-acrylamido-2-methylpropanesulfonic acid and polyethylene glycol diacrylate-600 (PEGDA-600) as crosslinking agent. The bound water content of the SAPs depended on the composition of the hydrogel. The total water absorbency of SAPs was determined by the abilities of interacting with water, which can be reflected by bound water content from the DSC results. The abilities of interacting with water in distilled water and NaCl solution (0.9 wt%) were different. For the distilled water, the sequence was AMPS>AA>AM, and for the 0.9% NaCl solution it was AMPS>AM>AA. For the ter-polymers, the distilled water absorbency increased with increasing amount of AA and AMPS and decreased with the reduction of the AM; however, for the 0.9% NaCl solution the absorbency increased with increasing amount of AM and AMPs and decreased with the reduction of the AA. The water absorbency and bound water content reached the maximum value when the monomer ratio was 1:1:3 both in distilled water and NaCl solution (0.9 wt%), while the change trend of water absorbency and bound water content was different.

References
[1] Buchholz F L 1996 Superabsorbent Polymers: An Idea Whose Time Has Come J. Chem. Educ. 73 512
[2] Zou X X 2002 Super Absorbents (Beijing: Chemical Industry Press) p 2
[3] Guo M Y and Liu M Z 2005 Preparation and Properties of a Slow-Release
Membrane-Encapsulated Urea Fertilizer with Superabsorbent and Moisture Preservation \textit{Ind. Eng. Chem. Res.} \textbf{44} 4206

[4] Raju M P and Raju K M 2010 Synthesis and Water Absorbency of Superabsorbent Ter-polymers. \textit{Int. J. Polym. Anal. Ch.} \textbf{8} 245

[5] Gosavi U R and Deopurkar R L 1999 Microbial Degradation of Superabsorbent HSPAN Gel by an Indigenously Isolated Bacterial Culture \textit{Macromolecules} \textbf{32} 4264

[6] Sahoo P K and Mohapatra R 2005 Characterization, Biodegradation, and Water Absorbency of Chemically Modified Tossa Variety Jute Fiber via Pulping and Grafting with Acrylamide. \textit{Int. J. Polym. Anal. Ch.} \textbf{10} 153

[7] Yilmaz S S 2007 Synthesis of a novel crosslinked superabsorbent ter-polymer with diazacyclooctadecane crown ether and its sorption capability \textit{Eur. Polym. J.} \textbf{43} 1923

[8] Hatakeyema T, Yamauchi A and Hatakeyema H 1984 Studies on bound water in poly(vinyl alcohol). Hydrogel by DSC and FT-NMR \textit{Eur. Polym. J.} \textbf{20} 61

[9] Li B H, Ding D T and Wang Y N 1999 NMR characterization of absorbed water in equilibrium swollen hydrogel P(AM-NaA) \textit{J. Appl. Polym. Sci.} \textbf{72} 1203

[10] Capitani D, Mensitieri G and Porro F 2003 NMR and calorimetric investigation of water in a superabsorbing crosslinked network based on cellulose derivatives \textit{Polymer} \textbf{44} 6589

[11] Lee D J and Lee S F 1995 Measurement of bound water content in sludge: The use of differential scanning calorimetry (DSC) \textit{J. Chem. Technol. Biot.} \textbf{62} 359

[12] Liu Y and Huglin M B 1995 Observations by DSC on bound water structure in some physically crosslinked hydrogels \textit{Polym. Int.} \textbf{37} 63

[13] Wang T and Gunasekaran S 2006 State of water in chitosan-PVA hydrogel \textit{J. Appl. Polym. Sci.} \textbf{101} 3227

[14] Guan Y L, Shao L and Liu J 1996 PH effect on correlation between water state and swelling kinetics of the crosslinked chitosan/polyether semi-IPN hydrogel \textit{J. Appl. Polym. Sci.} \textbf{62} 1253