Synthesis, Properties, and Humidity Resistance Enhancement of Biodegradable Cellulose-Containing Superabsorbent Polymer

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To improve the humidity resistance and water absorption capacity of the superabsorbent polymer (SAP), a biodegradable cellulose-containing polymer was successfully assembled through inverse suspension polymerization, using cellulose, acrylic acid, and acrylamide as monomers, Span-80 as dispersant, and potassium persulfate as initiator. The impact of conditions such as reaction temperature, ratio of oil to water, degree of neutralization, amount of cellulose, and cross-linking agents on the properties of the polymer were evaluated. The results showed that the as-prepared superabsorbent polymer exhibited the best water (859 g/g) and salt water (72.48 g/g) absorption rate, when the reaction temperature was 70°C, monomer ratio was 1:10, neutralization degree was 75%, and oil-water ratio was 3:1. Moreover, the humidity resistance of the polymer could be enhanced significantly by adding different cross-linking reagents such as epoxy chloropropane or diethylene glycol.

1. Introduction

Superabsorbent polymer with strong hydrophilic groups such as carboxyl and hydroxy can absorb water hundreds of times more than its own weight in a short time and exhibit good water retention even at high temperature and pressure [1–4]. The superabsorbent polymer is superior to other absorbing materials [5, 6]. It has been widely used in many fields such as diapers, sanitary napkins, oilfield chemistry, and water soluble coatings [7–10].


The superabsorbent polymer based on cellulose has the advantages of high gel strength, low soluble component content, strong water retention ability, being biodegradable, and high enzymolysis resistance [14]. Essawy et al. [15] obtained the acrylic acid and chitosan-cellulose hybrid superabsorbent hydrogels via graft polymerization. Fekete et al. [16] prepared superabsorbent hydrogels from aqueous solutions of four cellulose derivatives; the swelling properties of CMC gels with lower water uptake showed lower sensitivity to the ionic strength of the solvent. Montesano et al. [17] evaluated a novel class of cellulose-based superabsorbent hydrogels for agricultural use; the soil moisture at field capacity increased with the highest hydrogel percentage up to 400% compared to the nonamended soil. The as-prepared cellulose-based superabsorbent hydrogels showed to be suitable for potential use in agriculture. Mohammadi-Khoo et al. [18] synthesized a cellulose-based biodegradable hydrogel, which exhibited excellent swelling behavior in distilled water, tap water, and 0.9% NaCl solution; it can be employed as a suitable moisture-holding additive in the soil for agricultural purposes.

However, it was easy for the reported cellulose-based superabsorbent polymers to absorb moisture, which will
seriously affect their translation, storage, and usage [19]. Thus, methods to improve the moisture-proof of resins are highly desirable. In this paper, the superabsorbent polymer with high water absorbency and gel strength was prepared under optimum conditions. The ratio of oil to water, the degree of neutralization, the amount of cellulose, and cross-linking agents on the absorption of water were investigated. Furthermore, the moisture-proof ability of the resins after modification by different kinds of cross-linking agents was also discussed carefully.

2. Experimental

2.1. Materials. Carboxymethyl cellulose (CMC, chemically pure, Tianjin Fucheng Chemical Reagent Factory), cyclohexane (analytical grade, Tianjin Fucheng Chemical Reagent Factory), potassium persulfate (analytical grade, Shanghai Kaibo Chemical Reagent Factory), N, N’-methylenebisacrylamide (analytical grade, Shanghai Kaibo Chemical Reagent Factory), sodium hydroxide (analytical grade, Shanghai Kaibo Chemical Reagent Factory), Span-80 (analytical grade, Shanghai Kaibo Chemical Reagent Factory), anhydrous ethanol (analytical grade, Shanghai Kaibo Chemical Reagent Factory), diethylene glycol (analytical grade, Tianjin Fucheng Chemical Reagent Factory), epoxy chloropropene (analytical grade, Tianjin Fucheng Chemical Reagent Factory), ethylene glycol (analytical grade, Tianjin Fucheng Chemical Reagent Factory), polyethylene glycol (analytical grade, Tianjin Fucheng Chemical Reagent Factory), ethylenediamine (analytical grade, Tianjin Fucheng Chemical Reagent Factory), acrylamide (analytical grade, Tianjin Fucheng Chemical Reagent Factory), and acrylic acid (analytical grade, Tianjin Fucheng Chemical Reagent Factory) were distilled under reduced pressure before use.

2.2. Synthesis of Superabsorbent Polymer. A certain amount of cellulose, cyclohexane (100 g), acrylic acid (17.3 g), and acrylamide (2.98 g) was added to a four-neck flask equipped with gas line, mechanical stirrer, condenser, and thermometer and stirred at 45°C for 0.5 h under nitrogen. After the acrylic acid solution was neutralized by sodium hydroxide aqueous solution, the initiating agent potassium persulfate (KPS, 0.08 g) and the cross-linking agent N, N’-methylenebisacrylamide (MBA, 0.08 g) were added to the mixture. Then, the system temperature was raised to 75°C, and a polymeric gel was formed. Finally, the product was washed several times with ethanol and dried in vacuum at 100°C for 10 h. The white powdered superabsorbent polymer was obtained by smashing.

2.3. Infrared Spectrum. Fourier Transform Infrared Spectroscopy (IR) was measured with KBr direct compression, scanning for 5 times at the range of 4000–400 cm⁻¹.

2.4. Measurement of Water and Salt Water Absorbency. The dried powdered resin (0.1 g) was immersed in 500 mL distilled water and 0.9% physiological saline solution, respectively. The water-swollen gel was filtered by a sieve after soaking overnight and then weighted. The water-holding capacity was calculated by the following equation:

\[ Q = \frac{M_2 - M_1}{M_1} \]

where \( M_2 \) is the weight of water-swollen gel, \( M_1 \) is the weight of dried sample, and \( Q \) is the water absorbing capacity.

2.5. Experiment for the Moisture Resistance. A certain amount of resin was divided into several groups at random and tiled on the surface of watch glass at 25°C with humidity of 70%. The hygroscopic rate was measured and the curve was made at different times until the absorption reached saturation. Moreover, the results were compared with those of the untreated resin at the same conditions.

3. Results and Discussion

3.1. Infrared Spectrum Analysis. Figure 1 shows the IR spectra of CMC and SAP. The peak at 3448.44 cm⁻¹ is the stretching vibration peak of –OH group. The peaks at 2923.30 cm⁻¹ and 1618.33 cm⁻¹ are attributed to =C–O symmetric stretching vibration peak and C=O stretching vibration peak, respectively. Compared with the IR spectrum of CMC (Figure 1(a)), the peaks at 1406.74 cm⁻¹ and 1458.09 cm⁻¹ (Figure 1(b)) are due to the O=C=O and –CH₂– in-plane bending vibration, which are the characteristic adsorption bands of sodium polycrylate [15]. The peak at 1166.87 cm⁻¹ is the =C–O stretching vibration of =C–O–C and the peak at 1068.69 cm⁻¹ is –C–O stretching vibration of C–O–C, which indicated that CMC was successfully grafted in SAP.

3.2. Effect of the Amount of Cellulose on the Absorption Properties of SAP. Figures 2 and 3 show the effect of the amount of cellulose on water and salt water absorption. When the monomer ratio was less than 1:10, the water and
salt water absorption rate significantly increased with the increasing ratio of the monomer. The maximum absorption rate for water and salt water reached 706.14 g/g and 72.48 g/g, respectively. However, when the monomer ratio exceeded 1:10, the absorption rate of SAP for water and salt water decreased with the ratio increase. The results showed that the optimized monomer ratio for the absorption of water and salt water was 1:10. The possible reason is that, with the monomer ratio increase, the viscosity of the reaction system increased. It weakened the probability of the active collision between monomers and shortened polyacrylic acid acrylamide graft chains, which is adverse to the formation of polymer network structure [20–24]. On the other hand, the amount of cellulose is important for the graft polymerization and too little amount of cellulose has an adverse influence on the graft polymerization.

3.3. The Effect of Neutralization Degree on the Absorption Properties of SAP. As shown in Figures 4 and 5, the optimum neutralization degree is 75%. The possible reason is as follows: the acidity of the solution increases with the decreasing of neutralization degree, which can accelerate the polymerization. With the increasing of neutralization process, the ionization of the carboxyl groups on the molecular chain increased [25]. Thus, the repulsive force of carboxyl groups is enhanced, which makes the molecular chain become more straight and the network structure become larger. On the other hand, the enhancement of affinity and osmotic pressure makes the water and salt water absorption rate increase. Furthermore, the ion concentration becomes higher and the hydrogen bond between the water molecule and ion becomes stronger under the neutralization degree larger than 75%, which limits the freedom of the molecular diffusion and makes the microporous polymer play insufficient role in the water and salt water storage [20].

3.4. Effect of Oil-Water Ratio on the Absorption Properties of SAP. As shown in Figures 6 and 7, with the increase of the oil-water proportion, the water absorption rate of the resin took on the trend with increasing firstly and decreasing
The water absorption rate

The oil-water ratio

2:1 2.5:1 3:1 3.5:1 4:1

The water absorption rate

Temperature (°C)

Figure 6: Effect of oil-water ratio on the water absorption of superabsorbent polymer.

Figure 7: Effect of oil-water ratio on the salt water absorption of superabsorbent polymer.

Figure 8: Effect of the temperature on the water absorption of superabsorbent polymer.

Figure 9: Effect of the temperature on the salt water absorption of superabsorbent polymer.

The optimum proportion of oil-water ratio was 3:1. When the ratio was higher than 3:1, the water and salt water absorption decreased obviously. This is because the acrylic acid superabsorbent resin contains a large number of hydrophilic groups, which make the SAP fully swelling in water. Actually, the ratio of oil to water has larger influence on the elasticity of hydrophilic groups (such as carboxyl and amino groups), and then it controls the swelling degree of copolymers. When the oil-water ratio is relatively high, the water in the aqueous phase can be dispersed into small droplets, and the water content in the monomer drops is low, which induces the polymer difficult to be crossed. Accordingly, the water absorption capacity decreased. When the ratio of oil to water is low, the water content in the monomer drops increased, the resin macromolecular chain could be fully extended, the cross-linking degree increased, and the water absorption rate decreased too [21].

3.5. Effect of Reaction Temperature on Absorption Properties of SAP. Figures 8 and 9 show the effect of reaction temperature on the absorption of water and salt water. Absolutely, the optimum reaction temperature is 70°C. Since the low reaction temperature reduces the activity of radical, slows down the decomposition rate of initiator agent, decreases the concentration of radical, and impedes the delivery of polymerization reaction chain, the prepared SAP with low reaction temperature shows relatively low molecular weight and water absorbency. As the reaction temperature increased, the concentration of radical increased, the conversion ratio of monomer raised, and the ability for the absorption of water and salt water increased. However, the heat is difficult to dissipate under the higher reaction temperature, explosive polymerization easily occurred, and gel disks would form.

3.6. Effect of Different Kinds of Cross-Linking Agent on the Properties of SAP. Table 1 shows the properties of SAP modified by different kinds of cross-linking agents. The results showed that the strength and dispersity of the as-prepared SAP can be improved with the addition of cross-linking reagent; however, the water absorption capacity decreased.
Table 1: The absorption of SAP after modification by different surface cross-linking reagents.

<table>
<thead>
<tr>
<th>Types of cross-linking agents</th>
<th>Water absorption rate (g/g)</th>
<th>Moisture absorption (humidity resistance)</th>
<th>Gel strength</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>903</td>
<td>Easy</td>
<td>Low and viscous</td>
<td>Poor</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>861</td>
<td>Easy</td>
<td>High, viscous</td>
<td>Better</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>859</td>
<td>Poor</td>
<td>High, relatively dry</td>
<td>Better</td>
</tr>
<tr>
<td>Epoxy chloropropane (ECH)</td>
<td>832</td>
<td>Poor</td>
<td>High, dry</td>
<td>Good</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>878</td>
<td>Easy</td>
<td>High, viscous</td>
<td>Better</td>
</tr>
<tr>
<td>Polyethylene glycol</td>
<td>856</td>
<td>Easy</td>
<td>High, viscous</td>
<td>Poor</td>
</tr>
</tbody>
</table>

Table 2: Effect of epoxy chloropropane dosage on the water absorption.

<table>
<thead>
<tr>
<th>Epoxy chloropropane dosage</th>
<th>Water absorption (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>902</td>
</tr>
<tr>
<td>5%</td>
<td>883</td>
</tr>
<tr>
<td>10%</td>
<td>859</td>
</tr>
<tr>
<td>15%</td>
<td>835</td>
</tr>
<tr>
<td>20%</td>
<td>794</td>
</tr>
<tr>
<td>25%</td>
<td>782</td>
</tr>
</tbody>
</table>

3.6.1. Effect of Epoxy Chloropropene (ECH) Dosages on the Properties of SAP. Figure 10 shows the spectrum of the SAP before and after ECH modification. The peak at 610–630 cm⁻¹ is the stretching vibration peak of C–Cl, which indicated that epoxy chloropropene was successfully grafted in SAP.

Effect of Epoxy Chloropropene Dosages on the Water Absorption Properties of SAP. Table 2 shows the results of the water absorption for the different epoxy chloropropene dosages. The water absorption was tested at different mass ratios of ECH and C₂H₅OH (ECH/C₂H₅OH = 5%, 10%, 15%, 20%, 25%), and water absorption of the resin significantly decreased with an increasing amount of epoxy chloropropene. The possible reasons are as follows: With the increasing of epoxy chloropropene dosage, the cross-linking sites, strength, and density of the SAP increased, while the molecular weight between net structure site and liquid capacity of SAP decreased.

Effect of Epoxy Chloropropene Dosages on the Moisture Resistance of SAP. Figure 11 shows the hydroscopicity of SAP with different dosages of epoxy chloropropene. To improve the moisture resistance of SAP, the surface particles of the resin were treated by thermal cross-linking to produce a high cross-linking degree coat. The SAP was modified by the mixture of 2 mL distilled water, 5 mL ethanol, and different amount of epoxy chloropropene. The results showed that, with the increasing amount of epoxy chloropropene, the moisture resistance was improved obviously. But when the amount was more than 20%, the moisture resistance was no longer significantly increased.

Effect of Distilled Water Quantity on the Moisture Resistance of SAP. Absolute ethanol was used as hydrophilic solution in the process of thermal cross-linking of the resin. It was found that the effect of the absolute ethanol on the moisture resistance of SAP was not very good, when it was used as solvent. The
cross-linking agent only reacted with a spot of free hydroxyl groups on the surface of the resin and remaining cross-linking agents vaporized on heating. So the cross-linking effect was not stable and the moisture resistance was poor. However, adding a small amount of distilled water, cross-linking agent would permeate into the resin in the help of distilled water; the thickness of surface cross-linking and moisture resistance were increased after heating treatment. Distilled water at different mass ratios (\(\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 20\%, 40\%, 60\%, 80\%\)) was added in the mixture of 15% epoxy chloropropane and absolute ethanol, and the moisture resistance was tested. When the mass ratio of \(\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}\) reached 40%, the SAP exhibited the best moisture resistance. If the amount of distilled water kept increasing, the resin would swell seriously, adhesion among the particles occurred, and the moisture resistance reduced. The high cross-linking density coat, which formed on the particle surface of the resin by epoxy chloropropane treatment, increased the strength and dispersity of the SAP. Combined with the dry surface of resin particles, the moisture resistance of resin was improved to certain extent. In conclusion, when the mass ratio of \(\text{ECH/C}_2\text{H}_5\text{OH}\) reached 15% and \(\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}\) reached 40%, the properties of the SAP were the best (Figure 12).

3.6.2. Effect of Diethylene Glycol (DEG) Dosages on the Properties of SAP. Figure 13 shows the spectrum of the SAP before and after DEG modification. The peak at 1114–1120 cm\(^{-1}\) is stretching vibration peak of the ether groups, which indicated that diethylene glycol was successfully grafted in SAP.

**Effect of Diethylene Glycol Dosages on the Water Absorption Properties of SAP.** Table 3 shows the results of the water absorption for the different diethylene glycol dosages. The water absorption was tested at different mass ratios of \(\text{ECH}\) and \(\text{C}_2\text{H}_5\text{OH}\) (\(\text{ECH/C}_2\text{H}_5\text{OH} = 0\%\), 1\%, 3\%, 7\%, 10\%). Obviously, the amount of diethylene glycol dosage had a great effect on the water absorption. The results indicated that the particles in the resin bonded together performed with poor dispersivity when the mass ratio of \(\text{ECH/C}_2\text{H}_5\text{OH}\) exceeded 10\% (Figure 14).

**Table 3: Effect of diethylene glycol dosages on the water absorption.**

<table>
<thead>
<tr>
<th>Diethylene glycol dosage</th>
<th>0%</th>
<th>1%</th>
<th>3%</th>
<th>5%</th>
<th>7%</th>
<th>10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water absorption (g/g)</td>
<td>902</td>
<td>894</td>
<td>871</td>
<td>856</td>
<td>833</td>
<td>782</td>
</tr>
</tbody>
</table>

**Figure 12:** Effect of distilled water quantity on the moisture performance of SAP.

**Figure 13:** The IR comparison of the SAP before and after diethylene glycol modification (a: the IR of the SAP before DEG modification; b: the IR of the SAP modified by DEG).

**Figure 14:** The moisture absorption rate of SAP with different dosage of diglycol modification.
Table 4: The optimum reaction conditions.

<table>
<thead>
<tr>
<th>The cellulose monomer ratio</th>
<th>Neutralization degree</th>
<th>Oil-water ratio</th>
<th>Reaction temperature (°C)</th>
<th>The ratio of ECH/C_2H_5OH</th>
<th>The ratio of DEG/C_2H_5OH</th>
<th>Water absorption rate (g/g)</th>
<th>Salt water absorption rate (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10</td>
<td>75%</td>
<td>3:1</td>
<td>70</td>
<td>15%</td>
<td>5%</td>
<td>859</td>
<td>72.48</td>
</tr>
</tbody>
</table>

3.7. The Optimum Reaction Conditions. The optimum reaction conditions are as shown in Table 4.

4. Conclusions

In this study, the superabsorbent polymer has been synthesized through inverse suspension polymerization. The absorption experiments for water and salt water showed that the operating conditions such as monomer dosages, neutralization degree, oil-water ratio, temperature, and the cross-linking agent had great effects on the water absorption. The optimum reaction conditions were as follows: the cellulose monomer ratio: 1:10, neutralization degree: 75%, oil-water ratio: 3:1, and reaction temperature: 70 °C. The water and salt water absorption rate can reach as high as 859 g/g and 72.48 g/g, respectively. Moreover, the moisture resistance of the resin treated by ECH and DEG was improved significantly. The moisture resistance showed the best when the addition of ECH was 15%, and it increased with the increasing amount of DEG, but when the dosage of DEG exceeded 5%, the particles among the resin adhered seriously.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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