NOTES

Synthesis of Anti-Salt Absorbent Resins and Studies of Reaction Mechanism

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INTRODUCTION

Superabsorbent resins were first synthesized by the grafting reaction of starch and acrylonitrile by C. R. Rusell in America in 1961.[1] Since then, the syntheses of and studies about superabsorbent resins have received considerable attention, especially starch and acrylic resins. We manufactured resins with sodium alginate and acrylic acid (AA) under the initiator $(NH_4)_2Ce(NO_3)_6$, whose maximum absorption to 0.9% NaCl solution is 150 g/g and to running water is 250 g/g.[2] Also, we produced absorbent resins with polysaccharide compounds extracted from kelp, one kind of seaweed, whose absorption ratio is 70–120 and 650–1075 g/g in 0.9% NaCl solution and distilled water, respectively.[3] This article is mainly about the development of the reaction conditions and the studies of the reaction mechanism. The experiments proved that the developed reaction could be controlled and repeated more easily.

EXPERIMENTAL

Polymerization of AA (Sodium) (PAA)

Acrylic acid (100 g), NaOH (41.7 g), and H_2O (170 g) were poured into a vessel and N_2 was passed through the vessel for 5–10 min to initiate the reaction at 40°C with an initiator (0.2 g $K_2S_2O_8$ + $NaHSO_3$). After reacting for 3–5 h in a temperature range of 40–80°C, a shallow pink PAA solution, which was very sticky and transparent, was received.

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Preparation of Anti-Salt Absorbent Resins

We mixed the PAA prepared above with an NaAgl solution until homogeneous in ratios of 1:1, 2:1, 3:1, 4:1, 5:1, and 10:1, putting the right amount of the epichlorohydrin crosslinking agent into every mixture, and then stored them at 120 ± 1°C. The anti-salt absorbent resins, whose absorption to 0.9% NaCl solution is from 50 to 150 g/g, were produced.

RESULTS AND DISCUSSION

Relations between Characteristics of Resin and Concentration of Crosslinking Agent

The effect of the crosslinking agent concentration on the absorption ability to the 0.9% NaCl solution was studied (Fig. 1). It is clear from the figure that with an increase of the crosslinking agent concentration from 0.6×10^{-4} to 6×10^{-4} (w/w), the absorption ratio of the resin decreases rapidly. However, if the concentration of crosslinking agent is lower than 0.6×10^{-4} (w/w), the resin dissolves in water. That is to say, epichlorohydrin can react with PAA and NaAgl as a crosslinking agent and produce a resin with a network structure which can absorb water or 0.9% NaCl solution. But the PAA and NaAgl have linear molecular structures. However, the crosslinking density depends on the amount of epichlorohydrin, and the higher the crosslinking density is, the lower the absorption ability to water or 0.9% NaCl solution the resin has.

Effect of PAA and NaAgl Amount on Absorption Ability of Resin

The effect of the PAA and NaAgl amount on the absorption ability to the 0.9% NaCl solution was investi-

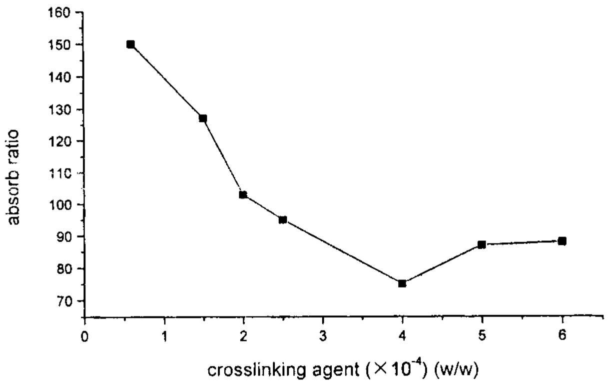


Figure 1 The variation of the absorbing ratio with the concentration of the crosslinking agent.

gated (Table I). In the investigation the ratio of PAA and NaAgl was varied from 1:1 to 10:1, and the absorption ability to the 0.9% NaCl solution was changed from 87 to 150 g/g. But we found no regularity in these experiments.

IR Spectra

The IR spectra of the resin and the mixture of NaAgl and PAA without crosslinking agent were recorded in the form of potassium bromide pellets and are shown in Figure 2. It is observed that both spectra show similar absorption bands. However, the spectra of the resin shows an additional peak at 1740 cm^{-1} and a stronger absorption at 1000 cm^{-1}, which are the characteristics of an ester. We proved that the crosslinking reaction introduced an additional chemical group into the resin.

Table I Absorption of Resin to 0.9% NaCl Solution with Various Ratios of PAA to NaAgl

PAA:NaAgl	1:1	2:1	3:1	4:1	5:1	8:1	10:1
Absorption to 0.9% NaCl aq.	87	98	115	133	105	115	150

DTA Curves

The thermal behaviors of the resin and relative reactants were examined through DTA curves within a temperature range of 20–560°C and with a heating rate of 10°C/min, as shown in Figure 3. In the mixture without crosslinking reagent, the decomposition tem-

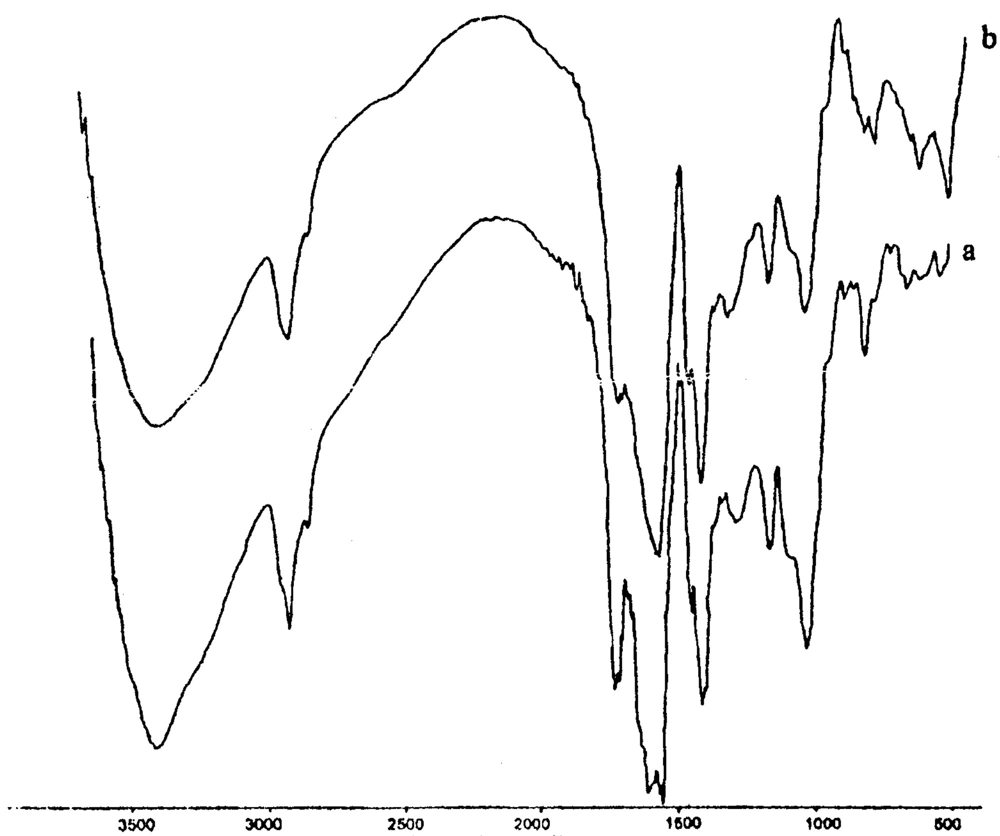


Figure 2 The IR spectra of (a) the resin and (b) the mixture of NaAgl and PAA.

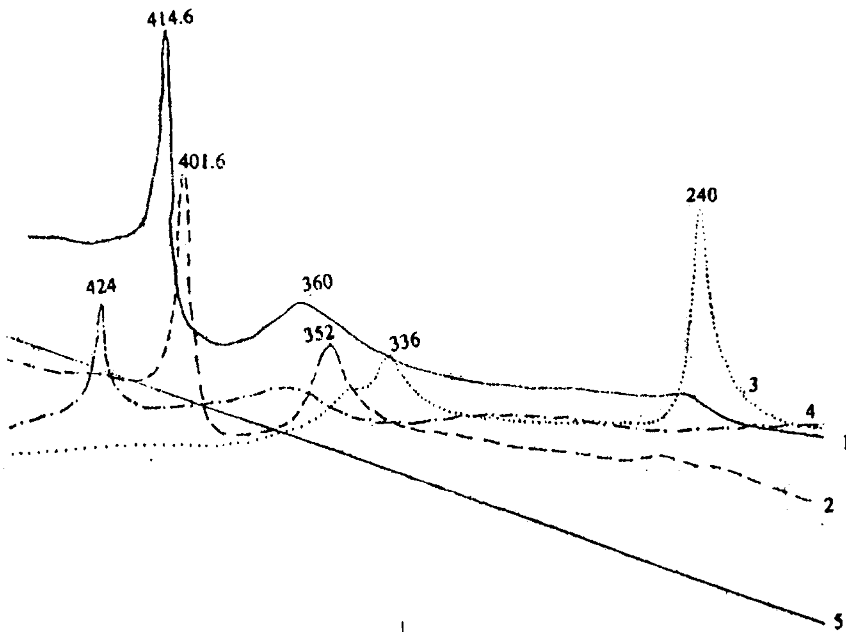
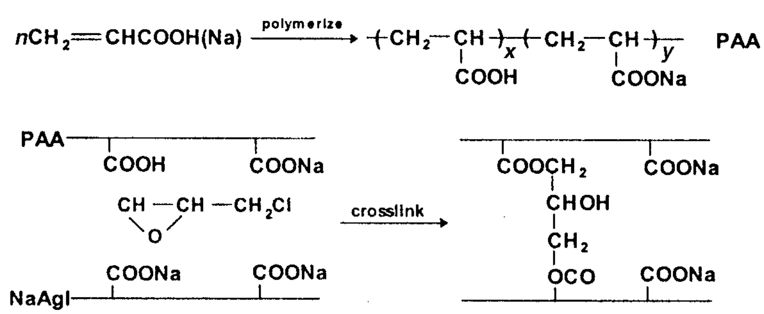


Figure 3 A DTA diagram of the resin (curve 1), the mixture of PAA and NaAgl (curve 2), NaAgl (curve 3), PAA (curve 4), and the heating rate (curve 5) of 10°C/min.

perature is at 352 and 401.6°C. However, the decomposition temperature of the resin is at 360 and 414.6°C. It is evident from this analysis that the thermal stability of the absorbent resin is better than that of the mixture, which may be ascribed to the additional chemical bonds introduced into the resin molecule during the crosslinking process.

CONCLUSION

1. The physical property of the resin is quite different from PAA and NaAgl. The resin absorbs water or 0.9% NaCl solution easily, but PAA and NaAgl are both soluble in water.
2. The spectroscopic data confirm that the crosslinking agent epichlorohydrin can introduce a chemical group ($-\overset{\displaystyle O}{\overset{\|}{C}}-O-$) into PAA and NaAgl to produce a network structure.
3. The thermal analysis data show that the resin is more thermally stable than both PAA and NaAgl, considering the decomposition temperature. The increase in the decomposition temperature may be ascribed to the additional chemical bond introduced into the molecule during the crosslinking process.
4. To explain the experimental results, the following reaction mechanism is suggested:



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