Synthesis and Characterization Superabsorbent-Ethanol Polyacrylic Acid Gels

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ABSTRACT: In this article, superabsorbent-ethanol polyacrylic acid gels were synthesized by free-radical aqueous polymerization method by using γ rays as initiator and varying the concentration of the Zn^{2+} from 0.1 to 0.3%, which acts as crosslinker. Effect of irradiation dose, monomer concentration, kind, and concentration of the crosslinker on swelling behaviors of polyacrylic acid gels were investigated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3458–3461, 2007

Key words: superabsorbent-ethanol polyacrylic acid gels; irradiation dose; crosslinker

INTRODUCTION

It is well known that superabsorbent gels are three-dimensional network structures that can absorb a large amount of water. Therefore, many researches on super water-absorbing gels have been done and lots of reports have been published.[1–5] Gels are synthesized by means of inverse suspension polymerization, with the highest absorbing rate 30 g/g for methanol.[6] A new super alcohol absorbing gel, in which $Ni(NO_3)_2 \cdot 6H_2O$ was selected as the crosslinker, has been polymerized from acrylic acid by plasma-induced polymerization at low temperatures in water solution. The gel has absorbencies of 64 g/g for methanol and 48 g/g for alcohol, respectively.[7] Most of the reported methods on absorbent-alcohol gels were both complex and with the highest alcohol-absorbing rate just under 50 g/g. But to the above gels, once in the mixtures of water and ethanol, the swelling behaviors would drop significantly, some even totally fail to absorb anything. So it is necessary to place importance on finding new types of super ethanol-absorbing gels in which ethanol has little or no effect. Herein, we reported a facile and effective method to synthesize a polyacrylic acid gel using γ rays as the initiator and where Zn^{2+} ions act as the crosslinker. This method is much easier than those have been reported, and the obtained gels with a highest ethanol-absorbing capacity 159 g/g. It is possible to use superabsorbents to absorb leaks comprised water and solvents.

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EXPERIMENTAL

Materials

Zinc oxide, nickel oxide, cadmium oxide, acrylic acid, and ethanol were reagent grade and used without further purification obtained from Shanghai Chemical Co.

Synthesis of polyacrylic acid gels

Analytical-grade ZnO and acrylic acid were dissolved in water, respectively, to form clear solutions. After the solutions were bubbled with N_2 for 20 min to eliminate the O_2 dissolved in them, the mixture was irradiated by γ rays. Finally, the polyacrylic acid gels were obtained.

Swelling

The obtained crosslinked gels were cut into small pieces and left to dry at 40°C in the oven until the gels were of constant weight. A piece of gel of known weight was immersed in ethanol at 25°C until the swelling equilibrium was reached (almost 72 h). The gels was removed, blotted quickly with absorbent paper, and then weighed. For accuracy, the experiment was repeated twice for each sample. The following equation was used to determined ethanol uptake.

$$\text{Ethanol absorbency} = (W_s - W_g)/W_g$$

where W_s and W_g represent the weights of swelled and dry polyacrylic acid gels, respectively.

RESULTS AND DISCUSSION

To investigate the effect of the monomer concentration on the ethanol-absorption capacity, various polyacrylic acid gels were synthesized, keeping all other variables constant. Added concentrations of acrylic acid were 2.08, 2.78, 3.47, 4.16, and 4.86 mol/L. The results of the ethanol-absorption capacity are shown in Figure 1. It is well known that in free-radical-chain-polymerization increase in the monomer concentration, polymerization is facile occurred. However, a further increase in the monomer concentration makes the radical concentration excessive, causing the rate of termination reactions to increase, the conversion to decrease, and the chain length between each crosslink to decrease.[8] These can affect the ethanol-absorption capacity of the gels. As shown in Figure 1, there is a maximum point at 3.47 mol/L of acrylic acid concentration. When the monomer concentration is smaller than that at the maximum point, the ethanol absorbency increases with an increasing monomer concentration. The monomer concentration of the acrylic acid is larger than that at the maximum point; however, the ethanol absorbency decreases with an increasing concentration of the acrylic acid because of the excessive radicals. These results are agreement with above explanation.

The effect of the irradiation dose on the alcohol absorbency was investigated. Keeping all other variables constant, the polymerization of the acrylic zinc was irradiated with 840, 1050, 1260, 1470, 1680 Gy, respectively. The results indicated that the hydrogel swellability in ethanol increases with irradiation dose to reach its maximum value around 1050 Gy. Thereafter, any increase in irradiation dose leads to a decrease in polyacrylic acid gels ethanol absorbency (Fig. 2).

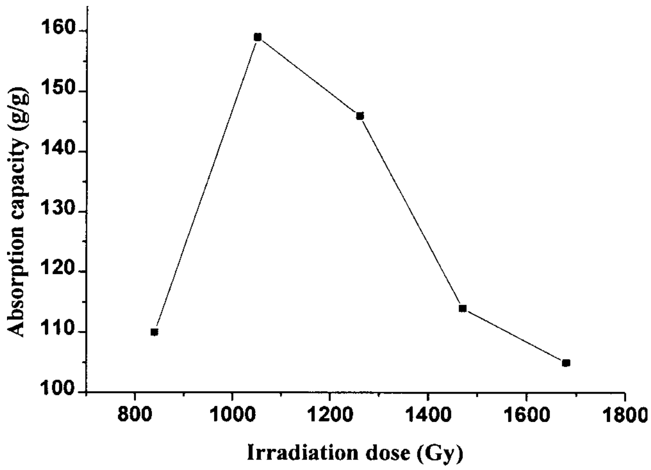

Figure 2 Relationship of ethanol-absorption capacity of the obtained gels and irradiation dose. Concentration of the Zn^{2+}: 0.017 mol/L.

At low irradiation doses, the decrease in polyacrylic acid gels ethanol absorbency may be because of the high-soluble fraction content in copolymer. However, at high doses, the reduction in the polyacrylic acid gels ethanol absorbency is attributed to the formation of hydrogel, containing a high degree of crosslinking. It was reported that, as the irradiation dose increases, the number of the small chains increased and the crosslinking density of copolymer system increased. At the same time, the number–average molar mass between the crosslinks is smaller than at the lower-ray doses.[5,8]

Figure 3 shows that when the concentration of Zn^{2+} was about 0.0104 mol/L, the resin with the highest ethanol-absorbing capacity of 159 g/g was obtained. It is well known that polyacrylic gels are

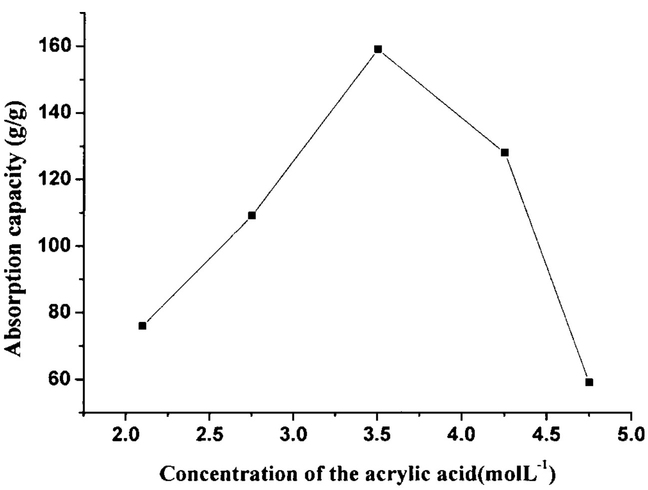

Figure 1 Relationship of ethanol-absorption capacity of the obtained gels and concentration of the acrylic acid. Concentration of the Zn^{2+}: 0.017 mol/L.

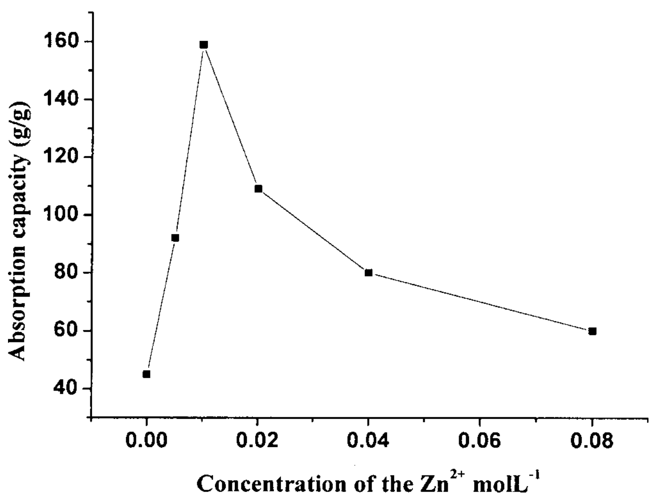

Figure 3 Relationship of ethanol-absorption capacity of the obtained gels and concentration of the Zn^{2+}. The gels were prepared with dose rate 41.96 Gy/min, concentration of acrylic acid 25%, and total radiation dose 1386 Gy.

three-dimensional network structures, and zinc acrylic play a part in the crosslinking of the network of the gels. By hydrogen bonding, van der Waals interaction of the ethanol molecules with chains of the polyacrylic acid, the ethanol molecules entered into the network of the gels, and the highest ethanol-absorbing capacity was obtained. With the increase or decrease of the concentration of Zn^{2+}, the cross-link of the three-dimensional structure of the ethanol-absorbing resin would be excessive or insufficient, with the result of the decrease of the ethanol-absorbing capacity. Besides, if the concentration of Zn^{2+} ions was more than 0.0832 mol/L, the obtained resin would absolutely fail to absorb any alcohol and turn rigid, with the color white.

From Figure 4, we can see that with the increase of the concentration of ethanol, the absorbing capacity of obtained gels would drop. There are several features between the swelling behavior of a crosslinked polymer in solvent and the dissolving of the linear polymer in the solvent. A solvent that can dissolve a linear polymer could also swell the polymer network, which would conform to the dissolving rules of linear polymer or the Hildebrand equation:[9]

$$\Delta H_M/(V\Phi_1\Phi_2) = (\delta_1 - \delta_2)$$

where ΔH_M is the enthalpy change on mixing of a polymer and solvent, V is the whole volume of the solution, Φ_1 and Φ_2 are volume fractions for the solvent and the polymer, and δ_1 and δ_2 are the solubility parameters for the solvent and polymer. This equation predicts that a solvent can dissolve a polymer if the solubility parameters for the solvent and the polymer are close to each other. The polyacrylate gel has the highest absorbency when the water is absorbed. The water solubility parameter is 23.2 and this value can be regarded as the solubility parameters for polyacrylate gel. The solubility parameters for a mixing solvent can be calculated using the following equation:[10]

$$\delta_{mix} = \Phi'_1\delta_1 - \Phi'_2\delta_2$$

where Φ'_1 and Φ'_2 are the volume fraction for the two solvents, and δ_1 and δ_2 are the solubility parameters for the two solvents.

When the volume fraction for water increase, the δ_{mix} will increase and the gels will absorb more water.

The effect of the kind of the crosslinker on the ethanol absorbency of gels was investigated. From Figure 5, we can see that concentrations of the Zn^{2+}, Cd^{2+}, Ni^{2+} are same in the polymer network; ethanol absorbency of the polyacrylic zinc gels, polyacrylic nickel gels, polyacrylic cadmium gels are not same. This may be caused by the metal ions differing in their complexing ability with carboxylic acids, so that they crosslink the polymer with different efficiencies, thus yielding different absorbencies at same nominal concentration of metal. These results should be further investigated in future. In addition, from Figure 5 we can see that concentrations of the metal ions are too high; the obtained resin would absolutely fail to absorb any ethanol and turn rigid.

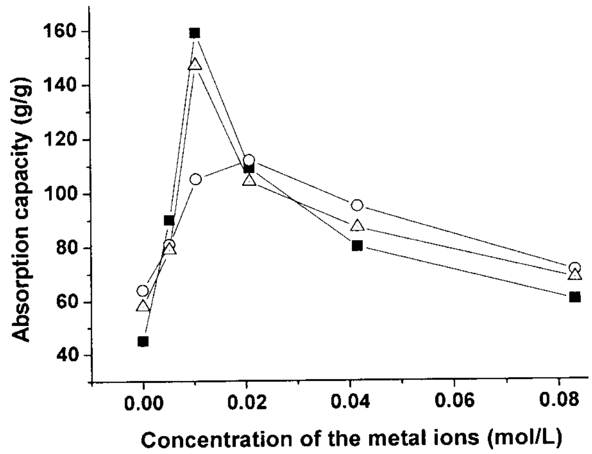

Figure 5 Effect of the metal ion on ethanol-absorption capacity of the obtained gels; ■ polyacrylic zinc gels, ○ polyacrylic nickel gels, and △ polyacrylic cadmium gels. The gels were prepared with dose rate 41.96 Gy/min, concentration of acrylic acid 25%, total radiation dose 1386 Gy.

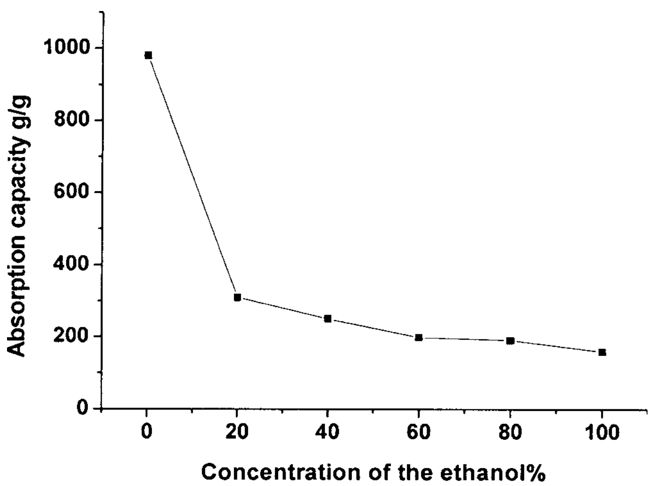

Figure 4 Relationship of absorption capacity of the obtained gels and concentration of the ethanol. The gels were prepared with dose rate 41.96 Gy/min, concentration of acrylic acid 25%, and total radiation dose 1386 Gy.

CONCLUSIONS

Superabsorbent-ethanol polyacrylic acid gels were synthesized by free-radical aqueous polymerization method using γ rays as initiator. Effect of irradiation dose, monomer concentration, kind, and concentration of the crosslinker on swelling behaviors of gels were investigated.

References

1. Doo-Won, L.; Kyong-Geun, S.; Kee-Jong, Y.; Sohk-Won, K. Eur Polym J 2002, 38, 579.
2. Lokhande, H. T.; Varadarajan, P. V.; Vatsala, I. J Appl Polym Sci 1992, 45, 2031.
3. Rathna, G. V. N.; Damodaran, S. J Appl Polym Sci 2001, 81, 2190.
4. Gugliemilli, L. A.; Weaver, M. O.; Russell, C. R; Rist, C. E. J Appl Polym Sci 1969, 13, 2007.
5. Abd El-Rehim, H. A.; El-Sayed, A. H.; Abd El-Mohdy, H. L. J Appl Polym Sci 2004, 93, 1360.
6. Xiulin, Z.; Zhenping, C.; Jianmei, L. Chin J Colloid Polym 2000, 18, 25.
7. Chen, Z. P.; Lu, J. M.; Zhu, J. Petrochem Technol 2000, 29, 571.
8. Sahiner, N.; Saraydin, D.; Karadag, E.; Güven, O. Polym Bull 1998, 41, 371.
9. Hilderbrand, J.; Scott, R. L. Solubility of Nonelectrolytes, Reinhold Publishing: New York, 1949.
10. He, M.; Chen, W.; Dong, X. Macromolecular Physics, Fudan University Press: Shanghai, 1990.