

PREPARATION OF SUPER ABSORBENT BY IRRADIATION POLYMERIZATION

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ABSTRACT

A kind of absorbent is prepared by gamma-rays irradiated by reversed-phase suspension polymerization. Drying particles have 1400(g/g) absorbency in deionized water.

Effects of reactive conditions, e.g.: dose-rate, dose, monomer concentration, degree of monomer neutralization and crosslinking agents on absorbency in deionized water are discussed. The cause of absorbing deionized water by polymer is related to its network structure and ionic equilibrium in particles. Accordingly, a suitable reactive condition is chosen for preparation of hydrogel spheres.

INTRODUCTION

The polyacrylate has been used as super absorbent in the napkin paper and paper diaper widely[1]. We have reported its preparation method initiated by heating[2]. The polymerization reaction may be carried out at room temperature by irradiation initiation, and this method has been used to prepare the super absorbent in many reports[1,3]. In this paper, the hydrogel microsphere is prepared by gamma rays irradiation using reversed-phase suspension way. Drying particles have 1400(g/g) absorbency in deionized water.

EXPERIMENTS

1. Reagents

Acrylic acid(Industrial grade); Tween 20(C.P); N,N-Methylene bisacrylamide(C.P); Span 60(C.P); Sodium dodecyl sulfate(C.P); 732# Resin(Industrial grade); Triethylene glycol diacrylate(C.P).

2. Experiment Process

The Acrylic acid is added into the solution of sodium hydroxide slowly, then the solution is put into a flask containing crosslinking agent, surface active agent and organic solvent. The reaction system is protected by Nitrogen and irradiated by Cobalt-60 gamma rays at room temperature. The hydrogel microsphere is obtained by filter.

3. Analysis Methods

3.1 Determining of the Absorbency

The ability of absorbency(Q) can be calculated by formula (1):

$$Q=(Wt-Wo)/Wo \quad (1)$$

Wo is the weight of the dry absorbent;Wt is the weight of absorbent absorbed solution(such as deionic water,0.1mol/LNaCl or Urine)saturated.

3.2 Determining of the Sol-fraction

The sol-fraction(S) can be abtained in the Soxh extractor,and can be calculated by formula (2):

$$S=1-(Wt-Wo)/Wo \quad (2)$$

Wo is the weight of the dry absorbent;Wt is the weight of absorbent having been extracted.

3.3 Determining of the Remaining Concentration of Monomer

The remaining concentration of monomer can be titrated by Bromide[2].

RESULTS AND DISCUSSION

1.Effect of Irradiation Dose on Absorbency(Fig.1)

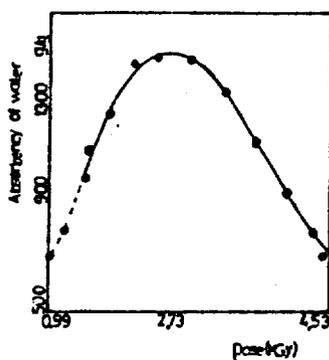


Figure 1 Effect of irradiation dose on absorbency of deionic water 16°C,Dose-rate:0.339kGy/h

In the system of reversed-phase suspension, the monomer containing water is dispersed in the organic solvent. Its diameter is between 10 μ m and 100 μ m. There are a lot of surface active agents between the two phases. The water loving end groups stretch into the liquid drop of water, otherwise, the oleophilic end groups stretch out, so that the metastable electric structure forms in the drop of water, and the drop of water are dispersed among the organic solvent stably. When the system is irradiated by gamma rays, the polymerization will

happen on free radical mechanism. The absorbency of the polymeric compound increases, then, decreases along with the increasing of irradiation dose because the irradiation crosslinking and irradiation splitting decomposition exist at the same time in the course of irradiation[4]. When the irradiation dose is lower, the crosslinking is in the dominant position, the absorbency increases along with the increasing of the irradiation dose; When the irradiation dose is higher, the splitting decomposition is in the dominant position, the absorbency decreases.

2. Effect of Irradiation Dose Rate on Absorbency(Fig.2)

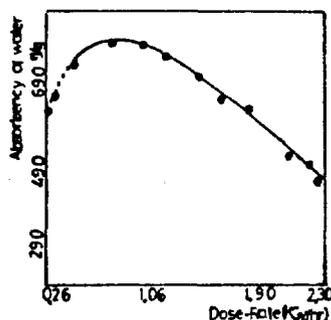


Figure2 Effect of irradiation dose-rate on absorbency of deionized water, 16°C, Dose: 3.00KGy

There is an extreme value of absorbency along with the dose-rate. When the dose-rate is lower, the reaction rate is lower, a lot of oligomers are produced, so the solubility of the absorbent becomes larger, the absorbency becomes lower. The initiating rate and reaction rate are faster along with the increasing of dose-rate, meanwhile, the gel-effect becomes notable, so the molecular weight and the absorbency become larger. If the dose-rate becomes enough large that the crosslinking points become more, the molecular weight of the segments in the crosslinking network becomes smaller, the absorbency becomes lower.

3. Effect of Monomer Concentration on Absorbency(Fig.3)

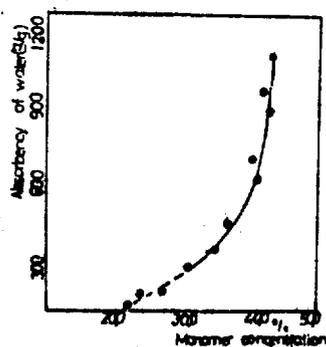


Figure 3 Effect of monomer conc. on absorbency of deionized water, 16°C, dose rate is 0.339KGy/h, dose is 2.7KGy, degree of neutralization is 98.5%

At the same conditions of irradiation, the reaction rate becomes faster with the increasing of monomer concentration, so the gel-effect becomes notable, the molecular weight becomes larger, the absorbency becomes higher.

4. Effect of Neutralization Degree of the Monomer on Absorbency(Fig.4)

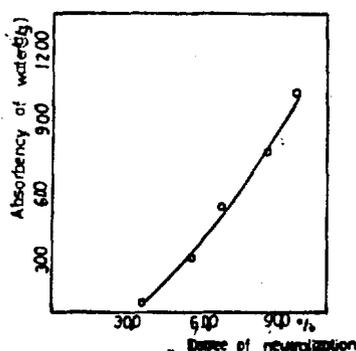


Figure 4 Effect of degree of neutralization on absorbency of deionic water, 16 C, Dose-rate: 0.339KGy/h, Dose: 3.00KGy, Monomer conc.: 39.2%

The absorbency of the absorbent increases with the increasing of the neutralization degree of the monomer. Because neutralization degree being higher, the viscosity of the solution is lower, the spreading rate of the monomer is faster, the molecular weight of the polymer is bigger. On the other hand, the ions concentration in gel-sphere becomes higher, its osmotic pressure increases at the theory of Dannan equilibrium.

5. Radiation Gelation-dose and Irradiation Yield

At the range of irradiation dose in experiments, the relation of irradiation crosslinking dose and gel-fraction is shown as formula (3) at the theory of Charlesby-Pinner:

$$S + S^{1/2} = p_0/q_0 + 1/q_0ur \quad (3)$$

S is the sol-fraction of the polymer; p_0 is the density of splitting decomposition; q_0 is density of crosslinking; u is the number-average molecular weight; r is the irradiation dose.

The gel-dose can be obtained ($D_g = 0.526 \text{ KGy}$) from the relation of $(S + S^{1/2})$ and $1/r$ (Fig.5). The radiation yield of the solution can be calculated by the formula of Rosick ($G = 24.6$).

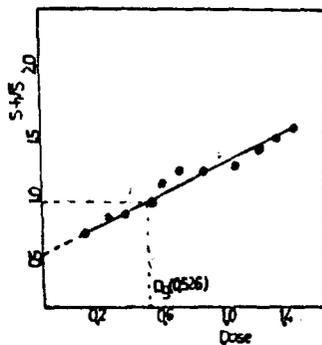


Figure 5 Relation of $S+5/2$ to $1/R$ by Charlesby-Pinner equation

6. The Absorption Mechanism of the Absorbent

A lot of anions (COO^-) and cation (Na^+) are fixed on the network of hydro gel. That is the reason for osmotic pressure. The structure model of hydro gel absorbing deionic water is shown in Fig.6. The gel spheres expand immersed in water, the foiled molecular of the polymer will extend, and water can be contained in the network of it. When osmotic pressure equals to molecular elastic force, the system reaches absorbing equilibrium.

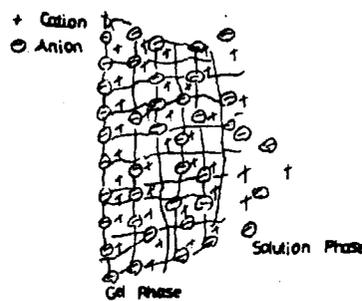


Figure 6 Model of hydro-gel absorbong deionio water

7. The Relativity of Quaity between Heating Initiation Polymerization and Irradiation Initiation Polymerization

The relative results is shown in table below:

	Initiation of heating	Initiation of irradiation
Absorbency in deionic water(g/g)	1286	1427
Yield(%)	98.7	99.8
Left of monomer(%)	0.3	0.0
Initiation temperature(°C)	59	21
Rate of lose in press(30g/cm ² ,%)	40	8.7
0.1mol/LNaCl(g/g)	165	167
Urine(g/g)	74	67

CONCLUSIONS

- 1.The super absorbent is prepared at suitable dose, dose-rate, concentration and degree of neutralization of the monomer.
2. The absorbing mechanism of the absorbent is discussed, the irradiation yield is calculated.
3. The properties of the hydro gel prepared using irradiation initiation polymerization is better than that of using heating initiation polymerization.

REFERENCES

1. Zou Xinxu, Super Absorbent,, Chemical industry publishing house, 1991.
- 2.Hua Fengjun,Qian Mengping,Tan Chunhong,Super Absorbent Prepared Using Heating Initiation Polymerization,Functional Polymer(in press).
- 3.Li Qian,Irradiation Research and Technology,1992:12-16.
- 4.Charlesby A.,Atomic Radiation and Polymerization,WNT,Warsaw,1962.
- 5.Yukiniko Naka,Radiation Physics and Chemistry,402:83-8.
- 6.Loretta Y.,Journal of Applied Polymer Science,45:1412-23.