

Influence of Chemical- Environment Parameters on ability Water Absorption of Biocopolymer Synthesized by Inverse Suspension Polymerization

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Abstract—Highly water-absorbing polymers of neutralized poly(acrylic acid-co-HPMA) onto Gelatin were synthesized in an effort to investigate the influences of environment parameters on water absorption. In addition, the extent of water absorption and the absorption rate were studied to determine their relationship with the environment parameters. This article explains the synthesis technique, characterization of the water-absorbing copolymers, and their properties.

Keywords—2-hydroxypropylmetacrylate , acrylic acid, water absorption, Gelatin

I. INTRODUCTION

Highly water-absorbing polymers have drawn much interest since Fanta et al. at the Northern Regional Laboratory of the United States Department of Agriculture succeeded in grafting monomers onto starch and other polysaccharides, which yielded products with water absorption of several hundred to thousand times its dried weight. Research and development of highly water-absorbing polymers from starchbased polymers to petrochemical-based polymers, which are nonbiodegradable with a long service life, has been carried out for more than two decades. To synthesize the highly waterabsorbing polymers in a bead form, an inverse suspension process is generally used. In an inverse suspension polymerization, the aqueous monomer mixture is suspended in a hydrophobic oil phase. The suspended droplets of monomer solution strongly depend on the chemical and physical properties of the dispersing agents or on nonionic steric stabilizers blended to achieve an overall HLB of between 4 to 6, used to stabilize the suspension. This article investigates the reaction parameters and their influences onto water absorption behaviour[1].

II. EXPERIMENTAL

A. Synthesis of hydrogel

A1-Liter three-neck reactor equipped with a reflux condenser and a mechanical stirrer was used. In general, 0.50-1.5 g Gellatin was dissolved in 35 mL distilled water. The stirrer speed was maintained at 300 rpm. To control the reaction temperature, the rector was placed in a water bath preset at desired temperature. After complete dissolving Gellatin, (0.08-0.2g in 5ml H₂O) initiator, APS, was added

to the Gellatin solution and allowed to stir for 15 min. Then, 1-5 ml of AA and 1-5 ml of 2-hydroxypropylmetacrylate monomer and MBA (0.03-0.15 g) were charged into the reactor. The graft copolymerization was set at 55 °C for 60 min. after the reaction completed, the produced hydrogel was cooled to ambient temperature. To neutralization of the introduced AA in the hydrogel, dilute NaOH solution was used and the hydrogel was neutralized to pH 8. Then 350 mL methanol was purred to the hydrogel and allowed to dewater for 48 h. the dewatered hydrogel filtered and dried in an oven for 24 h at 65 °C.

III. RESULTS AND DISCUSSIONS

A. Synthesis and spectral characterization

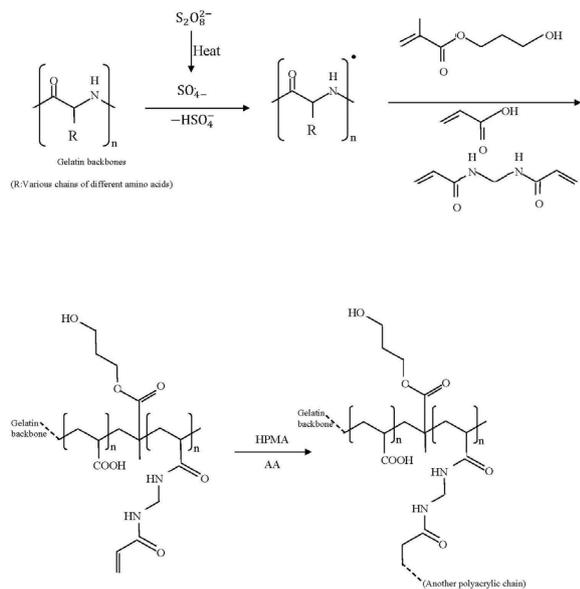
The mechanism for crosslinking graft copolymerization of AA and HPMA onto Gelatin backbones in the presence of KPS and MBA is shown in Scheme 1. At the first step, the thermally dissociating initiator, i.e. KPS, is decomposed under heating (65°C) to produce sulfate anion-radical. Then the anion-radical abstracts hydrogen from one of the functional groups in side chains (i.e. COOH, OH, and NH₂) of the substrate to form corresponding radical. So, these macroradicals initiate sodium acrylate grafting onto collagen backbones led to a graft copolymer. In addition, crosslinking reaction was occurred in the presence of a crosslinker, i.e., MBA, so that a three dimensional network was obtained.

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 1 shows the FTIR spectra of the Gelatin and the synthesized hydrogel. The bands observed at 1451 cm⁻¹ 1565 m⁻¹ can be attributed to C=O stretching (symmetric and asymmetric stretching modes) in carboxamide functional groups of substrate backbone (Fig. 1). The broad band at 3440cm⁻¹ is due to stretching of -OH groups of the Gelatin[2].

lower than that of NaCl solution. This phenomenon is arisen from ionic crosslinking of these cations with carboxylate anions that causes low water absorbency. However, swelling capacity of both hydrogel in NaCl is yet higher than that of the conventional PAANa superabsorbent.

Changing of environmental ionic strength affects significantly the swelling capacity of superabsorbents.

Fig 2 shows the effect of the various salt solutions on the water absorbency of Gelatin-g-PAANa-HPMA.



Scheme 1. Proposed mechanistic for synthesis of the hydrogel

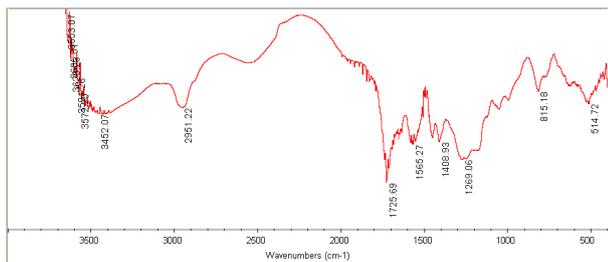


Figure 1. FTIR spectra of the synthesized hydrogel .

The decrease of the swelling capacity of the hydrogel is due to the screening effect and a loss of the osmotic pressure difference between the hydrogels and the fluids. In salt solutions, the perfect anion-anion repulsion of the carboxylate groups is prevented by the M^{n+} cations that shield the carboxylate groups, so the swelling capacity is decreased. In addition, the swelling of the superabsorbents depends on the valency of the cations. Multivalent cations decrease drastically the swelling capacity.

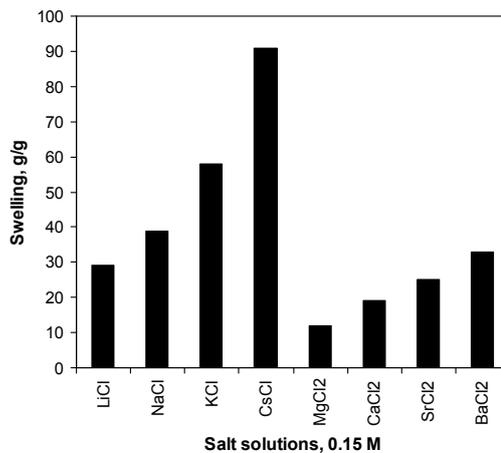


Figure 2. Swelling capacity of the hydrogel in different chloride salt solutions (0.15M).

B. Swelling in various salt solutions

The decrease is attributed to the complexing ability of carboxylate groups inducing interchain complexes formation and consequent enhancing of the network crosslink density [2]. The composite comprises carboxylate anions ($-\text{COO}^-$). The water absorbency of the composite in the presence of the Ca^{2+} and Al^{3+} cations is

C. Swelling kinetics

In practical applications, not only a higher swelling capacity is required, but also a higher swelling rate is needed. Buchholz has suggested that the swelling kinetics for the superabsorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area and composition of polymer. Figure 3 represents the dynamic swelling behavior of the superabsorbent samples with various particle sizes in water. Initially, the rate of water uptake sharply increases and then begins to level off. The time required to reach the equilibrium swelling capacity was achieved after ~ 20 min. A power law behavior is obvious from Fig. 3. The data may be well fitted with a Voigt-based equation (Eq. 4):

$$S_t = S_e (1 - e^{-t/\tau}) \quad (4)$$

where S_t (g/g) is swelling at time t , S_e is equilibrium swelling (power parameter, g/g); t is time (min) for swelling S_t , and τ (min) stand for the "rate parameter". The rate parameters for superabsorbent are found to be 4.5, 6.2, and 11.3 min for superabsorbents with particle sizes of 100-250, 250-400 and 400-550 μm , respectively. It is well-known that the swelling kinetics for the superabsorbent polymers is significantly influenced by particle size of the absorbents. With a lower the particle size, a higher rate of water uptake is observed. An increase in the rate of absorption would be expected from the increase in surface area with decreasing particle size of hydrogel.

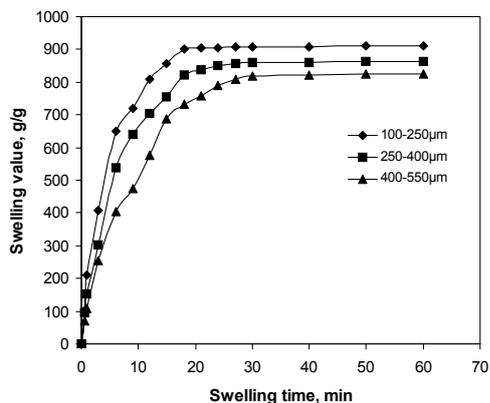


Figure 3. Representative swelling kinetics of the superabsorbent hydrogel with various particle sizes.

IV. CONCLUSION

In the research, we prepared a novel superabsorbent hydrogel by crosslinking graft copolymerization of polyacrylic acid and 2-hydroxypropylmetacrylate onto a

Gelatin. Swelling measurement of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in solutions with monovalent cations. However, swelling loss in salt solutions, in comparison with distilled water, can be attributed to charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively. Finally, dynamic swelling kinetics of the hydrogels shows that the rate of absorbency is increased with decreasing the particle size of superabsorbing samples.

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