Temperature Sensitive Superabsorbent Hydrogels from Poly(*N*-t-butyl acrylamide-co-acrylamide) Grafted on Sodium Alginate

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Summary: Temperature-sensitive hydrogels based on *N*-t-butylacrylamide (TBA), acrylamide (AAm), and sodium alginate were prepared by free radical polymerization method. Methylenebisacrylamide (MBA) and amonium persulfate (APS) were applied as water soluble crosslinker and initiator, respectively. The chemical structure of the hydrogels was confirmed by FT-IR spectroscopy and thermogravimetric analysis (TGA) methods. Morphology of the samples was examined by scanning electron microscopy (SEM). By changing the initial TBA/AAm mole ratios, hydrogels with different swelling properties were obtained. The rate parameters were found to be 2.0, 2.4, and 3.5 min for the superabsorbents with AAm/TBA weight ratio of 1.0, 1.3 and 2.0 respectively. The swelling behavior in distilled water and different pH solutions was investigated. A preliminary swelling kinetics and the absorbency under load (AUL) were also studied. At the applied pressure (2.07 kPa), maximum swelling was found to be 17, 19, and 21 (g/g) for the superabsorbent hydrogels with AAm/TBA weight ratios of 1.0, 1.5 and 2.0, respectively.

Keywords: crosslinking; hydrogels; radical polymerization

Introduction

Hydrogels are three-dimensional polymer networks, which swell significantly on contact with water. Interest in hydrogels has gained momentum recently because these materials can be actuated by a variety of stimuli such as pH,[1,2] temperature,[3,4] electrical current,[5,6] salinity,[7] and antigens.[8] Temperature-sensitive hydrogels are probably the most commonly studied class of environmentally sensitive polymer systems in drug delivery research.[9,10] Most hydrogels are formed by copolymerization of vinyl monomers containing hydrophilic side groups with multifunctional vinyl monomers or by crosslinking reactive functional groups of hydrophilic polymers. By manipulating the chemistry of the hydrophilic segments in the polymers and the degree of crosslinking, hydrogels may be tailored to exhibit specific properties. Polysaccharides constitute the majority of the natural-based superabsorbent hydrogels because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability, and non-toxicity. In particular, sodium alginate (Na-Alg) is a renewable and biodegradable natural polymer that is used in a variety of commercial applications because of its capacity for gelatinization. Alginates and their derivatives are widely used in the food, cosmetics and pharmaceutical industries.[11,12] Following our continuous research on modification of carbohydrate polymers[13,14] and synthesis of natural-based superabsorbent hydrogels,[15–17] in the present work we attempted to synthesis a novel superabsorbent hydrogel through graft copolymerization of N-t-butylacrylamide (TBA) and acrylamide (AAm) on sodium alginate. The swelling behavior in distilled water and

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different pH solutions was investigated as well. The effects of the hydrogel composition on the swelling behavior and thermosensitive properties were investigated.

Experimental Part

Materials

The polysaccharide sodium alginate was purchased from Merck and used without further purification. Methylene bisacrylamide (Fluka), potassium persulfate (Fluka), acryl amide (Merk), and N-t-butyl acrylamide (Fluka) were used without further purification. All other chemicals were also analytical grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

Superabsorbent Synthesis

Synthesis of the hydrogel, alginate-g-poly (TBA-co-AAm), was carried out using APS as an initiator and MBA as a crosslinker in ethanol–water mixture (1:1 by volume). A general procedure for chemically crosslinking graft copolymerization of TBA and AAm onto sodium alginate was conducted as follows: sodium alginate (1.0 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three-blade propeller type, 300 rpm), including 20 mL deoxygenated doubly distilled water and 20 mL ethanol. The reactor was immersed in a thermostated water bath preset at the desired temperature (80 °C). After complete dissolution of sodium alginate to form a homogeneous solution, certain amounts of TBA (0.5–1.5 g), AAm (1.5–0.5 g), MBA (0.2 g in 5 mL H_2O) and APS (0.1 g in 5 mL H_2O) were simultaneously added to the reaction mixture. After 60 min, the produced hydrogel was poured into excess non solvent ethanol (250 mL) and remained for 24 h to dewater. Then Ethanol was decanted and the product was cut to small pieces. Finally, the filtered hydrogel was dried in an oven at 50 °C for 12 h. After grinding, the powdered superabsorbent was stored away from moisture, heat and light.

Swelling Measurements

The accurately weighed of alginate-g-poly (TBA-co-AAm) superabsorbent hydrogel (0.5 g) was immersed in a glass cups full of distilled water at 25 °C. Then the unabsorbed water was screened with 160 mesh nylon bag and the bag weighed to determine the weight of the swollen gel. The water absorbency (Q) was calculated using the following equation:

$$Q = (W_s - W_d)/W_d \tag{1}$$

Where, W_s and W_d are the mass of swollen gel and dry gel, respectively.

The accuracy of the measurements was ±3%. The standard deviation (s) for a sample of data that is of limited size is given in the following equation:

$$s = \sqrt{\frac{\sum_{i=1}^{N}(X_i - \overline{X})^2}{N-1}} \tag{2}$$

where $(X_i - \overline{X})$ is deviation from average of ith measurement and N is number of replicates of each measurement (here $N = 3$).

Measurement of Absorbency under Load (AUL)

A macro-porous sintered glass filter plate (porosity 0, $d = 80$ mm, $h = 7$ mm) was placed in a Petri dish ($d = 118$ mm, $h = 12$ mm), and the weighed dried hydrogel samples (0.9 ± 0.01g) were uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid load (Teflon, $d = 60$ mm, variable height) is put on the dry hydrogel particles while it can be freely slipped in a glass cylinder ($d = 60$ mm, $h = 50$ mm). Desired load (applied pressure 2.07 kPa) was placed on the hydrogel sample. Then, 0.9% sodium chloride solution was added so that the liquid level was equal to the height of the sintered glass filter. Whole of the set was covered to prevent surface evaporation and probable change in the saline concentration. After 60 min, the swollen particles were weighed again, and AUL (absorbency under load) was calculated using Eq. (1).

Morphologies of the Hydrogels

Scanning electron microscopy (SEM) of the superabsorbent hydrogels was performed to visualize the superabsorbent hydrogel's pores. The morphology of the dried samples was examined using a scanning electron microscope, SEM, (Philips, XL30) operated at 25 KV after coating the samples with gold film.

FT-IR Analysis

FT-IR spectra of samples in the form of KBr pellets were recorded using an ABB Bomem MB-100 FT-IR spectrophotometer.

Results and Discussion

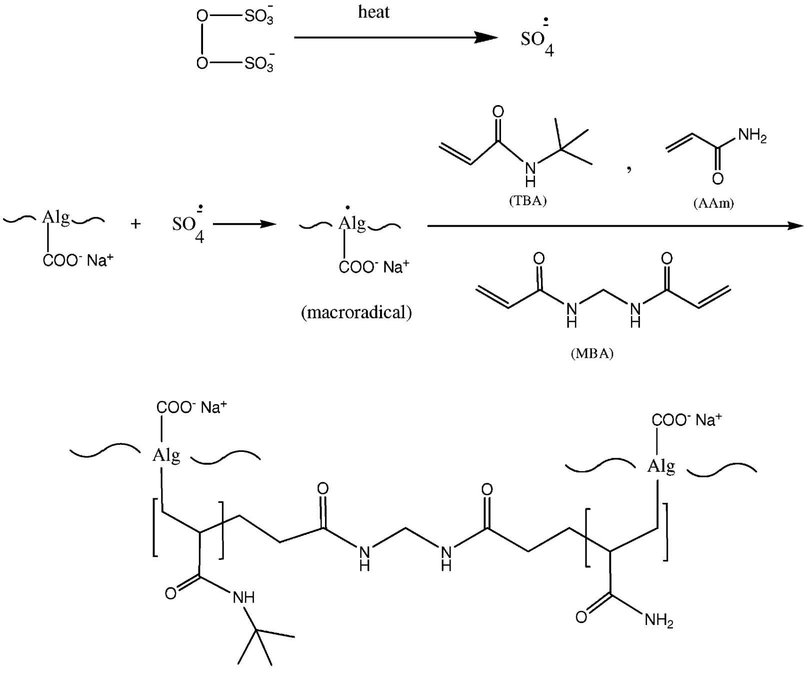
Synthesis and Characterization

A series of alginate-g-poly (TBA-co-AAm) hydrogels was prepared with various TBA/AAm weight ratios by free radical polymerization. Scheme 1 shows a simple structural proposal of the graft copolymerization of AAm and TBA on the alginate backbones and crosslinking of the graft copolymer.

The proposed mechanism for crosslinking and graft copolymerization was illustrated in previous works.[18] Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogels. Figure 1 shows the FT-IR spectra of the alginate and alginate-g-poly (TBA-co-AAm) superabsorbent hydrogel. The graft copolymer comprises alginate backbones with side chains that carry carboxamide functional groups that are evidenced by a new peak at 1683 cm^{-1}. This peak attributed to C=O stretching in carboxamide functional groups of PAM.

SEM Studies

Figure 2 shows the cross-sectional views of the scanning electron microscopic images of dry hydrogels obtained under various conditions. This figure shows the influence of the weight ratio of the monomers on the porosity. The porosity of the hydrogel



Scheme 1.
Outline of the synthesis of the alginate-based superabsorbent hydrogel.

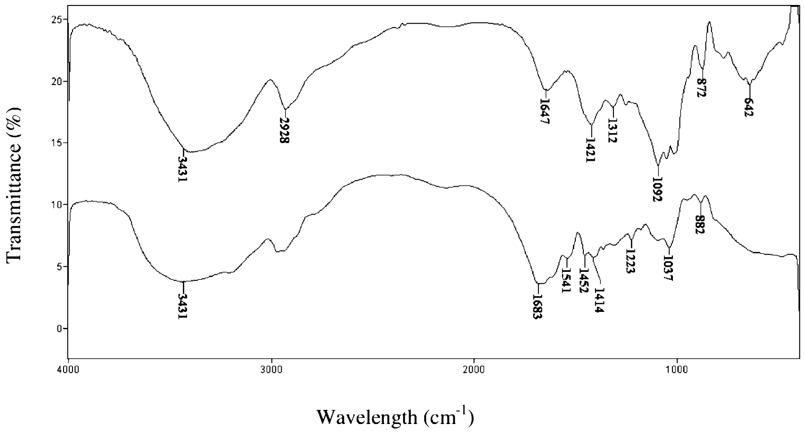


Figure 1.
FT-IR spectra of the alginate (a), and alginate-g-poly (TBA-co-AAm) (b).

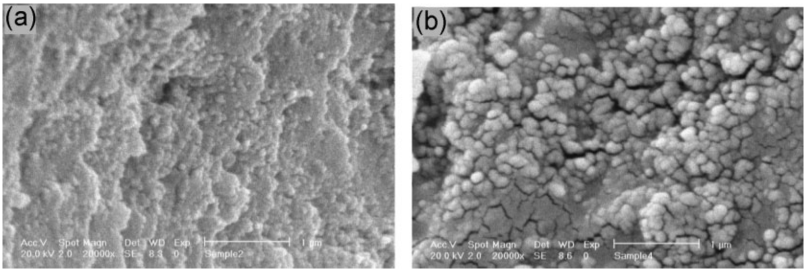


Figure 2.
Cross-sectional scanning electron microscopic (SEM) of the hydrogel with different AAm/TBA weight ratios.

particles in the sample 2b (AAm/TBA = 1) is greater than that in the sample 2a (AAm/TBA = 2). So increasing the AAm/TBA weight ratio decreases the porosity of the hydrogel. These results suggest that the hydrogel particles in the sample 2b are more porous and thus display a faster swelling response rate. The observed morphologies are confirmed by the observed swelling kinetics in Figure 6.

Thermal Analysis

Thermogravimetric analysis (TGA) method was employed to thermally characterize the hydrogel in comparison with the intact polysaccharide (Figure 3). In the TGA curve of alginate-g-poly (TBA-co-AAm) about 10–12% loss in weight is observed below 130 °C. This was attributed to the removal of the absorbed water. Figure 3 shows that degradation of native alginate is faster than that of grafted alginate. About 45% weight loss takes place in the temperature of 280 °C for alginate. A residual weight of 72% is observed at 280 °C for alginate-g-poly (TBA-co-AAm) sample.

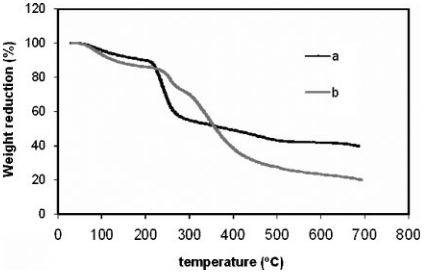


Figure 3.
Thermogravimetric analysis of the sodium alginate (a), and alginate-g-poly (TBA-co-AAm) (b).

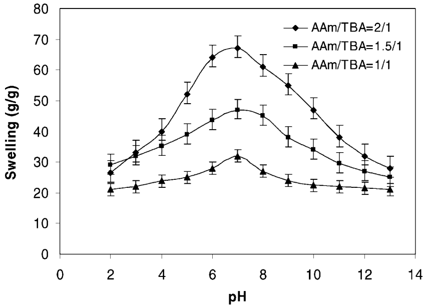


Figure 4.
Effect of AAm/TBA weight ratios on water absorbency of the superabsorbent hydrogels in various pH.

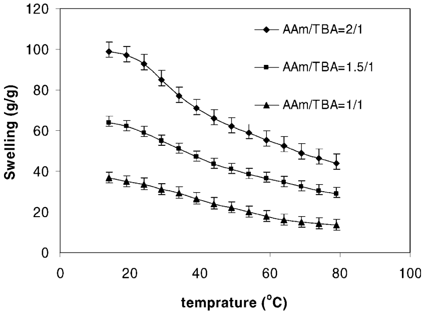


Figure 5.
Effect of temperature on swelling behavior of the superabsorbent hydrogel.

Effect of pH on Swelling

The swelling behavior of the superabsorbent hydrogels was studied at various pH values between 2.0 and 13.0 at room temperature (Figure 4). To prepare the pH media, standard HCl (pH 2.0) and NaOH (pH 13.0) solutions were diluted with distilled water to reach the desired acidic and basic pHs, respectively. The swelling of the superabsorbent hydrogel increased with increasing the pH from 2 to 7, but it is decreased in the pH range between 7 and 13. This can be attributed to the change in the ionic strength of the medium and to the effect of the counter ions. The maximum water absorbency of the hydrogel was achieved at pH 7.

Effect of Temperature on Swelling

The swelling behavior of the alginate-g-poly (TBA-co-AAm) superabsorbent hydrogels was also studied at different temperatures. Higher equilibrium swelling ratios were obtained at constant temperature by increasing the initial amount of the AAm (Figure 5). The hydrogels are swollen at low temperatures while they are shrunken at high temperatures. Thus, the swelling ratios of the hydrogels decreased with increasing the temperature of the aqueous medium. This behavior can attributed to the presence of *N-t*-butylacrylamide (TBA) as a temperature sensitive monomer in polymer network. At lower temperatures, water molecules in the vicinity of hydrophobic polymer chains are highly hydrogen bonded. Since these hydrogen bonding interactions lower the free energy of mixing considerably, the polymer chains swell in water at low temperatures. At higher temperatures, the hydrogen bonds weaken and the system tends to minimize the contact between water and hydrophobic surfaces, consequently the hydrophobic interaction increases. As a result, on heating the hydrogel, the swelling ratios of the hydrogels decreased dramatically. Also, with increasing the AAm content in the hydrogel structure the temperature sensitivity is slightly increased.

Swelling Kinetics

A preliminary study was conducted on swelling kinetics of the superabsorbent hydrogel. Figure 6 represents the dynamic swelling behavior of the alginate-g-poly

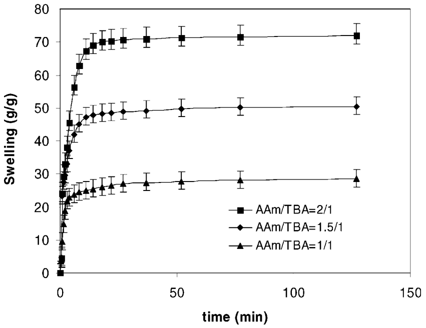


Figure 6.
Swelling kinetics of the superabsorbent hydrogels with different AAm/TBA weight ratios.

(TBA-co-AAm) superabsorbent hydrogel with various AAm/TBA weight ratios. Initially, the rate of water uptake sharply increases and then it begins to level off. The equilibrium swelling was achieved after 15 minutes. Higher equilibrium swelling rate were obtained at constant temperature by increasing the initial amount of the AAm. A power law behavior is obvious from Figure 6. The data may be well fitted with a Voigt-based equation (Eq. 3):[19]

$$S_t = S_e(1 - e^{-t/\tau}) \qquad (3)$$

Where St (g/g) is swelling at time t, Se is equilibrium swelling (power parameter, g/g), t is time (min) for swelling St, and τ (min) stand for the "rate parameter". The rate parameters were found to be 2.0, 2.4, and 3.5 min for the superabsorbents with AAm/TBA weight ratio of 1.0, 1.3 and 2.0 respectively. The rate parameter (r) is increased with increasing the AAm/TBA weight ratio. Therefore, with increasing the TBA/AAm weight ratio the hydrogels display a faster swelling response rate. This is confirmed with increasing in porosity as shown in Figure 2.

Absorbency Under Load

Absorbency under load (AUL) values is logically changed with mechanical strength of the swollen gel. Many efforts have been made to achieve superabsorbents having higher AUL or higher strength of the swollen gel.[20,21] To determine the swollen gel strength, we used the superabsorbent samples under load in sodium chlorid solution. Higher equilibrium swelling ratios were obtained at constant temperature by increasing the initial amount of the AAm. Figure 7 exhibit that AUL value decreases with increasing the TBA/AAm weight ratio. At the applied pressure (2.07 kPa), maximum swelling was found to be 17, 19, and 21 (g/g) for the superabsorbent hydrogels with AAm/TBA weight ratios of 1.0, 1.5 and 2.0, respectively. The minimum time needed for the highest AUL in the each sample is estimated to be 180 minutes. After this time, the AUL values were almost unchanged.

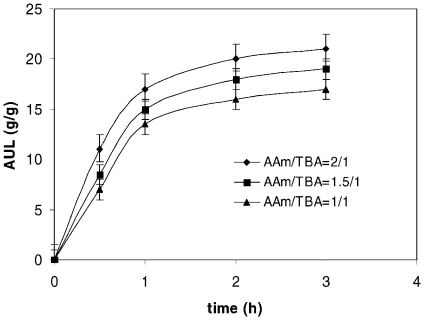


Figure 7.
Time dependence of the AUL values for the superabsorbent hydrogel sample swollen in saline solution (0.9% NaCl).

Conclusion

The alginate-g-poly (TBA-co-AAm) superabsorbent hydrogels was synthesized by graft copolymerization of AAm and TBA onto sodium alginate backbones under normal conditions of the atmosphere. The effect of TBA/AAM weight ratio on the swelling behavior of the superabsorbent hydrogels was investigated. The hydrogels have a good response to the temperature. The swelling ratios at various temperatures show that with increasing the temperature swelling is decreased. In addition, with increasing the initial amount of AAm the temperature sensitivity is slightly increased. The rate parameters were found to be 2.0, 2.4, and 3.5 min for the superabsorbents with AAm/TBA weight ratio of 1.0, 1.3 and 2.0 respectively. As a result, the swelling rate and the porosity of the hydrogel particles increased with increasing the initial TBA/AAM weight ratio. Both the free swelling and the AUL values decrease with increasing the TBA/AAm weight ratio. At the applied pressure (2.07 kPa), maximum swelling was found to be 17, 19, and 21 (g/g) for the superabsorbent hydrogels with AAm/TBA weight ratios of 1.0, 1.5 and 2.0, respectively. These hydrogels may find applications in biomedical field due to the super swelling in water as well as the temperature responsive character.

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