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Synthesis of biopolymer based on H-alginate-graft-poly (sodium acrylate-co-acrylamide)/MMT composite hydrogels

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Abstract

In this research, we synthesized a novel alginate-based composite hydrogel via graft copolymerization of mixtures of acrylic acid(AA) and acrylamide (AAm) onto alginate backbones in the presence clay powder. The composite hydrogel structures were confirmed by, SEM, TG,DTG and porosimeter. The rheological behavior of the prepared gels were measured by rheometer.

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Introduction

Highly swelling polymers, i.e. superabsorbent hydrogels, are hydrophilic, three dimensional networks that can absorb water from 10% up to thousands times of their dry weight. They are widely used in various applications such as hygienics, foods, cosmetics, and agriculture. This accounts for the worldwide increasing production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450000 tons in 1996. Nowadays, the worldwide production of SAPs is more than one million tons a year. Hence, the synthesis and characterization of superabsorbent hydrogels is the main goal of the several research groups in the world(Buchholz *et al.*1997; Peppas *et al.*1990; Wu *et al.*2003) .

The properties of the swelling network (e.g. pH, ionic strength and the counter ion and its valency) affect the swelling characteristics. The hydrogels which sharply and reproducibly respond to the network conditions are referred to as “responsive”, “smart” or “intelligent”. Among these, pH-sensitive hydrogels have been extensively investigated for potential use in site-specific delivery of drugs in specific regions of the gastrointestinal tract and have been prepared for delivery of low molecular weight protein drugs. Although hydrogels made of synthetic polymers, such as polyacrylate, possess excellent water-absorbing properties, their toxicity and non-biodegradability might pose long term environmental problems and limit their use in drug delivery systems and consumer products. Natural-based SAPs polymers have attracted much attention in medical and pharmaceutical fields because of their non-toxic, biocompatibility and biodegradability(Kirk *et al.*1992). Alginate is a biomaterial with the mentioned essential properties. Generally, crosslinking in alginate is used for various purposes such as capsule shells and subsequent partial release of drug contents, alginate swelling, alginate composite hydrogels as biodegradable implants to deliver small and macromolecular drugs, anticancer research and models of alginate microspheres. Recently, attentions have been drawn to employing alginate substrate to produce hydrogels with a specific response to a biological environment. Therefore, following is a continuous research on synthesis of natural-based composite hydrogels. The chemical reaction has a pronounced effect on the molecular structure of polymers. In addition, rheological properties of polymers depend on their molecular mobility. Consequently, it is possible to monitor rheological properties of a reacting system ,i.e., viscosity or modulus (storage and loss modulus) by using a chemorheological approach due to the reaction. Chemorheology is a powerful tool to study chemical cross-linking reactions at which a transition from the liquid to the solid state takes place. A reactive thermosetting resin can be used in an industrial production process with respect to its curing performance(Pourjavadi *et al.*2004; Pourjavadi *et al.*2005). In this paper we attempted to synthesize a novel alginate-based composite hydrogel polymer and investigate the rheological behavior of the prepared gels.

Experimental

Materials

The polysaccharide,Sodium alginate (chemical grade, MW 50000), was used without further purification. Acrylamide (from Merck), MBA (from Fluka) and APS (from Merck) and montmorolonite (from Khorassan Co., Iran, KPS grade, particle size<5µm) were used as received. Acrylic acid (AA, Merck), was used after vacuum distillation. All other chemicals were of analytical grade.

Preparation of Hydrogel

A 1-Liter three-neck reactor equipped with a reflux condenser and a mechanical stirrer was used. In general, 0.75g the polysaccharide was dissolved in 40 mL distilled water. The stirrer speed was maintained at 300 rpm. After complete dissolution of polysaccharide, various amounts of montmorolonite powder (0.25-0.75 g) were added to the alginate solution and allowed to stir (300 rpm) for 15 min. To control the reaction temperature, the rector was placed in a water bath preset at desired temperature. After complete dissolving alginate, 0.1g initiator, APS, was added to the polysaccharide solution and allowed to stir for 5 min. Then, (1-4.5) g of AcA, (.5-3.5) g of AAm monomers (dissolved in 5 mL H_2O) and MBA (0.08 g in 3 mL H_2O) were charged into the reactor. The graft copolymerization was set at 80 °C for 1 h. after the reaction completed, the produced hydrogel was cooled to ambient temperature (Pourjavadi *et al.*2005). To neutralization of the introduced acrylic acid in the composite hydrogel, dilute NaOH solution was used and the composite hydrogel was neutralized to pH 8. Then 400 mL methanol was purred to the composite hydrogel and allowed to dewater for 48 min. the dewatered composite hydrogel filtered and dried in an oven for 24 h at 50 °C.

Results and discussion

One of the most important properties that must be considered is composite hydrogel microstructure morphology. Figure 1 shows scanning electron microscope (SEM) photographs of the surface (Fig. 1A) and the cross-sectional area (Fig. 1B) of the composite hydrogel with interconnected pores. The composite hydrogel has a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. The cross-sectional view of composite hydrogels (Fig. 1B) also exhibited large, open, channel-like structures(Sadeghi *et al.*2010).

The results of BET analysis showed that the average pore diameter of the synthesized composite hydrogel was 12.3 nm. In general, the size of the pores can be controlled by adjusting the various factors such as the type and amount of surfactant, porosigens and gas forming agent during crosslinking polymerization, and the amount of diluent in the monomer mixture (i.e., monomer–diluent ratio). For example, as the amount of diluent (usually water) in the monomer mixture increases, the pore size also increases up to the micrometer (μm) range.

BET surface area analysis is a technique used to determine the specific surface area of powders, solids and granules; the values are expressed in meter square per gram. The BET surface area measurement is crucial for understanding the behavior of a material, as the material reacts with its surroundings via its surface. A higher surface area material is more likely to react faster, dissolve faster and adsorb more gas than a similar material with a lower surface area(Pourjavadi *et al.*2005; Sadeghi *et al.*2010).

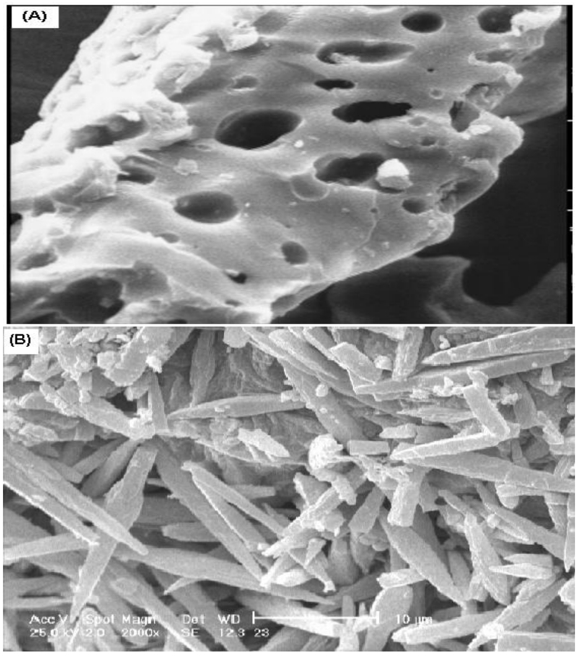

Fig. 1. SEM photograph of the alginate (a), and H-alginate-g-Poly(AcA-co-AAm)/MMT composite hydrogel (b).

Thermogravimetric analysis

As Shown in Figure 2a, TGA of alginate have a weight loss in two distinct stages. The first stage ranges between 121 and 329 °C and shows about 31% loss in weight. This may correspond to the loss of adsorbed and bound water. No such inflexion was observed in the TGA curve of composite hydrogel. This indicated that the composite hydrogel was resistant to moisture absorption. The second stage of weight loss starts at 332 °C and continues up to 448 °C during which there was 28% weight loss due to the degradation of alginate. Grafted samples, however, show almost different behavior of weight loss between 93 and 555 ºC (Fig. 2b). The first stage of weight loss starts at 98 ºC and continues up to 345 ºC due to the degradation of alginate. The second stage from 418 to 555 ºC may contribute to the decomposition of different structure of the composite hydrogel. The appearance of these stages indicates the structure of alginate chains has been changed, which might be due to the grafting of poly AcA and AAm chains. This means that the grafting of monomers onto alginate increases the thermal stability of alginate in some extent(Chen *et al.*2000 ; Cai *et al.*2001).

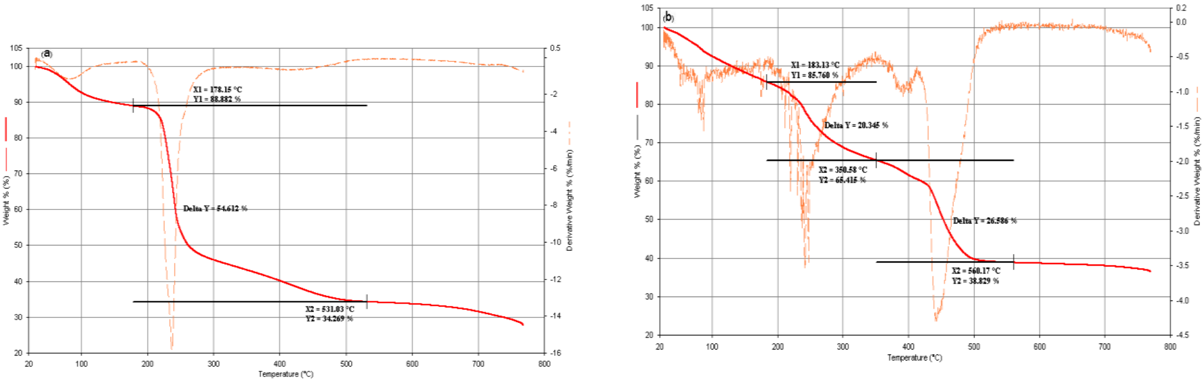

Fig. 2. TGA of crude alginate (a) and H-alginate-g-Poly(AcA-co-AAm)/MMT composite hydrogel (b).

Rheological Properties of hydrogel

The rheological test is carrie out with UDS 200 AntoanParr bob and cup rheometer. On the contrary, dynamic oscillatory measurements allow accurate determination of the gel time of thermosetting systems. In these experiments, the evolution of the storage modulus (G') and the loss modulus (G'') is measured in small amplitude oscillatory shear as a function of cross-linking time while, frequency is kept constant throughout the experiment(Muzumdar *et al.*1996) . As an example, a plot of the G' and G'' versus time at 120°C is presented in Figure 3. Trends in changes of storage and loss moduli at different isothermal temperatures are the same.

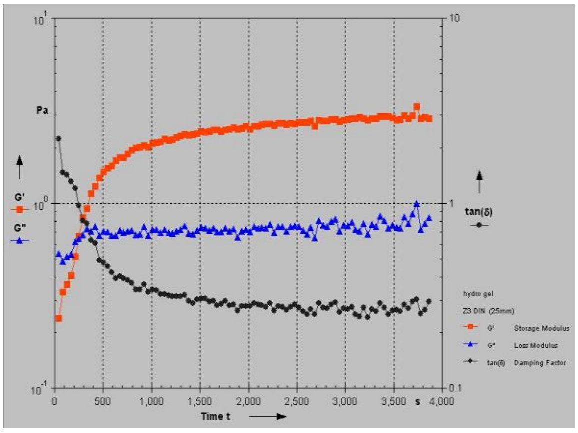

Fig. 3. Evolution trend of storage modulus (G') and loss modulus (G'') versus time at isothermal temperature of 120°C.

Rheological properties such as G' and G'' are very sensitive to changes in molecular structure and phase transitions occurring in thermosetting polymer system. Cross-linking of thermosetting polymers can be modeled as a cluster formation process. During the initial period of reaction, micro-gels are formed with branched and partially cross-linked molecules of colloidal sizes. The polymer continues reactivity to form larger clusters of various sizes distributed randomly in the system(Dean *et al.*2005). Rheologically, the thermosetting resin at the early stage of curing is in liquid state and the viscous behavior dominates the initial part of the curing process, consequently G''>G'. Both of the dynamic moduli increase as a result of increasing cross-link density and molecular weight of the curing polymer system. at the gel point an infinitely large cluster extends throughout the whole system, and a three-dimensional continuous network is formed and a crossover of G' and G'' curves occurs. The cross-over point of G' and G'' during thermoset curing can be applied as a criterion of elasticity domination in a reactive system and has been considered at the gel point. Effects of shear thinning for alginate reactive formulation is shown in fig. 4. As seen, at low shear rates the viscosity increases and with the increase of the shear rate the viscosity decreases. With the progression of the reaction, high molecular weight polymer chains are formed. Consequently, the application of shear rate can induce a shear thinning behavior in long chain entangled macromolecules. The application of the shear rate causes orientations of molecular chains which leads to shear thinning behavior and the dilution effect of shear rate on viscosity (shear thinning behavior) seems to be dominant. Hence, the viscosity of the reactive formulation at higher shear rates is lower than that at lower shear rates (Hong *et al.*2004).

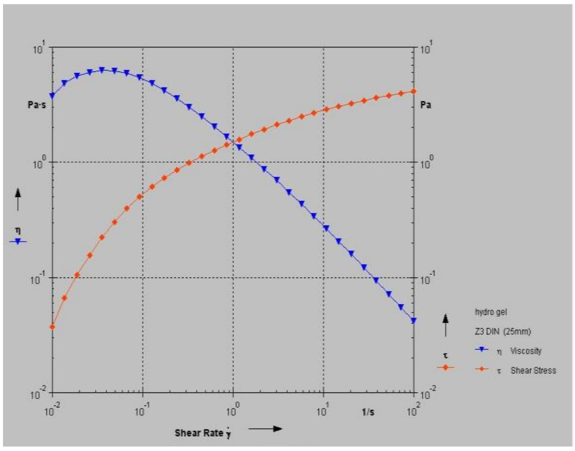

Fig. 4. Shear thinning effect of isothermal curing temperature on the viscosity change of the alginate reactive formulation.

Conclusion

The composite hydrogel based on alginate-*g*-poly(NaAA-co-AAm) was synthesized through simultaneous crosslinking and graft polymerization of acrylic acid/acrylamide mixtures onto alginate. The hydrogel structures were confirmed by SEM and TG/DTG analyzes . In this study, the rheometry results showed that temprature sensivity is times lower below the alginate point than temprature sensivity above it. With the progression of the reaction and formation of long chain macromolecules shear thinning behavior was observed in viscoelastic regions. The evolution of the storage modulus (G') and the loss modulus (G") is measured in small amplitude oscillatory shear as a function of cross-linking time while, frequency is kept constant throughout.

References

Buchholz FL, Graham AT. 1997. Modern Superabsorbent Polymer Technology. Elsevier: Amsterdam.

Peppas, LB.; Harland, RS. 1990. In Absorbent Polymer Technology; Elsevier: Amsterdam.

J. Wu, Y. Wei, J. Lin, S. Lin. 2003. Study on Starch-g-Acrylamide/ Mineral Powder Superabsorbent Composite. Polymer **44**, 6513-6520.

Kirk RE, Othmer DF. 1992. Encyclopedia of Chemical Technology, Vol. 4, Kroschwitz JI, Howe-Grant M. (eds). John Wiley & Sons: New York, 942.

A. Pourjavadi, AM Harzandi, H Hosseinzadeh. 2004. Modified Carrageenan. 3. Synthesis of a Novel Polysaccharide-based Superabsorbent Hydrogel via Graft Copolymerization of Acrylic Acid onto kappa-carrageenan in Air. European Polymer Journal **40**, 1363.

A. Pourjavadi, M. Sadeghi, H. Hosseinzadeh. 2005. Modified Carrageenan. 4. Preparation, Swelling Behavior, Salt- and pH- Sensitivity of Partially Hydrolyzed Crosslinked Carrageenan-graft-Polymethacrylamide Superabsorbent Hydrogel. Polymers for Advanced Technologies **22**, 43-56 .

M. Sadeghi and H. Hosseinzadeh. 2010. Synthesis and super-swelling behavior of a novel low salt-sensitive protein-based superabsorbent hydrogel: collagen-g-poly(AMPS) Turkish Journal of Chemistry **34** ,739-752.

Chen J, Zhao Y. 2000. Relationship Between Water Absorbency and Reaction Conditions in Aqueous Solution Polymerization of Polyacrylate

Superabsorbents. Journal *of* Applied Polymer Science **75**, 808.

Cai J.J., Salovey R. 2001. Chemorheology of model filled rubber compounds during curing. Polymer Engineering & Science **41**, 1853-1858.

Muzumdar S.V., Lee J.L. 1996. Chemorheological analysis of unsaturated polyester-styrene copolymerization, Polymer Engineering & Science **36,** 943-953.

Dean D., Walker R., Theodore M., Hampton E., Nyairo E. 2005. Chemorheology and properties of epoxy/layered silicate nanocomposites, Polymer **46**, 3014-3021.

Hong B.T., Roh S.S., Kim D.S. 2004. Chemorheologicalstudies on a dicyanate resin modified with poly(ether sulfone). Polymer International **53,** 640-645.