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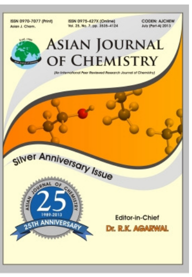

Investigation of Rheology Biocopolymer Based on Starch-poly(sodium acrylate-co-acrylamide)

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In the present paper, attention is paid to investigates rheology of a superabsorbent hydrogel based on starch and polyacrylonitrile. The physical mixture of starch and polyacrylonitrile was hydrolyzed by NaOH solution to yield starch-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel. A proposed mechanism for hydrogel formation was suggested and the structure of the product was established using FTIR spectroscopy.

Key Words: Starch, Polyacrylonitrile, Hydrogel, Rheology.

INTRODUCTION

Loosely crosslinked hydrophilic polymers (hydrogels) being able to absorb and retain hundreds of their own weight of water are known as superabsorbents[1]. The swelling properties of these hydrogels have attracted the attention of researchers and technologists and have found wide-spread applications in drug delivery systems, agriculture, separation processes and many other fields[2,3].

The modification of natural polymers is a promising method for the preparation of new materials. Graft copolymerization of vinyl monomers onto natural polymers is an efficient approach to achieve these materials. Superabsorbing resins were first developed with a view to utilizing agricultural materials and are typed by the hydrolyzed corn starch-g-poly(acrylonitrile), HSPAN[4]. Since then, starches from different resources as well as other polysaccharides, for example, cellulose, hydroxyethyl cellulose, agar, sodium alginate and guar gum were graft copolymerized to achieve water absorbing polymers. Polyacrylonitrile (PAN), polyacryamide and poly(acrylic acid) have been frequently grafted, mostly onto starch, using different initiators especially the ceric-saccharide redox system. Radical polymerization, however, has several disadvantages[5]. The reproducibility of this method is poor and there is little control over the grafting process, so the molecular weight distribution is polydisperse. In addition, the necessity for inert gases (*e.g.*, argon) to prepare an oxygen-free atmosphere and the need for initiators, toxic and/or expensive monomers and crosslinkers are other disadvantages of free-radical polymerization reactions. These problems have been reviewed in detail. For the first time, Fanta[6], with a new method, tried to synthesize of HSPAN superabsorbent hydrogel. They indicated by a solubility test that crosslinks were formed during graft copolymerization, by coupling of the two growing polyacrylonitrile radicals and during saponification, by the attack of starch alkoxide ions on the nitrile groups as the initioation reaction of nitrile polymerization in the early stages of saponification. The nitrile groups of polyacrylonitrile were converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis followed by *in situ* crosslinking of the grafted polyacrylonitrile chains. The initially formed oxygen-carbon bonds between the starch hydroxyls and nitrile groups of the polyacrylonitrile chains remained crosslinking sites. Then, Fanta[6] attempted to extend this idea to the preparation of superabsorbent hydrogels by the saponification of polyacrylonitrile in the presence of polyhydroxy polymers. Finally, Buchholz and Graham[1] reported the preparation of superabsorbing polymers from mixtures of polyacrylonitrile and various saccharides or alcohols.

EXPERIMENTAL

Starch (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). Polyacrylonitrile (PAN) was synthesized through a method mentioned in the literature[4]. Double distilled water was used for the hydrogel preparation and swelling measurements.

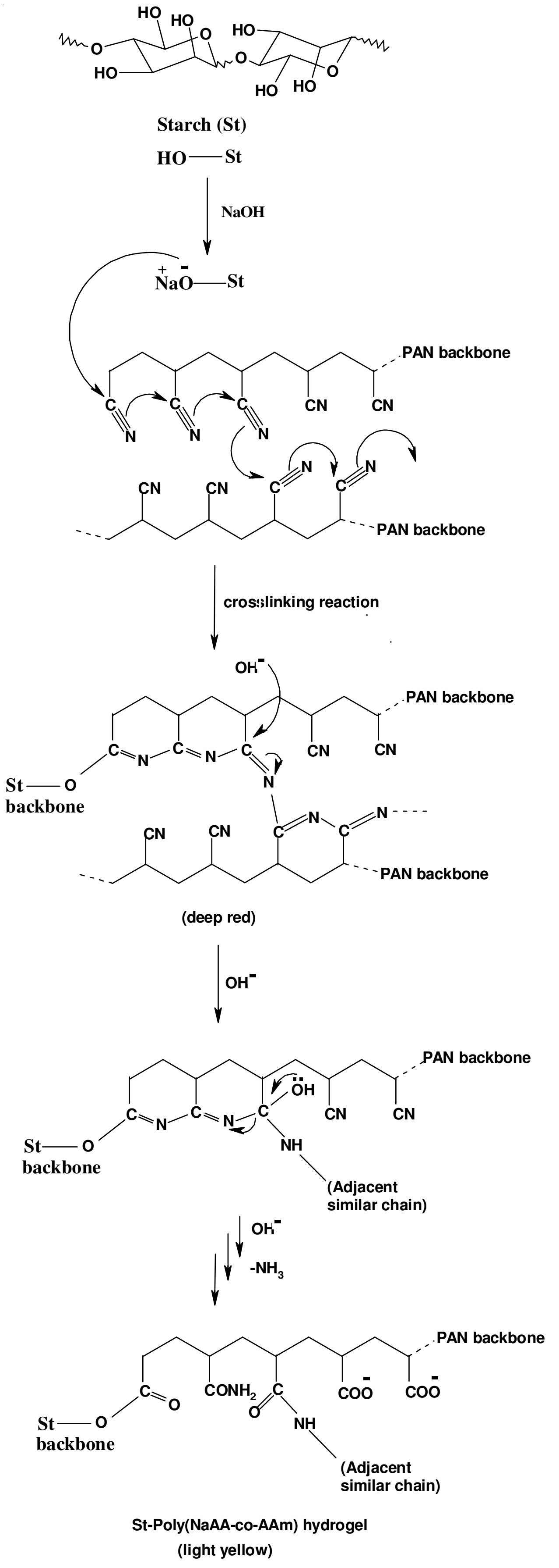
Hydrogel preparation: A facial one step preparative method was used for synthesis of starch-poly(sodium acrylate-co-acrylamide) hydrogel, starch-poly(NaAA-co-AAm), hydrogel. A general procedure for alkaline hydrolysis of starch-polyacrylonitrile mixture was conducted as follows. Starch (0.50-1.33 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 50-500 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath. After complete dissolution of starch to form a homogeneous solution, certain weight per cent of sodium hydroxide (2.0-20.0 wt %) was added to the starch solution at desired temperature (alkalization temperature, 50-90 ºC). The mixture was allowed to stir for certain times (alkalization times, 30-360 min). The various amount of polyacrylonitrile (0.50-1.50 g) was dispersed in the reaction mixture to saponify for certain times and temperatures (alkaline time and temperature). During the saponification NH_3 gas was evolved and a colour change from red to light yellow. This discoloration was an indication of the reaction completion. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8.0 by addition of 10 wt % aqueous acetic acid solution. Then the gelled product was scissored to small pieces and poured in ethanol (200 mL) to dewater for 5 h. The hardened particles were filtered and dried in oven (50 ºC, 10 h). After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light.

Infrared spectroscopy: FTIR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Mechanism of hydrogel formation: A general reaction mechanism for starch-poly(NaAA-co-AAm) hydrogel formation is shown in **Scheme-I**. At the first step, hydroxyl groups of starch substrate was converted to corresponding alkoxide ions using sodium hydroxide solution (**Scheme-I**). Then, these macroalkoxides initiate crosslinking reaction between some adjacent polyacrylonitrile pendant chains. This reaction leads to intermediate formation of naphthyridine cyclic structures (including imine, -C=N-, conjugated bonds) with deep red colour. The intermediate was then hydrolyzed using residual sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups (**Scheme-I**) with a resulting colour change from red to light yellow. This sharp colour change was used as an indication to halt the alkaline treatment. However, incompletely hydrolyzed structures may also give rise to a few crosslinking points result in a loosely crosslinked network. It has been reported, in the case of HSPAN, a maximum conversion of 70 % of nitrile to carboxyl groups and the remaining 30 % are amide groups[7]. In fact, details of the chemical processes and mechanism involved in HSPAN synthesis are not yet well understood. For instance, the incomplete hydrolysis is interpreted as being related to steric and polar factors. It is suggested that condensation might also occur between carboxyl and amide groups to form imide structures. Therefore, in the case of our hydrogel, starch-poly(NaAA-co-AAm), we realized that precise control of the ratio is practically impossible.

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Fig. 1 shows the FTIR spectra of starch-polyacrylonitrile physical mixture and the



Scheme-I: Proposed mechanism for crosslinking during the hydrolysis of nitrile groups of the starch-polyacrylonitrile mixture to produce the starch-poly(NaAA-co-AAm) hydrogel

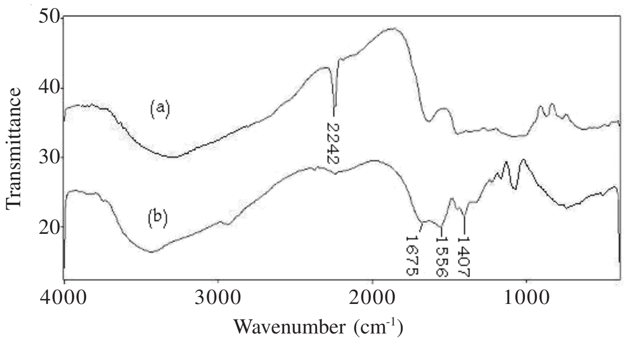


Fig. 1. FTIR spectra of (a) the physical mixture of starch and polyacrylonitrile and (b) the crosslinked starch-poly(NaAA-co-AAm) hydrogel

resulted hydrogel, starch-poly(NaAA-co-AAm). The band observed at 2242 cm^{-1} can be attributed to stretching of -CN group of polyacrylonitrile (Fig. 1a). The hydrogel comprise an starch backbone with side chains that carry carboxamide and carboxylate functional groups that are evidenced by three new peaks at 1407, 1556 and 1675 cm^{-1} (Fig. 1b). These peaks attributed to C=O stretching in carboxamide functional groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively[8]. The stretching band of -NH overlapped with the -OH stretching band of the starch portion of the copolymer. As shown in Fig. 1b and **Scheme-I**, after alkaline hydrolysis, most of the nitrile groups are converted to carboxamide and carboxylate groups.

To obtain an additional evidence of *in situ* crosslinking during alkaline hydrolysis, a similar reaction was conducted in absence of the polysaccharide. Since the resulted product became soluble, the crosslinks really formed between the alkoxide ions of starch and the nitrile groups of polyacrylonitrile. This fact practically proves that the starch hydroxyls are involved in the crosslinking.

Rheological properties of hydrogel: The rheological test is carried 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[9]. As an example, a plot of the G' and G" versus time at 120 ºC is presented in Fig. 2. Trends in changes of storage and loss moduli at different isothermal temperatures are the same.

Rheological properties such as G' and G" are very sensitive to changes in molecular structure and phase transitions occurring in thermosetting polymer systems[10]. 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[11].

Rheologically, the thermosetting resin at the early stage of curing is in liquid state and the viscous behaviour 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[11].

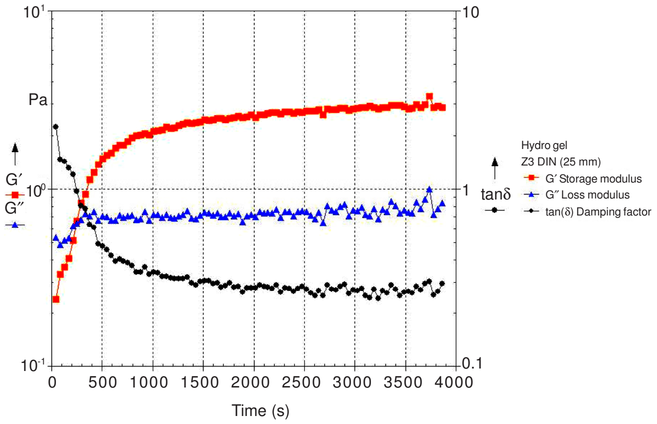


Fig. 2. Evolution trend of storage modulus (G') and loss modulus (G") *versus* time at isothermal temperature of 120 ºC

Effects of shear thinning for polysaccharide reactive formulation is shown in Fig. 3. 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 behaviour in long chain entangled macromolecules.

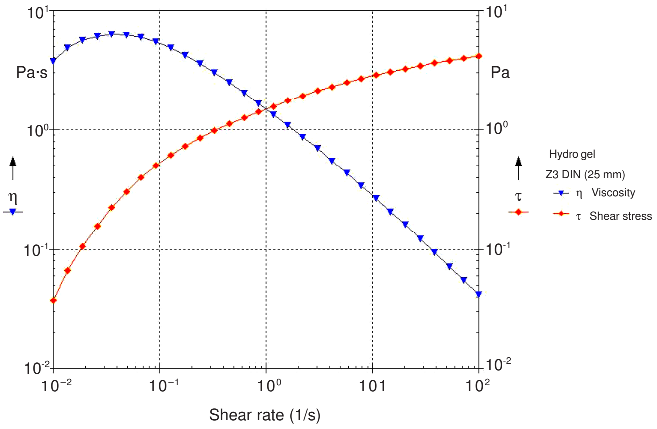


Fig. 3. Shear thinning effect of isothermal curing temperature on the viscosity change of the starch reactive formulation

The application of the shear rate causes orientations of molecular chains which leads to shear thinning behaviour and the dilution effect of shear rate on viscosity (shear thinning behaviour) seems to be dominant. Hence, the viscosity of the reactive formulation at higher shear rates is lower than that at lower shear rates[12].

Conclusion

The biocopolymer, starch-g-polyacrylonitrile, was synthesized through alkaline hydrolysis of starch-polyacrylonitrile physical mixture. The reaction of starch alkoxide anions with nitrile groups of polyacrylonitrile, forms crosslinking points and results in a three-dimensional network. The rheometry results showed that temperature sensivity is times lower below the polysaccaride point than temprature sensivity above it. With the progression of the reaction and formation of long chain macromolecules shear thinning behaviour 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. The polysaccaride time was obtained from the modulus cross-over.

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