



Rheology Behaviour of a Biopolymer Based on Chitosan-g-poly(Acrylamide-co-AcA) Hydrogels

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Acrylamide monomer was directly grafted onto chitosan using ammonium persulfate as an initiator and methylenebisacrylamide as a crosslinking agent under an inert atmosphere. Infrared spectroscopy and thermogravimetric analysis were carried out to confirm the chemical structure of the hydrogel. Moreover, morphology of the samples was examined by scanning electron microscopy. The rheology behavior of the synthesized hydrogels was preliminarily investigated with oscillating and rotational rheometer.

Key Words: Chitosan, Polyacrylamide, Biopolymer, Superabsorbent, Reochemical.

INTRODUCTION

In recent years, there has been considerable interest in water-swallowable super absorbent polymers capable of absorbing and holding a large amount of water while maintain the physical dimension structure. Super absorbents are three-dimensional networks of hydrophilic polymers held together by crosslinks of covalent bonds or ionic and/or secondary forces in the form of hydrogen bonds or hydrophobic interactions¹⁻³. Their affinity for water makes them useful especially for agriculture, personal hygiene products, industrial absorbents, medicine and cosmetics⁴⁻⁶.

Because of their exceptional properties, *i.e.*, biocompatibility, biodegradability, renewability and non-toxicity, polysaccharides are the main part of the natural-based super absorbent hydrogels. Graft copolymerization of vinyl monomers onto polysaccharides is an efficient rout to preparation of hydrogels. The hydrogel forming ability through graft copolymerization of vinyl monomers onto polysaccharides such as starch, chitosan, sodium alginate, carrageenan and cellulose has been well documente^{7,8}. Because of the presence of certain functional groups along the polymer chains, hydrogels are often sensitive to the conditions of the surrounding environment, which are referred to as "intelligent materials" or "smart materials". For example, the water uptake of these materials may be sensitive to temperature, pH, or ionic strength of the swelling solutions, or even to the presence of a magnetic field or ultraviolet light⁹. These smart hydrogels are of general interest for biomedical applications, such as artificial muscles or switches, biomedical separation systems and controlled release systems.

Chitosan is a linear natural polysaccharide composed of a partially deacetylated material of chitin. It is a basic polymer, having amine side groups^{10,11}. Due to its excellent biocompatibility and biodegradability, chitosan and its derivatives were widely applied to fabrication of biomedical materials, enzyme and cell immobilization, especially for drug delivery. Since chitosan is easily soluble in acidic solutions, crosslinking of chitosan to form a network is the only way to prepare chitosan hydrogels. Conventional chitosan crosslinking reactions have involved a reaction of chitosan with formaldehyde and dialdehydes, such as glutaraldehyde, diglycidyl ethers, or epoxides. By crosslinking chitosan with dialdehydes, one can obtain a hydrogel with a swelling ability in acidic media. When anionic monomer such as acrylic acid is grafted onto chitosan (in the presence of a divinyl crosslinking agent monomer), an ampholytic hydrogel containing both cationic and anionic charges is prepared. So, by introducing anionic charges (-COO⁻) onto chitosan, a hydrogel with swelling ability at various pHs is prepared. In our previous works, we reported about synthesis of novel ampholytic hydrogels by hydrolysis of chitosan-g-poly(acrylonitrile) and binary graft copolymerization of the acrylamide (AAM) and acrylic acid monomers onto chitosan^{12,13}. In the present work, we study the the preparation and characterization rheology of chitosan-g-PAAm hydrogels.

EXPERIMENTAL

Chitosan (from Fluka, with m.w. = 22742 and degree of deacetylation of 0.7) was used as received. Acrylamide (AAM, Fluka) was used after recrystallization from acetone (for removing of inhibitor) below 30 °C. Ammonium persulfate

(APS) was used without purification. Methylenebisacrylamide (MBA, Fluka) was used as received. All other chemicals were of analytical grade.

Synthesis of hydrogels: Chitosan solution was prepared in a 1 L reactor equipped with a mechanical stirrer and an inert gas inlet (argon). Chitosan was dissolved in degassed, distilled water containing 1 wt % of acetic acid. In general, 0.50 g of chitosan was dissolved in 30 mL of the acetic acid solution. The reactor was placed in a water bath at 60 °C. Then 0.10 g of ammonium persulfate was added to the chitosan solution and stirred for 10 min at 60 °C. Following this, acrylamide (2 g) was added to the chitosan solution. Methylene bisacrylamide (0.05 g) as a crosslinker was added to the reaction mixture after the addition of monomer and the mixture was continuously stirred for 1 h under argon atmosphere. After 1 h, the reaction product was allowed to be cooled to ambient temperature. The resulting hydrogel was neutralized to pH 8 by addition of 1 N NaOH solution. Then methanol (500 mL) was added to the gel product while stirring. After complete dewatering for 24 h, the product was filtered, washed with fresh methanol (2 mL × 50 mL) and dried at 50 °C.

The chitosan-g-PAAm (0.50 g), was then saponified using 20 mL aqueous 1.0 N NaOH solution in a loosely stopper 100 mL flask at 100 °C for 1 h. The hydrolyzed chitosan-g-PAAm (H-chitosan-g-PAAm) product was then allowed to be cooled to ambient temperature and neutralized to pH 8 by addition of 10 wt % acetic acid solutions. Methanol (200 mL) was added to the gel product while stirring. After complete dewatering (for 3 h), the yellow product was filtered, washed with fresh methanol (2 mL × 50 mL) and dried in an oven at 50 °C.

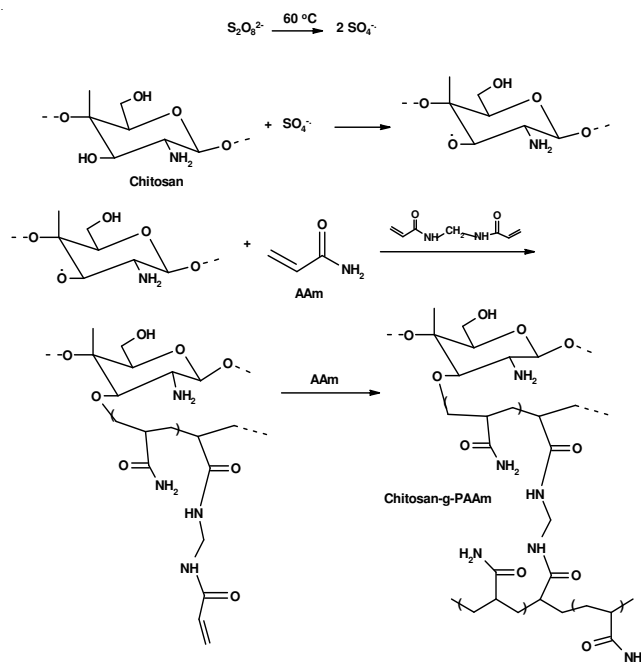
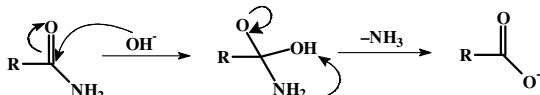
Infrared analysis: The dried samples were crushed with KBr to make pellets. Spectra were taken on an ABB Bomem MB-100 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Super absorbent hydrogels were prepared by graft copolymerization of acrylamide onto chitosan in the presence of MBA as a crosslinking agent. Ammonium persulfate was used as an initiator. The persulfate is decomposed under heating and produced sulfate anion-radicals that remove hydrogen from -OH groups of chitosan backbones. So, this persulfate-saccharide redox system results in active centers capable to radically initiate polymerization of acrylamide leading to graft copolymer. Since the crosslinking agent, MBA, is presented in the system, the copolymer comprises a crosslink structure. A possible mechanism of the polymerization of acrylamide onto chitosan in the presence of MBA was shown in **Scheme-I**.

To obtain a hydrogel with a high swelling capacity, the chitosan-g-PAAm hydrogel copolymer was hydrolyzed with NaOH solution, the hydrolyzed chitosan-g-PAAm being termed H-chitosan-g-PAAm. During the saponification, ammonia evolves and amide groups are converted to carboxylate salts. This reaction can be shown as below:

The absorbency, pH-sensitivity and salt-sensitivity of these hydrogels were investigated. Fig. 1 shows FTIR spectra of



Scheme-I: General mechanism for APS-initiated graft copolymerization of acrylamide onto chitosan in the presence of MBA

chitosan-g-PAAm and H-chitosan-g-PAAm hydrogels (in dried stat). In the spectrum of chitosan-g-PAAm (Fig. 1a), two absorption band in 3206-1660 cm^{-1} region correspond to the primary amides and amide -NH stretching vibrations, respectively. Under saponification conditions, the amide groups were converted to carboxylate groups. In the hydrolyzed hydrogel (Fig. 1b), the intense characteristic band at 1566 cm^{-1} is due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by another sharp peak at 1406 cm^{-1} which is related to a symmetric stretching mode of the carboxylate anion. A combination of absorptions of the carboxylate and alcoholic O-H stretching appears in the wide range¹⁴⁻¹⁶ of 3500-2550 cm^{-1} .

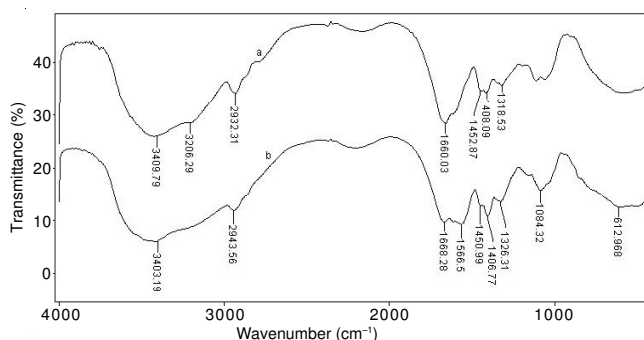


Fig. 1. FTIR spectra of (a) chitosan-g-PAA and (b) H-chitosan-g-PAA

Scanning electron microscopy: The surface morphology of the samples was investigated by scanning electron microscopy. Fig. 2c shows an SEM micrograph of the polymeric hydrogels (H-chitosan-g-polyAAm) obtained from the fracture surface. The hydrogel have 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.

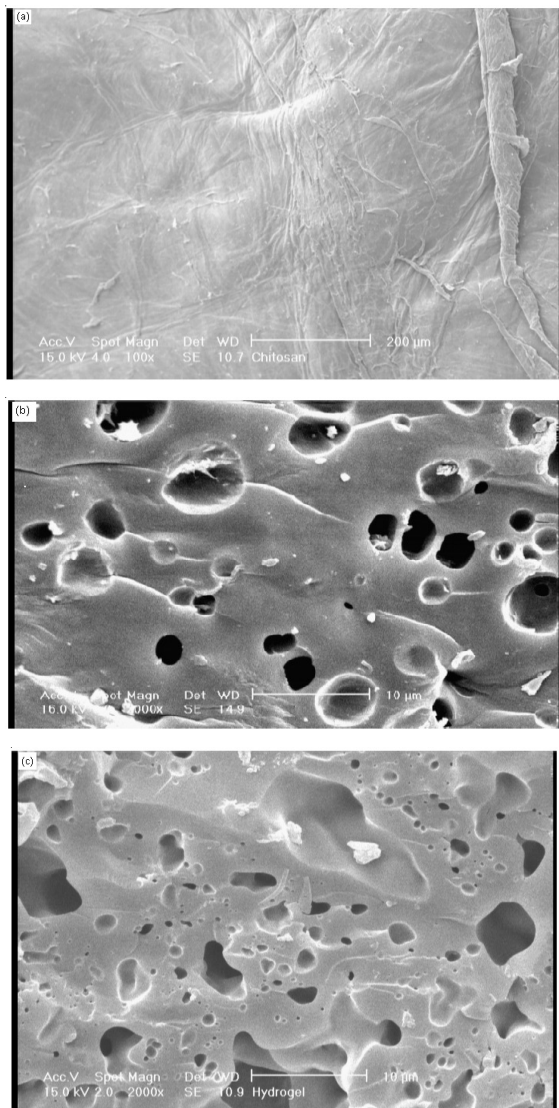


Fig. 2. SEM photograph of the chitosan (a), chitosan-g-PAAm copolymer (b) and H-chitosan-g-PAAm-co-PAA hydrogel (c)

Rheometric tests: The prepared hydrogel rheological behaviours were studied with UDS 200 Parr Physica rheometer with two oscillation and rotation modes of measurement. Dynamic oscillatory measurements allow to determination of the gel systems states. Small amplitude sinusoidal oscillatory testing as function of test frequency is a rapid and often used method to measure the viscous and elastic properties of a polymer simultaneously. Two parameters are most often reported-Storage (elastic) modulus (G') and Viscous (loss) modulus (G'') which represent the relative degrees of the material to recover (elastic response) or flow (viscous response) respectively as the rate of deformation changes¹⁷. A typical response for a polymer melt is to exhibit elastic dominated behavior at high frequencies and viscous dominated behaviour at low frequencies. This means that there is a critical frequency at which the two responses are equal. This is obviously a well defined point and conveniently this "cross-over" frequency and modulus has been shown to depend on the molecular weight and molecular weight distribution of some linear polymers. At cross-over point gel is formed completely and this point gelation point. The frequency sweep test result is shown in Fig. 3.

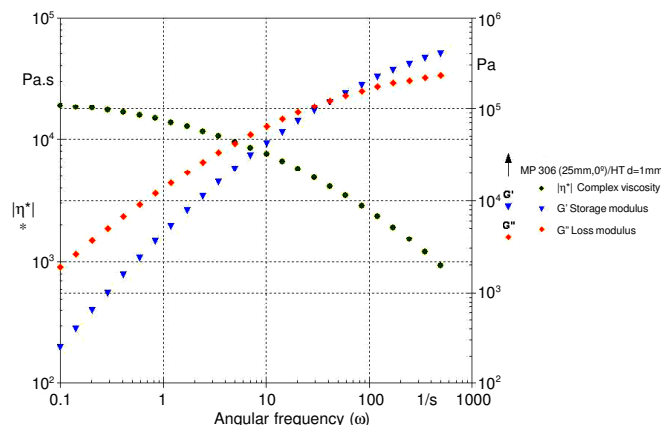


Fig. 3. Frequency Sweep test for gel. The cross-over point is determined by the average molecular weight and molecular weight distribution

A potential advantage of utilizing this point as a quality control tool is that the cross-over of elastic and viscous moduli occurs at significantly higher frequencies than the point at which a constant value of shear viscosity occurs. Testing times may therefore be considerably reduced when compared to making flow curve measurements or performing creep tests¹⁸.

Flow curves to measure the shear viscosity *versus* shear rate or shear stress. At sufficiently low shear rates a constant value for the viscosity will be attained. This so called zero shear viscosity has been shown to depend on the average molecular weight of the polymer and the length of the plateau (how high a rate before the viscosity decreases) is known to reflect the width of the molecular weight distribution. Flow curve test result for prepared gel is shown in Fig. 4. In these experiments, the evolution of the modulus $G(t)$ is measured in small amplitude oscillatory shear as a function of cross-linking time while, frequency is kept constant throughout the experiment¹⁹.

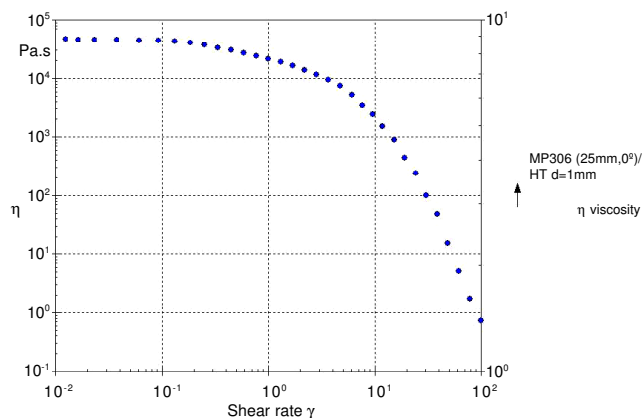
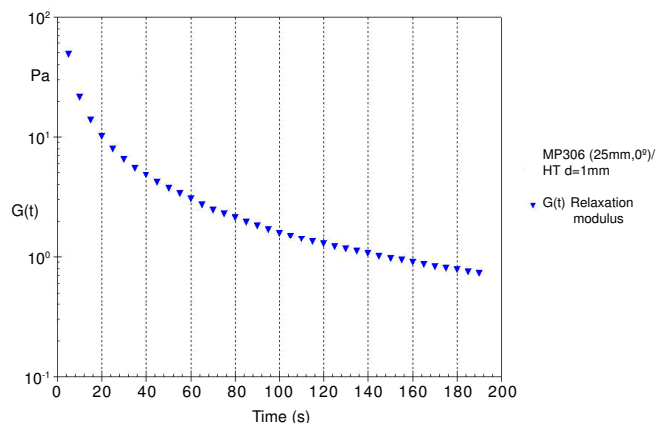


Fig. 4. Flow curve for hydrogel showing low shear rate plateau for viscosity. The magnitude of the zero shear viscosity is determined by the average molecular weight of the polymer

As an example, a plot of the $G(t)$ *versus* time at 120 °C is presented in Fig. 5. Trends in changes modules at different isothermal temperatures are the same. Fig. 5 shows that the prepared gel is a structural gel. Rheological properties such as $G(t)$ is sensitive to changes in molecular structure and

Fig. 5. $G(t)$ versus time at 120 °C for prepared hydrogel

phase transitions occurring in thermosetting polymer systems¹⁷. Cross-linking of thermosetting polymers can be modeled as a cluster formation process¹⁹. During the initial period of reaction, micro-gels are formed with branched and partially cross-linked molecules of colloidal sizes¹⁸. The polymer continues reactivity to form larger clusters of various sizes distributed randomly in the system²⁰. At final when the gel is formed completely, we have a broad distribution of macro molecules.

Depending on the type of oscillatory test the frequency, deformation and temperature can be varied. In an amplitude sweep the amplitude is varied and the frequency kept constant. This test provides information on the limit of the linear-viscoelastic (LVE) range and the structural character of the sample. The following characters are defined: Gel or paste character with $G' > G''$ and liquid character with $G'' > G'$. The structural strength of a substance is expressed by the G' value. Test result for amplitude sweep of the prepared gel is shown in Fig. 6. This fig shows that the hydrogel behavior is linear viscoelastic until 5 % of strain and the gel is maintainer it behavior until 30 % of strain. G' and G^* is very close to each other at this strain²¹.

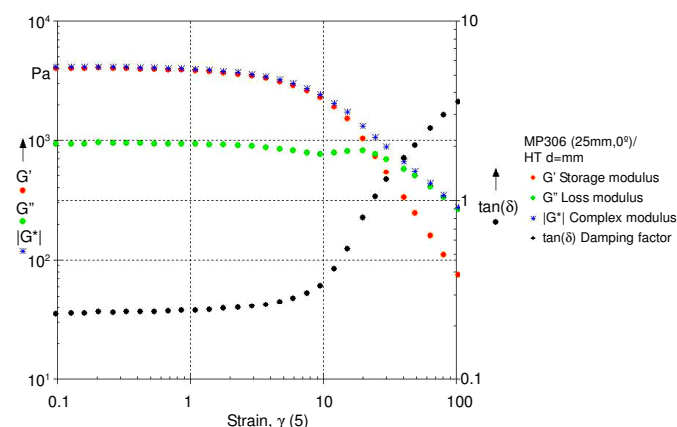


Fig. 6. Strain sweep test at 120 °C for prepared hydrogel

Time sweep test for prepared hydrogel is show in Fig. 7. This figure shows viscosity changes verses. time at 120 °C. It shows that the complex viscosity is near to the loss viscosity, thus the hydrogel is more flexible²¹.

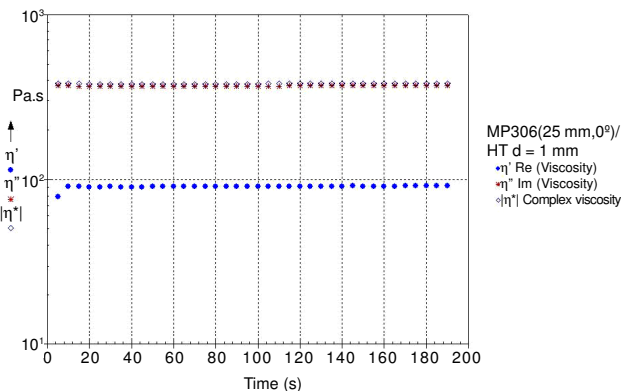


Fig. 7. Time sweep test for prepared hydrogel. Viscosity changes versus time at 120 °C

Conclusion

Super absorbent hydrogels, Chitosan-g-PAAm and H-chitosan-g-PAAm, were synthesized through grafting of acrylamide onto chitosan and saponification of chitosan-g-PAAm, respectively. Formation of long chain macromolecules of hydrogel is verified with rheology test. Shear thinning behaviour was observed in viscoelastic regions. The shear thinning phenomenon of long chain gelatin molecules counters the influence of the shear rate on the increase of the mobility of functional groups. The hydrogel behavior is linear viscoelastic up to 5 % strain. The changes of the modulus, with time and strain measured in small amplitude oscillatory shear as a function of cross-linking time while, frequency is kept constant throughout. Its shows the prepared hydrogel is completely a structural gel.

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