Synthesis, Characterization and Rheochemical of biocopolymer based on Gelatin

Esmat Mohammadinasab, Mohammad Sadeghi and Fatemeh Shafiei

Chemistry Department, Science Faculty, Islamic Azad University, Arak Branch, Arak, Iran.

ABSTRACT

In the present paper, a novel superabsorbent hydrogel composite based on gelatin have been prepared via graft copolymerization of acrylic acid (AA) in the presence of kaolin powder using methylenebisacrylamide (MBA) as a crosslinking agent and ammonium persulfate (APS) as an initiator. The composite structure was confirmed using FTIR spectroscopy. A new absorption band at 1728 cm⁻¹ in the composite spectrum confirmed kaolin-organic polymer linkage. The rheology behaviors of the synthesized hydrogels were preliminarily investigated with oscillating and rotational rheometer. The rheology test shows the prepared gels are structural gel.

Key words: gelatin, acrylic acid, composite, chemorheology.

Introduction

Vinyl graft copolymerization onto polysaccharide backbones is a well-known method for synthesis of natural-based superabsorbent hydrogels [1-4]. The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile, was synthesized using this method [5]. These biopolymer materials are crosslinked hydrophilic polymers, capable of absorbing large quantities of water, saline or physiological solutions [6]. They are widely used in many fields such as hygienic, cosmetics, and agriculture [7-9].

Because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability, and non-toxicity, polysaccharides and proteins are the main part of the natural-based superabsorbent hydrogels. The higher production cost and low gel strength of these superabsorbents, however, restrict their application widely. To improve these limitations, inorganic compounds with low cost can be used. The introduction of inorganic fillers to a polymer matrix increases its strength and stiffness properties. Among inorganic compounds, special attention has been paid to clay minerals in the field of nanocomposites because of their small particle size and intercalation properties. Mineral powders are hydrated layered aluminosilicate with reactive -OH groups on the surface. The interaction of mineral powders, reactive site of natural polymers and monomers result in a superabsorbent composite. Superabsorbent composites based on synthetic polymers [10,11] or natural polymers [12,13] have been reported.

Gelatin is a biomaterial with the above mentioned essential properties. Generally, crosslinking in gelatin used in various purposes such as capsule shells and subsequent partial release of drug contents, gelatin swelling, and gelatin hydrogels as biodegradable implants to deliver small and macromolecular drugs, anticancer research and models of gelatin microspheres.

In this work, we attempt to synthesize and characterize new superabsorbent composites based on gelatin in the presence of kaolin particles. The preparation of the biopolymer-based superabsorbent composites can also improve the mechanical properties of materials and can lower the cost of the finished product compared with the synthetic counterparts as well as providing biodegradable characteristics.

Rheological experiments give the trend of the changes in gel time especially in the critical point of gelation temperature. The result of rheological measurements in linear viscoelastic domain is only valid when the deformation is either quite small or very slow. However, in polymers forming operations the deformations are generally both large and rapid, and this necessitates the non-linear viscoelastic measurements to study polymer processing operations. In addition, for a cross-linking polymer, gel formation leads to evolution of a network-like structure throughout the system. These structures...
may be perturbed by application of shear rate in non-linear viscoelastic domain.

**Experimental:**

**Materials:**

Gelatin (Merck) was used as received. Acrylic acid (AA, Merck), was used after vacuum distillation. Ammonium persulfate (APS, Merck) was used without purification. Methylene bisacrylamide (MBA, Fluka), was used as received. All other chemicals were of analytical grade.

**Superabsorbent composite synthesis:**

A general procedure for chemically crosslinking graft copolymerization of AA onto gelatin backbones was conducted as follows. Variable amounts of gelatin (0.25-0.75 g) were added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 35 mL doubly distilled water. The reactor was placed in a thermostated water bath to control the reaction temperature at 70°C. After complete dissolution of gelatin, various amounts of kaolin powder (0.75-0.25 g) were added to the solution and allowed to stir for 10 min. Then, APS initiator (0.05-0.4 g, dissolved in 5 mL water) was added to the reaction mixture and the mixture was stirred for 10 min. MBA (0.05-0.2 g, dissolved in 5 mL water) and AA (1.0-5.0 g, completely neutralized with NaOH) were poured into the reactor. All of the reactions were carried out at 70 oC under an argon gas atmosphere and the reaction mixture was continuously stirred (300 rpm) for 1 h. At the end of the reaction, the gelly product was poured in ethanol (300 ml) and allowed to dewater for 24 h. Then, the product was filtered and washed with 100 mL ethanol. The filtered product was dried in an oven at 50°C for 10 h. After grinding, the powdered superabsorbent composite was stored away from moisture, heat and light.

**Results And Discussion**

**Synthesis and characterization:**

The superabsorbent composite was prepared by graft copolymerization of acrylic acid onto gelatin in the presence of a crosslinking agent and powdery kaolin. Ammonium persulfate was used as an initiator. The persulfate is decomposed under heating and produced sulfate anion-radicals that abstract hydrogen from one of the functional groups in side chains (i.e. COOH, SH, OH, and NH₂) of gelatin backbones. So, this persulfate-saccharide redox system results in active centers capable to radically initiate polymerization of acrylic acid led to a graft copolymer. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a crosslinked structure.

FTIR spectroscopy was used for identification of the hydrogel. The FTIR spectra of initial substrates and composite graft copolymer are depicted in Figure 1. Fig. 1a represents the spectrum of the physical mixture of kaolin and gelatin substrates. In the layer silicate structure, -OH groups show absorption bands at 3628-3675 cm⁻¹. The band observed at 1634 cm⁻¹ can be attributed to C=O stretching in carboxamide functional groups of substrate backbone. In the spectrum of the composite (Fig 1b), two new absorption peaks at 1558 and 1728 cm⁻¹ are appeared. The characteristic band at 1558 cm⁻¹ is due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by another peak at 1411 cm⁻¹ which is related to the symmetric stretching mode of the carboxylate groups [14]. The absorption band at 1728 cm⁻¹ can be corresponding to the ester groups that can be formed during the graft polymerization reaction. The carboxylate groups of the grafted poly(acrylic acid) can be react with the -OH groups on the kaolin surface. The replacement of -OH groups in the surface of kaolin by carboxylate anions results in the ester formation. The reaction can be shown as follows:

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Si-OH + O-CO
Surface of kaolin Carboxylate anions
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As shown in this figure, the absorption bands of -OH of kaolin at 3628-3674 cm⁻¹ are disappeared.

**Scanning electron microscopy:**

One of the most important properties that must be considered is hydrogel composite microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Figure 2b shows an SEM micrograph of the polymeric hydrogels composite (H-Gelatin-polyAA/Kaolin) obtained from the fracture surface. The composite 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.
**Fig. 1:** FTIR spectra of (a) physical mixture of gelatin and kaolin, and (b) gelatin-g-poly(acrylic acid)/kaolin composite.

**Fig. 2:** SEM photograph of pure gelatin (a) and the composite (b). Surfaces of composite was taken at a magnification of 2000, and the scale bar is 10 μm.
**Rheometric Tests:**

The prepared hydrogel rheological behaviors 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 changes [17]. A typical response for a polymer melt is to exhibit elastic dominated behavior at high frequencies and viscous dominated behavior 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. 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 tests [18].

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 experiment [19]. 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 very sensitive to changes in molecular structure and phase transitions occurring in thermosetting polymer systems [17]. Cross-linking of thermosetting polymers can be modeled as a cluster formation process [19]. During the initial period of reaction, micro-gels are formed with branched and partially cross-linked molecules of colloidal sizes [18]. The polymer continues reactivity to form larger clusters of various sizes distributed randomly in the system [20]. 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 maintained its behavior until 30% of strain, G’ and G* is very close to each other at this strain [21].

Time Sweep test for prepared hydrogel is shown in fig 8. 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 flexible [21].

**Conclusion:**

A novel natural-based superabsorbent composite polymer was prepared by graft copolymerization of acrylic acid onto gelatin backbones in the presence of a crosslinking agent. The resultant superabsorbent composite had a large degree of water absorbency. The study of FTIR spectra shows that in the composite spectrum a new absorption band at 1728 cm⁻¹ was appeared that attributed to the ester formation from replacement of hydroxyl groups of kaolin with grafted carboxylate anions onto polysaccharide backbones. The optimum reaction conditions was achieved at MBA 0.006 mol/L, initial AA 0.97 mol/L, APS 0.017 mol/L, gelatin 0.02 and kaolin 0.01 wt %. The effect of the kaolin amount and MBA concentration showed that with increasing of these parameters, the water absorbency of the superabsorbent composite are decreased.

Formation of long chain macromolecules of hydrogel is verified with rheology test. Shear thinning behavior 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.
**Fig. 3:** Frequency Sweep test for gel. The Cross-Over Point is determined by the average molecular weight and molecular weight distribution.

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

Fig. 6: Strain Sweep test at 120°C for prepared hydrogel.
Fig. 7: Time Sweep test for prepared hydrogel. Viscosity Changes vs. time at 120°C.

References