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Radiation synthesis and characterisation of the network structure of natural/synthetic double-network superabsorbent polymers

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ABSTRACT

In this study radiation synthesis and characterisation of the network structure of acrylic acid sodium salt/locust bean gum, (AAcNa/LBG) natural/synthetic double-network super absorbent polymers were investigated. Quartet systems composed of acrylic acid sodium salt/locust bean gum/N,N methylene bis acrylamide/water (AAcNa/LBG/MBAAm/water) were prepared at varying degree of neutralisations (DN) by controlling the DN value of AAc and irradiated with gamma rays at ambient temperature at a very low dose rate. The influences of the DN on the swelling and network properties were examined. It was observed that the DN strongly affected the gelation and super absorption properties of the gels. Molecular weight between crosslinks ($\overline{M}_c$), effective crosslink density (v_e) and mesh size (ξ) of SAPs were calculated from swelling and shear modules data obtained from compression and oscillatory frequency sweep tests. $\overline{M}_c$ values obtained from the uniaxial deformation experiments were very close to those obtained from the oscillatory shear experiments excluding the completely neutralised gel system. It was concluded that the uniaxial compression technique could be used for the characterisation of the network structure of a hydrogel as along with the rheological analyses; however, a very precise control of the gel size was also needed.

1. Introduction

Superabsorbent polymers (SAPs) are moderately crosslinked, 3-D, hydrophilic network polymers that can absorb and conserve considerable amounts of aqueous fluids even under certain heat or pressure. Because of the unique properties superior to conventional absorbents, SAPs have found potential application in many fields such as hygienic products, disposable diapers, horticulture, gel actuators, drug-delivery systems, as well as water-blocking tapes, coal dewatering, water managing materials for the renewal of arid and desert environment, etc. (Buchholz and Peppas, 1994). In recent years, naturally available resources, such as polysaccharides have drawn considerable attention for the preparation of SAPs. Since the mechanical properties of polysaccharide based natural polymers are low, researchers have mostly focused on natural/synthetic polymer/monomer mixtures to obtain novel SAPs (Gulrez et al., 2011).

The aim of this study is to synthesise novel double-network (DN) hydrogels as a SAP, and to characterise their network structures. Double network hydrogels with high mechanical strength were prepared by radiation induced polymerisation and crosslinking of AAcNa in the presence of natural polymer locust bean gum. Liquid retention capacities and absorbency under load (AUL) analysis of the SAPs synthesised were performed in water in order to determine their SAP character. For the characterisation of the network structure of the semi-IPN hydrogels, the average molecular weight between crosslinks ($\overline{M}_c$) were evaluated through uniaxial compression and oscillatory rheological measurements; and the advantages and disadvantages of these two techniques were compared.

2. Experimental

2.1. Radiation synthesis of double networks

For the preparation of the AAcNa salt (AAcNa)/LBG hydrogels a 4 ml of aqueous LBG solution (2% (w/v)) was mixed with a 0.4 ml of aqueous AAcNa solution. N,N′-methylenebisacryl amide, a bifunctional water soluble compound, was added (2% of AAc (w/w)) as a crosslinking agent in this solution. For the preparation of the AAc solutions in different DNs, 0.01 mol AAc was mixed with 0.01 mol NaOH to obtain a theoretically complete neutralization. Then, for the preparation of the 50, 60, 70, 80, or 90 mol% neutralised AAc, 0.005, 0.0040, 0.003, 0.002, or 0.001 mol of AAc was added into this solution and then 0.4 ml of this solution was mixed with 4 ml of aqueous LBG solution. The resultant solutions were placed in PE injectors with a diameter of 5 mm, and

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irradiated at ambient temperature up to 0.72 kGy in a Gammacell-220 type γ-irradiator at a dose rate of 30 Gy/h. The SAPs obtained in long cylindrical shapes were cut into shorter pieces (1–2 mm in height), and washed for three days by keeping them in distilled water to remove the soluble fractions. After that, samples was dried and using a grinder, they were first converted into powder form and stored for later evaluations.

For the determination of the water absorption under load, a macro porous sintered glass filter plate was placed in a Petri dish, and the dry hydrogel sample was uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid weight, which could slip freely in a glass cylinder was used to apply the desired pressure (2.1 kPa) to the dry hydrogel particles (Şen and Hayrabolulu, 2009). The sample was then covered by the solution so that the liquid level was equal to the height of the sintered glass filter. The dish and its contents were covered to prevent surface evaporation and probable change in the concentration. The swollen particles were weighed at regular time intervals and swelling degree was calculated using the equation, $S=(W_2-W_1/W_1)$, where, W_1 and W_2 were the weights of the dry and swelled gels, respectively.

Oscillatory rheological measurements to determine the elastic moduli of the gels were carried out at 25 °C in a Thermo MARS II Rheometer equipped with a PP20 (20 mm diameter plate/plate geometry). All measurements were performed in the linear viscoelastic region ($\gamma=0.01$–1% (depending on the sample)) in the frequency range of $\omega_o=0.01$–1 Hz. Using the phase shift, δ, and the ratio of the maximum amplitude of shear stress, τ_o, to the maximum amplitude of deformation, γ_o, the complex oscillatory modulus G^* and its components, elastic modulus (G') and viscous modulus G'', were measured. The elastic moduli of the hydrogels were also determined using a Zwick Z010 model Universal Testing Instrument with a uniaxial compression module (Uzun et al., 2003).

3. Results and discussion

3.1. Preparation of the double networks

When AAc and its sodium salt monomer were irradiated with gamma rays, in the presence of LBG, polymerisation and crosslink reactions took place simultaneously. Due to the gelation of the monomers in the presence of a polysaccharide-type natural polymer LBG, the gels prepared were called as double network hydrogels. Percentage gelation, i.e. the conversion percentage of the monomer and crosslinking agent into an insoluble double network, was 93, 86, 81, 73, or 51% for the 60, 70, 80, 90, or 100% neutralised systems, respectively. The decrease in the gelation with the degree of neutralization was attributed to the increase in the macroradical stability with the ionisation degree of AAc and the diminishing rates of the polymerisation and crosslink reactions during irradiation. The determination of the gelation percentage was based on the total weight of the monomers and LBG natural polymer in the initial mixture. Gelation percentage data showed that the polymerisation and crosslinking yield of the system were a function of the degree of neutralisation (DN) of AAc in the initial mixture.

3.2. Swelling properties of the double networks

For the characterisation of the network structure and determination of the effective crosslink density of the hydrogels prepared, their swelling properties in water were investigated first. For the identification of the effect of DN and pressure on the swelling behaviour of the hydrogels the swelling experiments were carried out under the pressures of 0.0 and 2.1 kPa.

Each swelling experiment was performed until a constant value of swelling was reached for the sample in question. The swelling kinetics of the AAcNa/LBG hydrogels in water under 0.0 and 2.1 kPa at 25 °C are presented in Figs. 1 and 2. As can be seen from the figures, the AAcNa/LBG hydrogels reached the equilibrium swelling in 10–20 min. On the other hand, the equilibrium swelling degree was lower under pressure than in pure water in each DN value (Fig. 3). This decrease was attributed to the increase in osmotic pressure on the gel system.

The experimental results indicated that one of the most important parameters affecting the swelling behaviour of the AAcNa/LBG hydrogels was DN. The swelling degree of the gels was increased from 245 to 587 with an increase in DN from 50 to 90 in the absence of force. This was attributed to the increase in the number of the carboxylate groups in the gel with DN and chancing of Donnan equilibrium. The higher the DN value of the gel the more the carboxylate groups in the gel; that is, the concentration of the fixed charge on the gel network increased, and the negative charge repulsion inside the polymeric network became stronger. The water absorbency of the completely-neutralised gel (AAcNa/LBG-DN100)

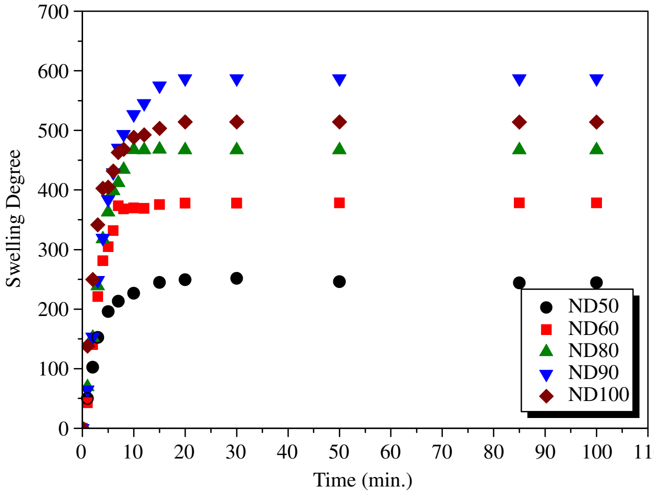

Fig. 1. Swelling kinetics of the AAcNa/LBG double network hydrogels under no pressure. The DN of AAc is indicated in legends.

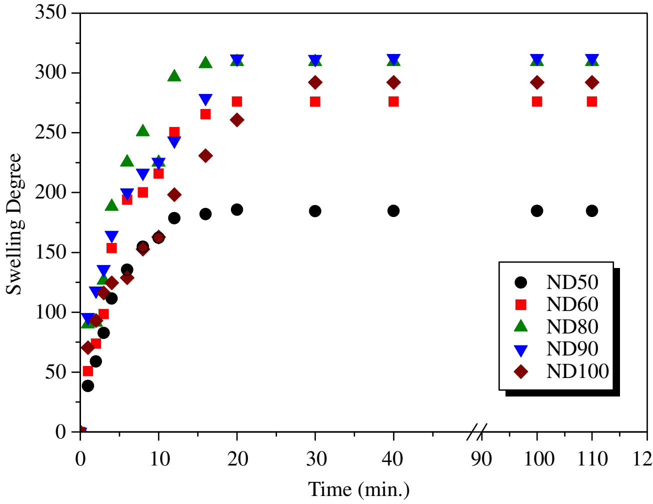

Fig. 2. Swelling kinetics of the AAcNa/LBG double network hydrogels under a pressure of 2.1 kPa. The DN of AAc is indicated in legends.