



Synthesis of new superabsorbent hydrogel based on lignin

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Abstract

Lignin as a polysaccharide has been chemically modified by graft copolymerization of 2-hydroxyethylmethacrylate (HEMA) in an aqueous medium using ammonium persulfate (APS) as an initiator under argon atmosphere. Evidence of grafting was obtained by comparison of FTIR and TGA spectra of initial substrates and superabsorbent hydrogel. Moreover, morphology of the samples was examined by scanning electron microscopy (SEM).

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Introduction

Highly swelling polymers, i.e. superabsorbent hydrogels, are hydrophilic, three dimensional networks that can absorb water in the amount from 10% up to thousands of times their dry weight $P_o R$. They are widely used in various applications such as drug delivery, hygienic, foods, cosmetics, and agriculture. This accounts for increase in the worldwide 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 in year. Hence, synthesis and characterization of superabsorbent hydrogels is the main goal of the several research groups in the. These smart hydrogels are of general interest for biomedical applications, such as artificial muscles or switches, biomedical separation systems, and controlled release systems (Zhang *et al.* 2000). The present investigation deals with the detailed study synthesis of crosslinked graft copolymer based on 2-hydroxyethylacrylate onto lignin, in the presence APS in aqueous medium as an initiator.

Materials and methods

Material

The polysaccharide, Lignin, and ammonium persulfate (all Fluka, Buchs, Switzerland), were used without further purification. 2-hydroxyethyl methacrylate monomer (Merck, Darmstadt, Germany) was used after vacuum distillation. All other chemicals were also of analytical grade.

Grafting procedure

A general procedure for chemically crosslinking graft copolymerization of HEMA onto lignin backbones was conducted as follows. Lignin (1.2 g) was 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 immersed in a thermostated water bath preset at 55 °C. Then a definite amount of APS solution (0.1 g in 5 mL H₂O) was added to lignin solution and was allowed to stir for 10 min. After adding APS, certain amount of monomer was added to the polysaccharide solution. MBA (0.01-0.13 g in 5

ml H₂O) as a crosslinker was added to the reaction mixture after the addition of monomer, and the mixture was continuously stirred for 60 min under argon atmosphere. After 60 min, 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 (2×50 mL), and dried at 50 °C.

Infrared analysis

Fourier transform infrared (FTIR) spectroscopy absorption spectra of samples were taken in KBr pellets, using an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature, with an average of 64 scans at 4 cm⁻¹ resolution. The sample/KBr ratio was 0.5 % and the IR peak signal-to-noise ratio was typically 30,000: 1 for 1 min scan time. The surface morphology of the gel was examined using scanning electron microscopy (SEM). Dried superabsorbent powder were coated with a thin layer of palladium gold alloy and imaged in a SEM instrument (Leo, 1455 VP). Thermogravimetric analyses (TGA) were performed on a Universal V4.1D TA Instruments (SDT Q600) with 8–10 mg samples on a platinum pan under nitrogen atmosphere. Experiments were performed at a heating rate of 20 °C/min until 600 °C.

Swelling measurements

samples (0.10 g) with average particle sizes between 40–60 mesh (250–350 μm) were put into a weighed teabag and immersed in 100 mL distilled water and allowed to soak for 2 h at room temperature. The equilibrated swollen gel was allowed to drain by removing the teabag from water (~20 min). The bag was then weighed to determine the weight of the swollen gel. The absorbency (equilibrium swelling) was calculated using the following equation:

$$\text{Absorbency} = (W_s - W_d) / W_d \quad (1)$$

where W_s and W_d are the weights of the samples swollen in water and in dry state, respectively. So,

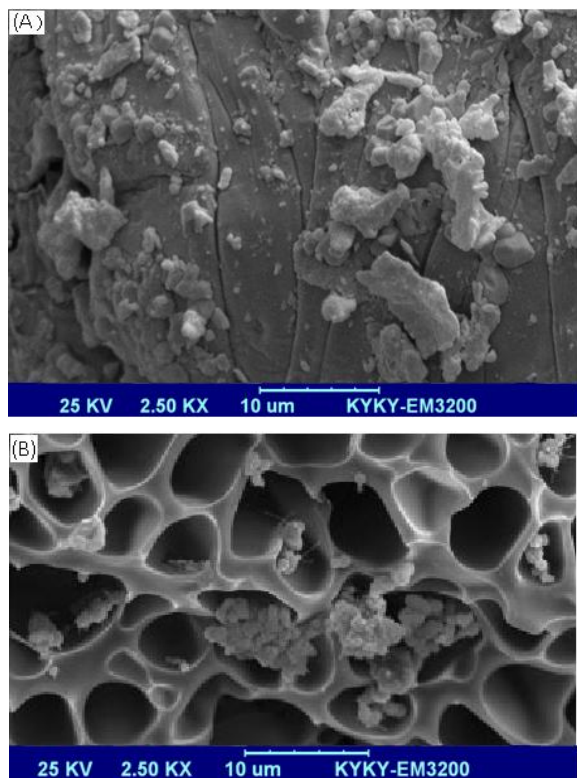


Figure 2. SEM photograph of the optimized superabsorbent hydrogel.

Thermogravimetric analysis

As Shown in Figure 3a, TGA of lignin have a weight loss in two distinct stages. The first stage ranges between 147 and 3150 °C and shows about 37% loss in weight. This may correspond to the loss of adsorbed and bound water. No such inflexion was observed in the TGA curve of hydrogel. This indicated that the hydrogel was resistant to moisture absorption. The second stage of weight loss starts at 347 °C and continues up to 435 °C during which there was 31% weight loss due to the degradation of chitosan. Grafted samples, however, show almost different behavior of weight loss between 97 and 602 °C (Fig. 3b). The first stage of weight loss starts at 105 °C and continues up to 364 °C due to the degradation of chitosan. The second stage from 402 to 555 °C may contribute to the decomposition of different structure of the hydrogel. The appearance of these stages indicates the structure of lignin chains has been changed, which might be due to the grafting of poly HEMA chains. This means that the grafting of lignin

increases the thermal stability of lignin in some extent (Pourjavadi *et al.* 2004; Zhang *et al.* 2007).

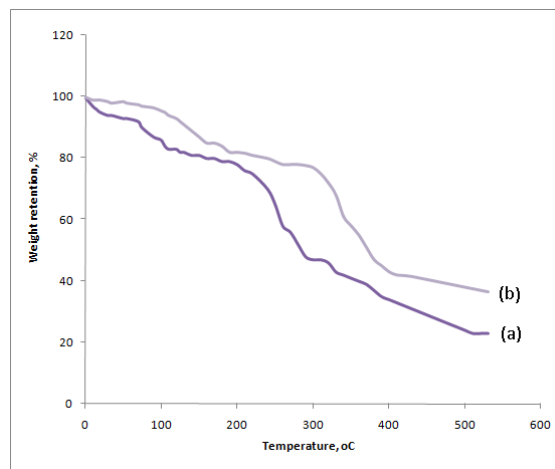


Figure 3. TGA thermograms of (a) lignin and (b) lignin-g-poly (HEMA) hydrogels.

Conclusion

A novel hydrogel was prepared by graft copolymerization of HEMA onto lignin the presence methylene bis acrylamide (MBA) as a crosslinking agent under an inert atmosphere. The resultant hydrogel had a large degree of water absorbency. The study of FTIR spectra shows that in the hydrogel spectrum a new absorption band at 1731 cm^{-1} was appeared that attributed to the ester groups related to monomer with grafted HEMA onto polysaccharide backbones.

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