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Carbohydrate Polymers 64 (2006) 37–40
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Controlled preparation of physical cross-linked starch-g-PVA hydrogel

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Received 28 November 2004; received in revised form 27 October 2005; accepted 27 October 2005
Available online 5 December 2005

Abstract

Physically cross-linked starch-g-PVA hydrogels with controllable grafted branch length were prepared. Polyvinyl acetate (PVAc) was grafted onto starch via radical copolymerization. The molecular weight of PVAc was tailored using the chain transfer reaction. In consequence, the branch length of starch-g-PVA, which derived from starch-g-PVAc, could be easily controlled. In this paper, the viscosity average molecular weight of grafted PVA segment ranged from 1.3×10^4 to 7.2×10^4. The structure of grafted copolymers was verified with FTIR. XRD analysis showed the crystallinity of starch-g-PVA was lower than that of starch. Starch-g-PVA hydrogels were obtained by freezing and thawing. It was found that the swelling ratio of hydrogels increased with the molecular weight of PVA.

Keywords: Starch-g-PVA; Hydrogel; Physical cross-linking; Controllable

1. Introduction

Biodegradable hydrogels were important scaffolds for tissue engineering and widely utilized as a matrix for drug delivery systems (Drury & Mooney, 2003; Hoffman, 2002). It was well known that starch was non-toxic, biocompatible, biodegradable and abundant. Starch-based hydrogels were mainly prepared by chemical cross-linking and irradiation (Zhai, Yoshii, Kume, & Hashim, 2002). On the other hand, Poly(vinyl alcohol) (PVA) was water-soluble and degradable (Chiellini, Corti, D'Antone, & Solaro, 2003). The way to form PVA-based hydrogels could be chemical or physical cross-linking (van Nostrum, Veldhuis, Bos, & Hennink 2004; Xiao, & Zhou, 2003).

A freeze/thaw process was used to form hydrogels. This is mild in the sense that the use of cross-linking agents and organic solvents could be avoided (van Nostrum, Veldhuis, Bos, & Hennink 2004). PVA hydrogels had been successfully prepared via such a physical cross-linking method. Thus, it could be anticipated that the grafting copolymer of starch and PVA could also form hydrogels by freezing/thawing technique either. The starch-g-PVA hydrogel would combine the advantages of both components.

To our knowledge, no physical cross-linked hydrogel that derived from starch and PVA had previous been prepared. Only starch/PVA blend hydrogel obtained by irradiating was reported (Zhai, Yoshii, Kume, & Hashim, 2002). In this paper, starch-g-PVA with a controlled PVA branch length was first prepared. Then, the corresponding hydrogels were formed by the freez/thaw process.

2. Experimental

2.1. Materials

Soluble starch was purchased from Shanghai Chemical Agents Ltd Co., China and dried before use. Vinyl acetate (Shanghai Chemical Agents Ltd Co., China) was purified by distillation. Potassium persulphate, 95% ethanol, sodium hydroxide, methanol and benzene were all analytical grade reagents and used as received.

2.2. Controlled synthesis of starch-g-PVA

The pure starch-g-PVA was prepared according to the literature (Fanta, Burr, Doane, & Russell, 1979) with some improvements. 5.0 g starch was dissolved in 50mL of distilled water at 70 °C. Nitrogen purging for 10 min was carried out to remove the dissolved oxygen from the solution. 0.0308 mol/L $K_2S_2O_8$ was added and allowed to react for 20 min. Then 10 mL vinyl acetate (VAc), in the presence or absence of

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0144-8617/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2005.10.020

a predetermined amount of methanol or ethanol, was added in drops and allowed to react for another 2 h. The constant stirring and the reaction temperature were maintained throughout the reaction period. The product was precipitated from ca. 60% ethanol and filtered. The crude product was extracted with benzene to remove homopolymer PVAc. Then starch-g-PVAc was dried to constant weight.

Starch-g-PVA was derived from alcoholysis of starch-g-PVAc. A mixture of 4.0 g starch-g-PVAc and 30 mL 5% NaOH/methanol was kept refluxing for 30 min. The product, yellowish-white powder, was filtered and dried in an oven at 60 °C to constant weight.

2.3. Infrared spectroscopy

Fourier transform Infrared (FTIR) spectra of starch, starch-g-PVAc, starch-g-PVA and the acid hydrolysate of starch-g-PVA were recorded on a Nexus 470 FTIR spectrophotometer using KBr for sample preparation.

2.4. X-ray measurements

X-ray diffraction profiles of starch and starch-g-PVA were collected with a Bruker D8-Advanced diffractometer using Nickel-filtered Cu Kα radiation ($\lambda = 0.15406$ nm) and scanned from 2 to 50° at a scan speed of 2°/min.

2.5. Intrinsic viscosity measurement

To separate the grafted PVA from starch, starch-g-PVA was subjected to acid hydrolysis via refluxing the copolymer in 1 N HCl for 1 h (Athawale, & Rathi, 1997). The clear solution was cooled and treated with excess 95% ethanol. PVA was precipitated from 95% ethanol, filtered and dried in an oven at 60 °C to constant weight. The intrinsic viscosity ([η], mL/g) of PVA was measured using an Ubbelohde viscometer at 30 °C. Then the viscosity average molecular weight (Mv) could be calculated according to the formula $[\eta] = K \times Mv^{\alpha}$(coefficients K and α were 6.65×10^{-2} mL/g and 0.64, respectively) (Qian, 1965).

2.6. Swelling behavior of starch-g-PVA films

To prepare films, starch-g-PVA samples were dissolved in distilled water, cast into a mould and dried in an oven at 70 °C to remove water. Dry 1.5×1 cm^2 film samples were weighed and immersed into phosphate-buffer saline (PBS) (0.1 M, pH7.4) for 24 h at ambient temperature (23 ± 1 °C), blotted with soft paper to remove surface water and weighed. Thus, the swelling ratio (SR) of starch-g-PVA samples could be calculated as $SR = W_{wet}/W_{dry}$, where W_{wet} and W_{dry} were the weight of swollen and dry starch-g-PVA samples, respectively.

The swollen samples were kept for another 24 h at −16 °C and 5 h at ambient temperature and SR of the corresponding samples were calculated. All experiments were done in triplicate and then the average was taken.

2.7. Preparation of starch-g-PVA hydrogel

An aqueous solution of starch-g-PVA (10% w/w) was prepared by dissolving the graft copolymer in distilled water. Then the starch-g-PVA hydrogels were obtained by subjecting the solution to several repeated freeze/thaw cycles, 24 h at −16 °C and 5 h at ambient temperature.

3. Results and discussion

3.1. Characterization of starch-g-PVA

The structure of the graft copolymers were analyzed with FTIR. On the IR spectrum of the extracted graft copolymer of starch and VAc, a characteristic peak was found at 1732 cm^{-1}, which was attributed to the carbonyl absorption. The same characteristic band was not present on the FTIR spectrum of starch (Fig. 1). Consequently, it was concluded that starch-g-PVAc was obtained. No carbonyl absorption band was found on the IR spectrum of the derivate of starch-g-PVAc, which was consistent with the alcoholysis mechanism. In addition, on the IR spectrum of the acid hydrolysate of the alcoholysis derivate, there was no absorption near 1730 cm^{-1} while the characteristic band of hydroxyl group (3330 cm^{-1}) remained. The evidence indicated that the alcoholysis derivate was the expected starch-g-PVA.

There were five peaks around 19.79° on the XRD pattern of starch, while only two peaks exhibited near 16.93° on that of starch-g-PVA (Fig. 2). The XRD profiles suggested that both starch and starch-g-PVA were semicrystalline. It could be calculated that the crystallinity of starch and starch-g-PVA were approximate to 8.03 and 7.74%, respectively. The XRD analysis results indicated that the morphology of starch was changed when PVA was grafted onto the backbone.

3.2. Tailoring graft branch length of starch-g-PVA

The grafted branch length in the starch-g-PVA could be controlled by adjusting the molecular weight of PVAc. This

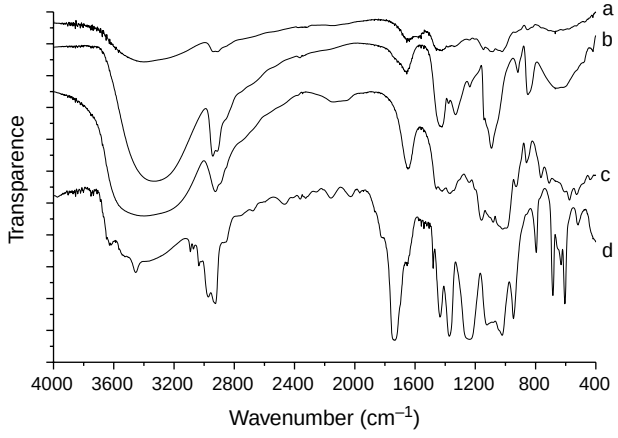

Fig. 1. FTIR spectra of starch and its derivates (a) acid hydrolysate of starch-g-PVA, (b) starch-g-PVA, (c) starch, (d) starch-g-PVAc).