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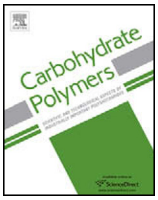

Short communication

Synthesis of starch-g-lactic acid copolymer with high grafting degree catalyzed by ammonia water

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ABSTRACT

The study of starch-g-lactic acid copolymer has gained much attention for its completely degradable property, but its intricate synthetic procedure and low graft degree inhibited its further application. In this work, the synthesis of starch-g-lactic acid copolymer was attempted via the catalysis of ammonia water by one-step process, and the structure of starch-g-lactic acid copolymer was characterized by means of IR, ^{13}C NMR and HMBC. The synthetic conditions were optimized as follows, the starch was activated for 2 h at 80 °C at first, starch and lactic acid with weight ratios of 1:4 reacted for 4 h at 90 °C in vacuum. The starch-g-lactic acid copolymer can be finally obtained with graft degree of starch 58.9%.

1. Introduction

Recently, the copolymer of starch graft with lactic acid has been explored widely owing to the excellent degradability of both starch and poly(lactic acid). Therefore, the starch-g-lactic acid copolymer has been synthesized by diverse procedures such as ring-opening polymerization of lactide with catalysis of stannous 2-ethyl-hexanoate (Xie, Shi, Xie, & Zhou, 2006), initiation by potassium tert-butoxide (You, Shen, Jiao, Li, & Zhu, 2002), or introducing some protective groups and substituent groups into raw materials and then to react (Dubois, Krishnan, & Narayan, 1999). Wang, Hu and Zhu (2012) prepared starch-g-lactic acid copolymer directly via the reaction of cornstarch with lactic acid catalyzed by sodium hydroxide with a grafting degree of 33.6%. However, either the procedures are very complex, or the grafting degree is too low. Thus, the synthetic method of starch-g-lactic acid copolymer needs to be further investigated to get more suitable condition and high grafting degree.

In this work, a new synthetic system was investigated in which the starch graft copolymerized with lactic acid was directly catalyzed by ammonia water under gentle condition in order to produce starch-g-lactic acid copolymer with high graft degree. The structure of starch-g-lactic acid copolymer was also characterized by means of IR, ^{13}C NMR and HMBC.

2. Experimental

2.1. Materials and equipments

Corn starch was obtained from Beijing Gusong Economics & Trade Co. Ltd. Ammonia water (A.R), Urea (A.R), ethanol (A.R) and acetone (A.R) were purchased from Beijing Chemical Works. Lactic acid (A.R) was obtained from Xilong Chemical Company.

Corn starch and graft copolymer were characterized by IR (Perkin-Elmer 100) in the wavelength range from 4000 to 450 cm^{-1}, XRD (D/max-Ra diffractometer) with CuK$_\alpha$ radiation (λ = 1.5406 Å) operating at 40 kV and 100 mA in the range of 3–35° of 2θ by steps of 0.02°, ^{13}C NMR and HMBC (Bruker AV-600) with d6-DMSO as solvent, and SEM (JEOL, JSM-7001F with resolution at 10 µm, 5.0 kV), respectively.

2.2. Synthesis of starch-g-lactic acid copolymer

The 30 mL urea solution, 15 mL $NH_3 \cdot H_2O$ (25%) and 5.00 g starch were added into the flask and stirred adequately at 80 °C for 2 h. Then lactic acid was added into the flask to react under vacuum at 90 °C for 4 h, and the mixture was precipitated by ethanol to remove excessive lactic acid and residual solvent after cooling to room temperature. Then it was dried to get crude product. And then the crude product was purified with soxhlet extraction at 80 °C for

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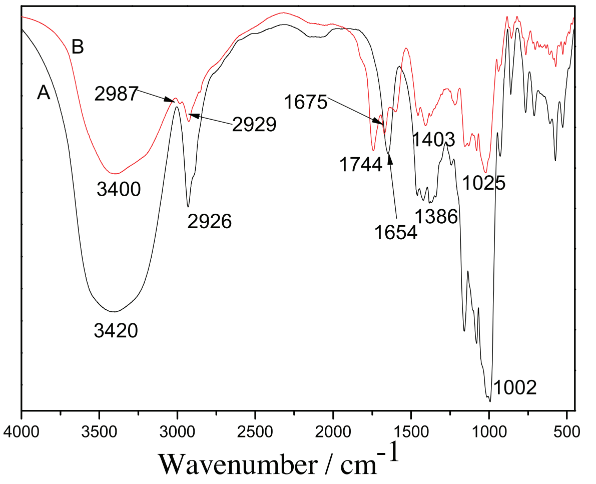


Fig. 1. IR spectra of starch (A) and starch-g-lactic acid copolymer (B).

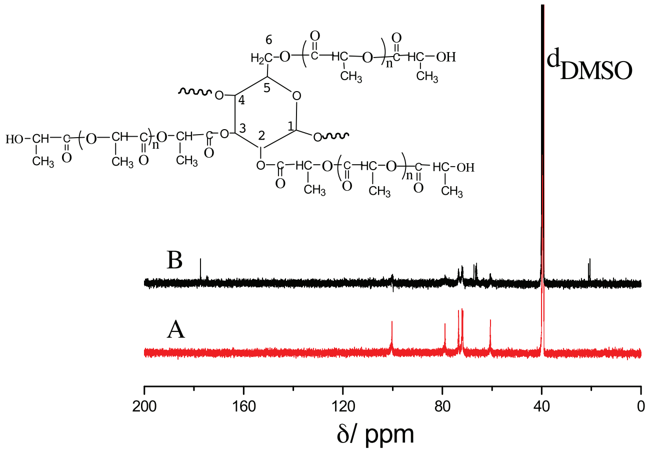


Fig. 2. ^{13}C NMR spectra of corn starch (A) and starch-g-lactic acid copolymer (B).

40 h to obtain the final starch-g-lactic acid copolymer. The grafting degrees were calculated with the following formula:

$$\text{grafting degree} = \frac{m_1 - m_0}{m_0}, \qquad (1)$$

where m_0 is the weight of raw corn starch, and the m_1 is the weight of the final copolymer product.

3. Results and discussion

3.1. *Characterizations of starch-g-lactic acid copolymer*

3.1.1. *IR spectra of starch-g-lactic acid copolymer*

The IR spectra of starch and starch-g-lactic acid copolymer were shown in Fig. 1. The broad and strong absorption peak in the 3252–3547 cm^{-1} region is attributed to the stretching vibration of —OH, and the peaks at 2929 cm^{-1}, 1654 cm^{-1}, and 1161–1002 cm^{-1} are assigned to the vibrational absorption of C—H bond, intramolecular hydrogen bond and C—O bond in starch respectively (Curve A). Compared to IR spectrum of starch, the IR spectrum of starch-g-lactic acid copolymer (Curve B) displayed two new absorption peaks, which are the characteristic absorption of carbonyl group stretching at 1744 cm^{-1} and the stretching vibration of C—H bond in poly(lactic acid) chain at 2987 cm^{-1}, respectively. The other absorption peaks all correspond to those of starch except that some peaks shift for a few wavenumbers owing to electric effects of ester group, which indicated that the starch-g-lactic acid copolymer was synthesized in this system.

3.1.2. *^{13}C NMR spectra analysis*

The ^{13}C NMR spectra of starch and starch-g-lactic acid copolymer were shown in Fig. 2. It was found from the ^{13}C NMR spectra of starch (Fig. 2A) that the chemical shift of the peak at δ100 ppm and δ79 ppm were assigned to carbons C_2, C_3 and C_6 attached to —OH of the starch unit respectively. The signal in the δ 71–72 ppm region is attributed to C_1, C_4 and the carbon C_5 attached to CH_2 occurred at δ60 ppm. Compared to the peaks of starch (Fig. 2A), Fig. 2B showed extra peaks belonging to long chain of poly(lactic acid). The methyl carbon at δ21 ppm, carbon of CH_2 and CH in the region of δ66–72 ppm and obvious carbonyl carbon peak at δ177 ppm in the ester, all corresponded with the typical structure of starch-g-lactic acid copolymer.

3.1.3. *Heteronuclear Multiple Bond Coherence (HMBC) analysis*

Fig. 3 displays the HMBC spectra of starch and starch-g-lactic acid copolymer. As for the HMBC spectra, the ^{13}C spectrum was presented along the vertical axis and the ^{1}H spectrum was shown along the horizontal axis. It is obvious that hydrogens are attached to carbons for cross peaks relating the two types of spectra in the field, and the cross peak of the ^{13}C peak at 40 ppm and the ^{1}H peak at 2.5 ppm are attributed to the methyl of DMSO as shown in Fig. 3. The blue arrow was taken from singlet of the peak at 54 ppm out to the correlation peak in the *x*–*y* field and dropped down to the horizontal axis at 3.6 ppm, which correspond to the signals of C_2 and C_3 in starch ring and related to the vertical axis at 40 ppm produced by C_6 in starch. The ^{1}H NMR shows that the signal at 2.6 ppm was caused by the hydrogen on the CH group which was related

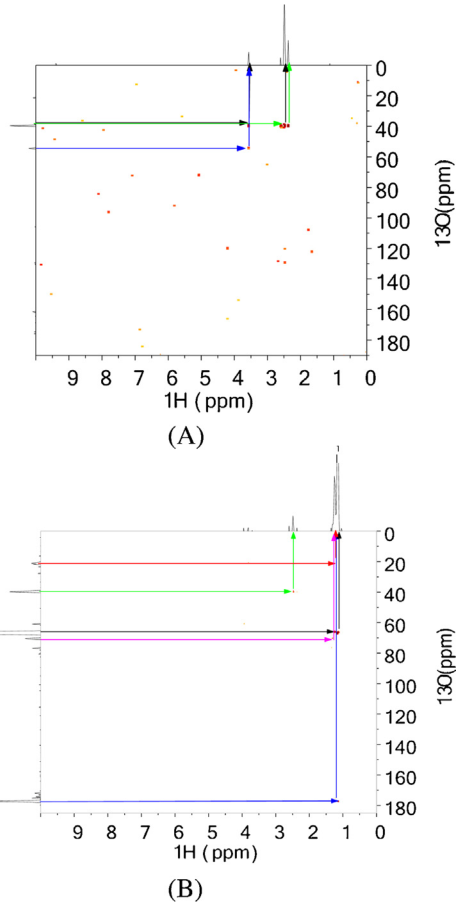
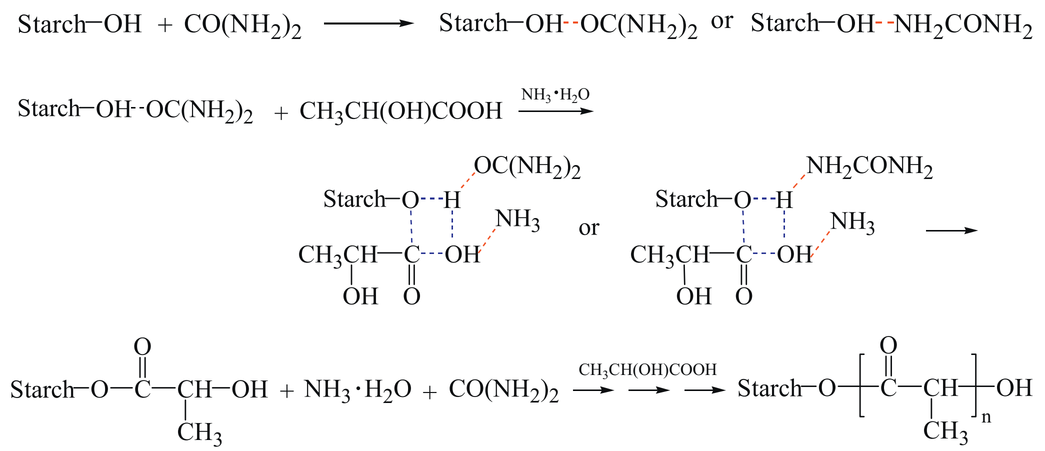


Fig. 3. HMBC spectra of starch (A) and starch-g-lactic acid copolymer (B).



Scheme 1. The reactive procedures of synthesis on starch-g-lactic acid copolymer.

to the oxygen in ether bond (Fig. 3A). Distribution of the ^{13}C NMR signal at 22 ppm to the carbon on the methyl group, connecting to the correlation peak and down to the horizontal axis indicates that the signal at 1.3 ppm was caused by the methyl hydrogen on the poly(lactic acid) chain (Fig. 3B). Multiplet of the proton spectrum at 1.3 ppm (horizontal axis) and 70 ppm (vertical axis) comes from the signal of CH of the graft copolymer. Similarly, the resulting signal at 1.2 ppm (horizontal axis) and 67 ppm (vertical axis) is produced by protons of methylene. And the ^{13}C NMR peak at 177 ppm for the carbonyl carbon forms vicinal coupling which is correlated to carbon with single hydrogen atom in Fig. 3B. The HMBC spectra further confirmed the structure of starch-g-lactic acid copolymer.

3.2. The effect of reaction conditions on the graft degree of starch

In order to investigate the synthetic efficiency of starch-g-lactic acid copolymer and the influence factors, urea was used as activating agent in the gelatification of starch. The non-toxic and easily obtained ammonia water was used as catalyst, the reactive procedures were inferred and shown in Scheme 1.

3.2.1. The effect of concentration of urea and $NH_3{\cdot}H_2O$ dosage on the graft copolymerization

Fig. 4A shows that concentration of urea has obvious effects on the copolymerization of starch with lactic acid and the highest grafting degree was obtained at 14 wt% of urea. It is proposed that this is because hydrogen bond of starch with urea can boost the dissolution of starch and favor the esterization of starch with lactic acid (Scheme 1). The amount of hydrogen bond increased with the increase of urea at beginning and decreased when the amount of urea exceeded a certain extent for the association of urea by the hydrogen bond itself, and the optimum dosage of urea was 14%.

The ammonia water was selected as catalyst since it is available and safe in operation. The effect of dosage of $NH_3{\cdot}H_2O$ on the grafting degree of starch was shown in Fig. 4B. Ammonia water could promote the esterization of starch with lactic acid (Scheme 1). It is found that the graft degree of starch becomes higher with the increase of ammonia water at initial stage, but the esterization of starch with lactic acid is reversible, excessive ammonia water could promote the hydrolysis of ester, so the grafting degree of starch descended quickly with the continual increase of ammonia water.

3.2.2. The effect of activation temperature and activation time on the graft copolymerization

The activation extent of starch directly affected the graft copolymerization, which was also dominated by the activation temperature and time. The variation of activation temperature and time on the graft copolymerization were summarized in Fig. 5. The two curves revealed the same trend that the grafting degrees of starch increased with increasing activation temperature and pro-

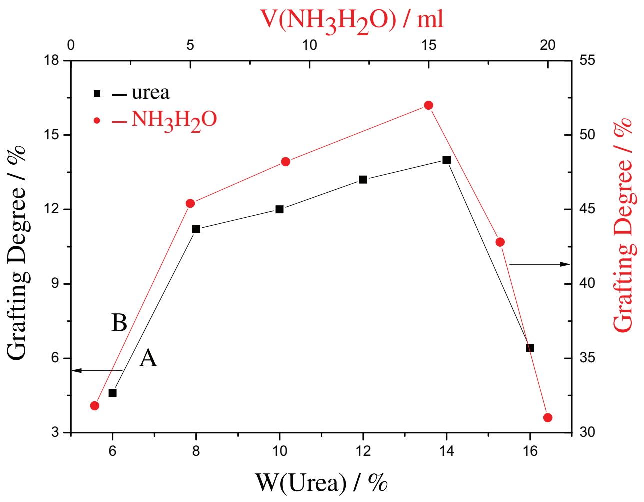


Fig. 4. The effect of urea and $NH_3{\cdot}H_2O$ to graft degree of starch.

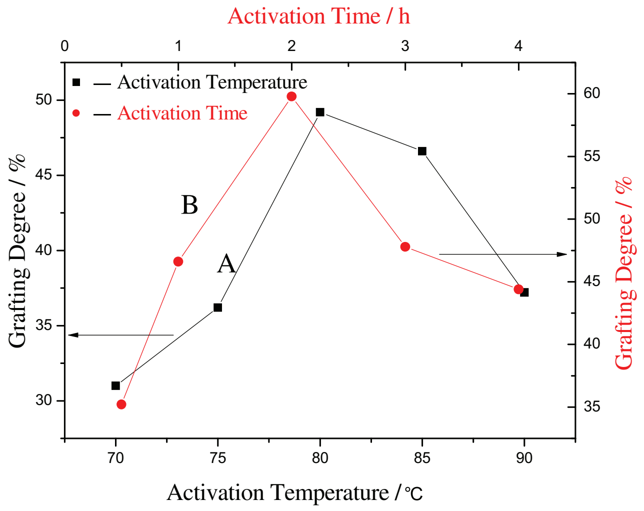


Fig. 5. The effect of activation temperature (A) and activation time (B) to graft degree of starch.

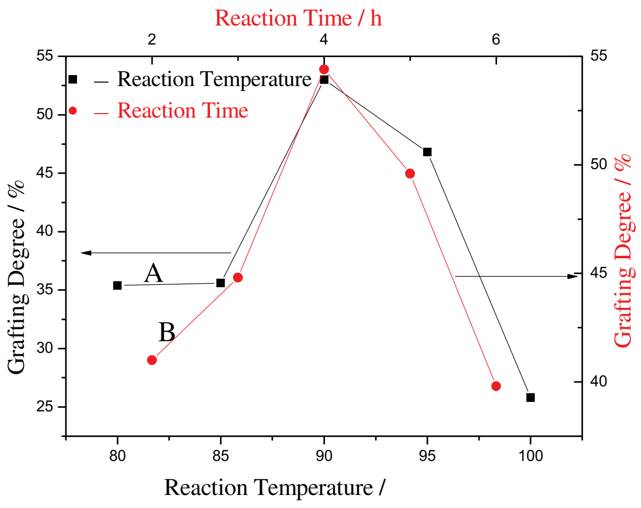


Fig. 6. The effect of reaction temperature (A) and reaction time (B) to graft degree of starch.

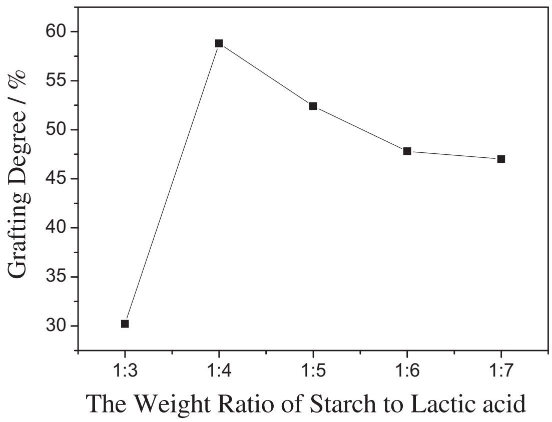


Fig. 7. The grafting degree curve of different weight ratio of starch to lactic acid.

longing activation time initially. However, the grafting degrees begin to decline when exceeding 80 °C or 2 h since the activation extent of starch was not enough below 80 °C or 2 h, and the excessive temperature and time would produce more hydrogen bonds of starch with urea dissociation.

3.2.3. The effect of reaction temperature and reaction time on the graft copolymerization

The variation of reaction temperature and reaction time on grafting degree of starch were shown in Fig. 6. The two curves also exhibit the same tendency that the grafting degrees of starch increased with increasing reaction temperature and prolonging reaction time at initial stage. The grafting degrees begin to decrease when exceeding 90 °C or 4 h. It was ascribed to that the esterification of starch with lactic acid is easier to appear and more completed with increasing reaction temperature and prolonging reaction time below 90 °C or 4 h, while the excessive reaction temperature and time may accelerate the hydrolysis of product.

3.2.4. The effect of weight ratio of starch to lactic acid on the graft copolymerization

Fig. 7 shows the effect of weight ratio of starch to lactic acid on the graft copolymerization. The grafting degree of starch sharply increased with the increase of lactic acid at first, and then it fell down to flat with continuous increase of lactic acid. As lactic acid was the major reactant, the amount of graft copolymer increased with the addition of lactic acid at first period. However, the excess lactic acid may lead to homopolymerization. Thus, the optimal grafting degree of starch reached 58.9%, much higher than the reported 33.6% in previous studies (Wang et al., 2012).

4. Summary

The starch-g-lactic acid copolymer was successfully synthesized by one-step process with the catalysis of ammonia water in a mild condition. The structures of the starch and starch-g-lactic acid copolymer were characterized by means of IR, ^{13}C NMR and HMBC, respectively. The synthetic conditions were systematically studied and the optimum condition has been drawn as follows: Starch activation for 2 h at 80 °C at first, and the weight ratios of starch with lactic acid was 1:4 with reaction in vacuum for 4 h at 90 °C. Accordingly, the optimized grafting degrees of starch obtained with 58.9% for the starch-g-lactic acid copolymer. This work may provide the fundamental feasibilities for broad applications of starch-g-lactic acid copolymer, and the investigation on its film forming procedures and mechanical performances is under way yet.

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