

Convenient synthetic method of starch/lactic acid graft copolymer catalyzed with sodium hydroxide

QINGLING WANG, YINGMO HU*, JIANHUA ZHU, YANG LIU, XUE YANG and JING BIAN

School of Material Science and Engineering, China University of Geosciences, Beijing 100083, China

MS received 8 March 2011; revised 9 July 2011

Abstract. Copolymer of starch grafted with lactic acid (LA) could be directly prepared by reaction of cornstarch with lactic acid and with sodium hydroxide (NaOH) as the catalyst. The structure of starch/LA copolymer was characterized by IR, XRD, SEM and $^1\text{H-NMR}$. The effects of NaOH concentration, ratios of starch and LA, reaction temperature and reaction time on the grafting degree were also investigated and the results showed that the highest grafting degree of starch could reach 33-60% when the graft copolymerization was carried out in 0.40 mol l^{-1} NaOH aqueous solution for 9 h at 90°C with 1: 6 ratio of starch and lactic acid.

Keywords. Starch; lactic acid; graft copolymerization.

1. Introduction

With the rapid development of plastic industry, 'white pollution' has become more and more serious, so more attention has been paid to the research and development of biodegradable polymers of sustainable materials for environmental protection. In many biodegradable polymers, starch is a potentially useful and completely biodegradable material for biodegradable plastics because of its nontoxic, low cost and its natural abundance which can be obtained from many crops including corn, wheat, rice, potato and so on (Tester and Karkallas 2002). Therefore, modification of starch, physically and chemically, has been extensively studied for the environmental and ecological concerns. Chemical modification, which can produce various starch-based products including chemical derivation and graft copolymerization, is the most widely used, and graft copolymerization, as a rational approach of chemical modification, has been extensively used in the modification of starch (Park and Inagaki 2003; Rouilly *et al* 2004; Gong *et al* 2006a). At present, grafted monomers are the main types of vinyl monomers and aliphatic polyester, although the copolymers of starch are grafted by vinyl monomers (Athawale and Lele 2000; Cho and Lee 2002; Zhai *et al* 2002; Fanta *et al* 2004) can improve the mechanical properties of starch and they do not biodegrade completely. However, starch graft copolymers by aliphatic polyester (Sang *et al* 1997; Choi *et al* 1999; Dubois *et al* 1999) are a kind of completely biodegradable polymer materials, but the coverage on them is limited. Recently, the copolymer of starch with lactic acid have been studied widely for its excellent degradability and the starch/LA copolymer has been prepared using different methods such

as ring-opening polymerization of lactide in the presence of stannous 2-ethyl-hexanoate (Gong *et al* 2006b), ring-opening polymerization of lactide initiated by potassium tert-butoxide (Shao and Zhao 2009), introducing some protective groups and substituent groups to the raw materials and then further reaction (Chen *et al* 2005; Shi *et al* 2005; Xie *et al* 2006) and so on. However, either the procedures are very complex or the grafting degree is too low, so study on the starch/LA copolymer needs to be further investigated.

In this study, a convenient method was introduced to synthesize starch/LA copolymer by the reaction of starch with lactic acid directly catalyzed with NaOH, the structure of starch/lactic acid copolymer was affirmed by means of IR, XRD, SEM and $^1\text{H-NMR}$.

2. Experimental

5 g of raw cornstarch was dispersed in 30 ml 0.40 mol l^{-1} NaOH (AR) aqueous solution and the mixture was heated to 75°C for gelatinization for about 1 h, then 15 ml dimethyl sulfoxide (AR) and 25 ml LA (AR) were added to the flask. Graft copolymerization was carried out at 90°C under about 0.095 MPa for 9 h. Then the system was cooled to room temperature, and the product was washed twice with acetone (AR) under vigorous stirring to remove unreacted LA monomer, and dried in a vacuum oven at 80°C for 12 h. And then the dried product was further purified by Soxhlet extraction with acetone for 48 h to remove the unreacted LA monomer completely as well as the PLA homopolymer. The final product was dried at 80°C under vacuum oven with a grafting degree of 33-60%. The grafting degree is calculated as follows:

$$\text{Grafting degree} = \frac{m_1 - m_0}{m_0}$$

*Author for correspondence (huyingmo@cugb.edu.cn)

where m_0 is the weight of dried raw starch and m_1 the weight of purified starch/LA copolymer.

The sample and cornstarch were characterized by IR (Perkin-Elmer 100) with the wave range from 4000 to 400 cm^{-1} , XRD (D/max-Ra diffractometer) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 100 mA and the sample was scanned from 3–50° of 2θ by steps of 0.02°, and $^1\text{H-NMR}$ (Bruker AV-400) with $\text{DMSO-}d_6$ as solvents. The morphology of sample and cornstarch was investigated by SEM (LEO-1450).

3. Results and discussion

From the IR spectra of starch (figure 1A), the strong and broad absorption peak at 3430 cm^{-1} is the characteristic absorption peak of the stretching vibration of $-\text{OH}$, the peaks at 2935 cm^{-1} , 1644 cm^{-1} and 1160–1010 cm^{-1} are respectively assigned to the vibrational absorption of C–H bond, intramolecular hydrogen bond and C–O bond in starch, while the peaks at 570.6 cm^{-1} , 762.5 cm^{-1} and 862.4 cm^{-1} are the swing vibration absorption peaks of C–H bond of starch. Compared with the spectrum of starch (figure 1A), the new strong absorption peaks at 1751 cm^{-1} and 2990 cm^{-1} are assigned to carbonyl of ester and C–H bond in poly(lactic acid) chain, appearing in the IR spectrum of starch/lactic acid copolymer (figure 1B), and the other peaks almost did not change, which indicates that the starch has been successfully grafted by the lactic acid, and starch/LA copolymer has been formed.

The X-ray diffraction pattern of starch (figure 2A) shows diffraction peaks at $2\theta = 15.8^\circ$, 19.3° and 21.6° which demonstrated good crystallizability of starch. Compared with the acute diffraction peaks of the starch, the starch/lactic acid copolymer (figure 2B) shows a broad dispersion peak at $2\theta = 18.7^\circ$, which indicates the starch/lactic acid copolymer is a kind of amorphous polymer, and the aggregation of starch has been changed and the original diffraction peaks completely disappeared after graft copolymerization of starch with lactic acid.

The scanning electron microscopic images of starch (A) and starch/lactic acid copolymer (B) are shown in

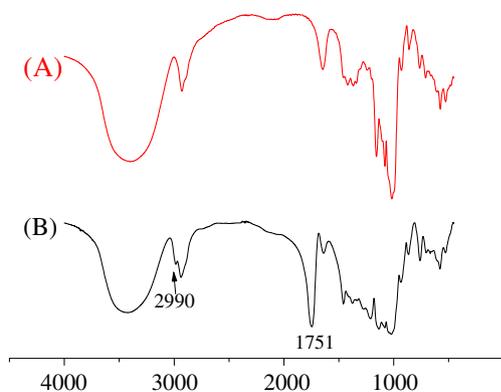


Figure 1. IR spectra of starch (A) and starch/LA copolymer (B).

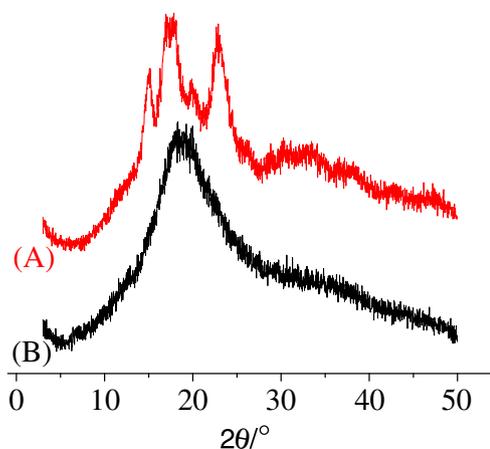


Figure 2. X-ray diffraction patterns of starch (A) and starch/LA copolymer (B).

figure 3. The particles of starch are spherical solid and regular, and have smooth surfaces and edges (figure 3A). Its surface has remarkable changes after modification becoming loose and irregular, because the external surfaces of starch have suffered certain corrosion from LA.

$^1\text{H-NMR}$ spectra of cornstarch and starch/LA copolymer are shown in figure 4. Seen from cornstarch (figure 4A), the signals at 5.40, 5.50 and 4.59 ppm are respectively assigned to proton signals of hydroxyl group on C–2, C–3 and C–6, while the proton signals assigned to CH and CH_2 of the starch unit are centred at about 3.60–3.40 ppm. Seen from the $^1\text{H-NMR}$ spectra of starch/LA copolymer (figure 4B), the signals at 5.11 and 4.18 ppm are respectively assigned to proton signals of terminal hydroxyl group (H_f) and the carbon adjacent to the terminal hydroxyl group (H_e), while the proton signals assigned to the starch unit and CH of poly(lactic acid) chain (H_d) are centred at 3.65–3.38 ppm, and the proton signals corresponding to H_c , H_b and H_a on the methyl groups of poly(lactic acid) chain are set at about 1.45, 1.27 and 1.08 ppm. So the $^1\text{H-NMR}$ analysis could demonstrate the microstructure of starch/LA copolymer.

The mechanism of grafting polymerization reaction of starch with LA is inferred and shown in figure 5. By mixing the dried starch with NaOH aqueous solution so that the starch can be fully gelatinized by water in NaOH aqueous solution and the hydroxyl groups on the starch can also be activated by NaOH to form ion-pair, which produce the reactive sites of polymerization reaction. Our previous study has shown that LA can be transformed into lactide under mild conditions (Gong *et al* 2006a, b). The ring of lactide can be opened and its terminal group formed ion-pair of sodium alkoxide via ester exchange reaction of oxygen anion on the ion-pair generated by the starch with carbonyl group of lactide. The ion-pair of sodium alkoxide continues to react with the carbonyl group of lactide and the polyester chain is prolonged, producing the long chain of polylactic acid on the bone of starch.

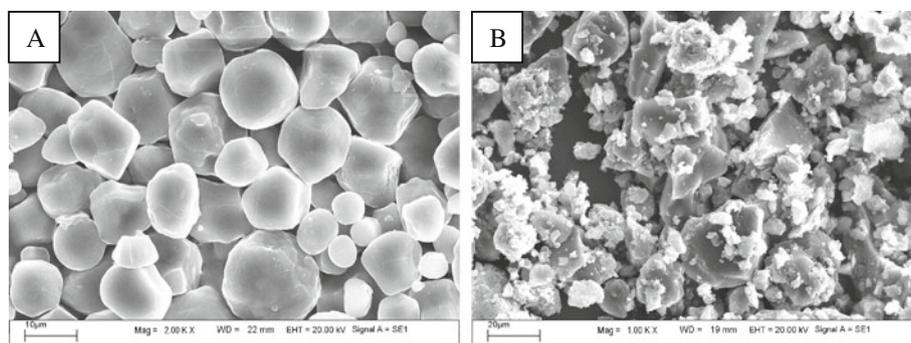


Figure 3. SEM images of starch (A) and starch/LA copolymer (B).

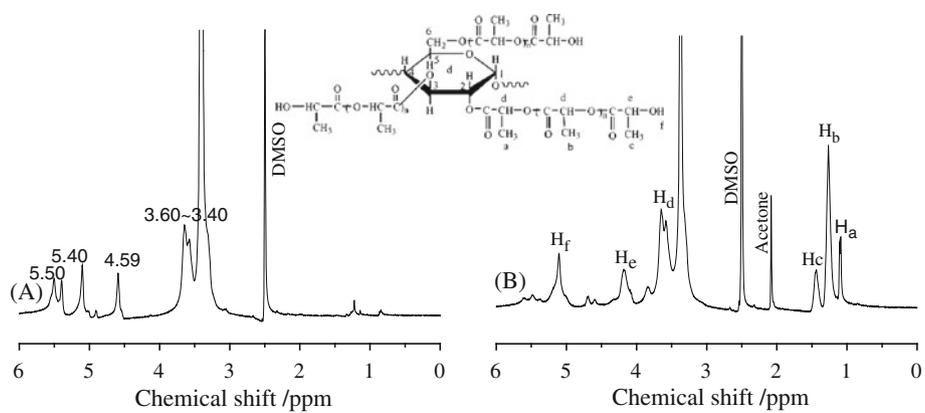


Figure 4. ¹H-NMR spectra of cornstarch (A) and starch/LA copolymer (B).

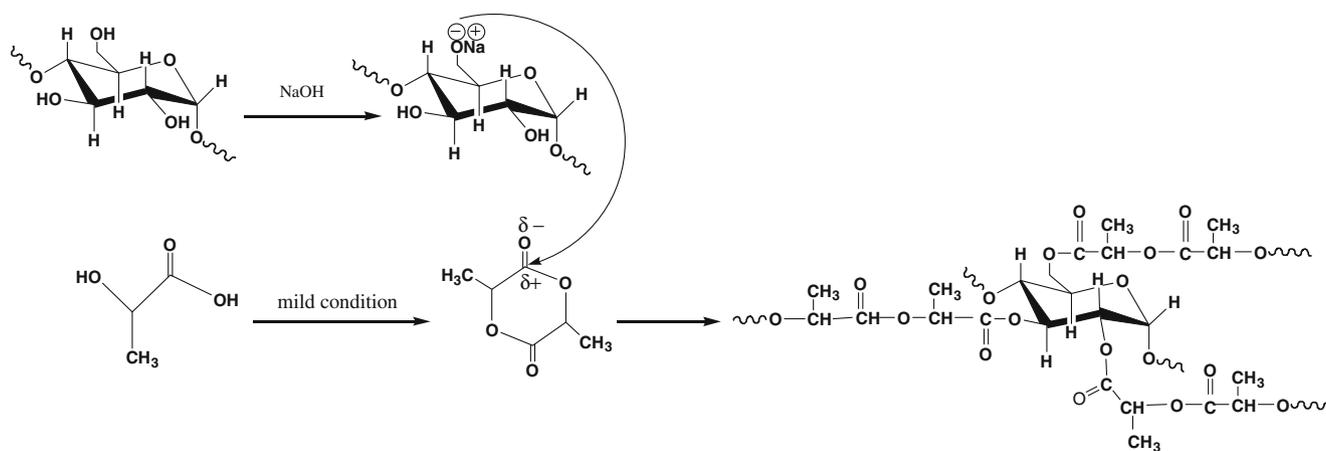


Figure 5. Reaction process of starch graft with lactic acid.

4. Conclusions

In conclusion, starch/LA copolymer can be successfully synthesized by direct reaction of starch with lactic acid catalyzed with NaOH aqueous solution. Its structure is also confirmed by IR, XRD, SEM and $^1\text{H-NMR}$, and the grafting degree of starch could reach 33.6% in experimental conditions.

Acknowledgement

This work is supported by the Fundamental Research Funds for the Central Universities (2011PY0171).

References

- Athawale V D and Lele V 2000 *Carbohydr. Polym.* **41** 407
Chen L, Qiu X Y and Deng M X 2005 *Polymer* **46** 5723
Cho C G and Lee K 2002 *Carbohydr. Polym.* **48** 125
Choi E J, Kim C H and Park J K 1999 *Macromolecules* **32** 7402
Dubois P, Krishnan M and Narayan R 1999 *Polymer* **40** 3091
Fanta G F, Felker F C and Shogren R L 2004 *Carbohydr. Polym.* **56** 77
Gong Q X, Tu K H and Wang L Q 2006a *Acta Polym. Sin.* **9** 1045
Gong Q X, Wang L Q and Tu K H 2006b *Carbohydr. Polym.* **64** 501
Park Y W and Inagaki N 2003 *Polymer* **44** 1569
Rouilly A, Rigal L and Gilbert R G 2004 *Polymer* **45** 7813
Sang H L, Kwang H L and Sung K H 1997 *J. Appl. Polym. Sci.* **64** 1999
Shao J and Zhao Y M 2009 *China Plastics* **23** 15
Shi H J, Li A D and Liu Z Z 2005 *J. Shenyang Inst. Chem. Technol.* **19** 200
Tester R F and Karkallas J 2002 *Starch* **53** 513
Xie D M, Shi Y F and Xie C L 2006 *J. Mater. Sci. Eng.* **24** 836
Zhai M, Yoshii F and Kume T 2002 *Carbohydr. Polym.* **50** 295