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An ionic liquid as reaction media in the ring opening graft polymerization of ε-caprolactone onto starch granules

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Abstract

A powerful and highly efficient direct solvent, 1-allyl-3-methylimidazolium chloride ([AMIM]Cl), has been used for the dissolution of starch and the homogeneous ring opening graft polymerization (ROGP) of ε-caprolactone (ε-CL) onto starch granules. The ROGP carried out smoothly and the grafting efficiency of PCL reached 24.42% when the ROGP proceeded at 110 °C for 28 h with ε-CL/starch 1:1 (wt/wt) and stannous octoate ($Sn(Oct)_2$) as a catalyst, which was calculated according to a standard curve newly created by an FT-IR method. The structure of starch grafted poly(ε-caprolactone) (starch-*g*-PCL) was characterized by FT-IR, DSC, WAXD and ^{13}C NMR, the good adhesion between the two components was evidenced by SEM observations. The homo-polymerization of ε-CL and the disconnection of grafted PCL from starch-*g*-PCL were the main competition reactions. A new homogeneous modification of starch by the ROGP of ε-CL in [AMIM]Cl was investigated, as well as a new FT-IR method to calculate the grafting efficiency of PCL.

Keywords: ε-Caprolactone; Graft polymerization; Homogeneous; Ionic liquid; Starch

1. Introduction

As the oldest class of such materials, starch as a carbohydrate polymer is a potentially useful, economic and most abundant biodegradable material. Various physical and chemical modifications of starch granules including blending (Dubois, Krishnan, & Narayan, 1999; Koenig & Huang, 1995; Kweon, Cha, Park, & Lim, 2000; Kweon & Lim, 2001; Lee, Lee, & Hong, 1997; Rodriguez-Gonzalez, Ramsay, & Favis, 2003; Singh, Pandey, Rutot, Degée, & Dubois, 2003) and grafting (Chen, Ni et al., 2005; Chen, Qui et al., 2005; Mani, Tang, & Bhattacharya, 1998; Rouilly, Rigal, & Gilbert, 2004) have been considered to improve its mechanical properties and process capability.

The grafting reaction is the representative modification of starch by chemical methods (Mani et al., 1998; Rouilly et al., 2004). The starch graft copolymers with vinyl polymer such as starch-*g*-acrylonitrile (Fanta, Felker, & Shogren, 2004), starch-*g*-polyvinyl alcohol (Zhai, Yoshii, Kume, & Hashim, 2002), starch-*g*-polystyrene (Cho & Lee, 2002) and starch-*g*-methacrylonitrile (Athawale & Lele, 2000) have been synthesized, but the biodegradability has also been limited for the 'non-degradable' part of the polymer.

Recently, the biodegradable polymer grafted starch has attracted much attention and poly(ε-caprolactone) (PCL) and poly(L-lactide) (PLLA) have been chosen as artificial segments for starch-*g*-PCL and starch-*g*-PLLA and can completely biodegrade under natural conditions and additionally have an improved performance (Chen, Ni et al., 2005; Chen, Qiu et al., 2005; Huang, Yu, Ma, & Jin, 2005; Mani et al., 1998; Rouilly et al., 2004; Rutot, Degee, Narayan, & Dubois, 2000). A facile way to introduce PCL and PLLA segments onto starch is the ring opening graft polymerization (ROGP) of ε-caprolactone (ε-CL) and L-lactide (L-LA) (Choi, Kim, & Park, 1999).

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Homogeneous functionalization of starch has been one focus of starch research for a long time, and the homogeneous reactions urgently need suitable solvents that can dissolve starch and provide a feasible reaction environment. Due to the stiff molecule and close chain packing *via* numerous intermolecular and intramolecular hydrogen bonds, starch is extremely difficult to dissolve. Usually, suspension and bulk polymerization are applied for the starch graft and the reactions are carried out in heterogeneous solvents (Chen, Ni et al., 2005; Chen, Qiu et al., 2005; Choi et al., 1999; Dubois et al., 1999). The solvent for the suspension grafting can be toluene, *N*,*N*-dimethylacetamide and, sometimes, a caustic media. However, the heterogeneous reaction and non-green solvents remain limitations in terms of volatility, toxicity, cost, difficulty for solvent recovery, or instability in processing.

Room-temperature ionic liquids (ILs), being considered as desirable green solvents for a wide range of separation and as reaction media for processes including catalysis, have recently received significant attention (Welton, 1999). Cellulose can dissolve in some ILs (Swatloski, Spear, Holbrey, & Rogers, 2002) and highly grafted cellulose derivatives such as carboxymethyl cellulose and cellulose acetate are synthesized using 1-*n*-butyl-3-methylimidazolium chloride ([BMIM]Cl) as a solvent, the degree of the polymerization ranging from 290 to 1200 without any catalyst and no degradation of the polymer is observed (Heinze, Schwikal, & Barthel, 2005). Very recently, Biswas, Shogren, Stevenson, Willett, and Bhowmik (2005) revealed that starch and zein can also dissolve in [BMIM]Cl up to 15% (wt/wt) concentration at 80 °C. What is more, just like [BMIM]Cl, 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) is found to have excellent capability for dissolving cellulose, and the solubility of cellulose in [AMIM]Cl is better than in [BMIM]Cl on the same dissolving conditions (90–100 °C, 3–5 wt%) (Ren, Wu, Zhang, He, & Guo, 2003; Wu et al., 2004). The ILs containing chloride anion, that can form strong hydrogen-bond contacts (Holbrey et al., 2003), seem to be most appropriate for biopolymers such as starch, cellulose and zein. And among them, the ILs containing one unsaturated substituent on the nitrogen of *N*-methyl-imidazole may be more effective.

The polymer synthesis using ionic liquids as solvents are systematically studied in last few years (Kubisa, 2004; Perrier, Davis, Carmichael, & Haddleton, 2003; Vygodskii et al., 2004). Strehmel, Laschewsky, Wetzel, and Golrnitz (2006) investigated the polymerization of *n*-butyl methacrylate in ionic liquids. Ionic liquids have no detectable influence on polymer tacticity but in them the degrees of polymerization are significantly higher compared to polymerization in toluene, and can even exceed the values obtained by bulk polymerization. Meanwhile, the microwave ring opening polymerization (ROP) of ε-CL in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, using zinc oxide as a catalyst, proceeds smoothly and high molecular weight PCL (M_w 28,500 g/mol) are obtained at 85 W for 30 min (Liao, Liu, Shi, & Zhang, 2005).

A homogeneous modification of starch by the ROGP of ε-CL was thus investigated with [AMIM]Cl as a reaction media in this research. The behavior of starch granules dissolving in the IL and the results of the ROGP are presented in this paper.

2. Experimental

2.1. Materials

Corn starch consisting of 75% amylopectin and 25% amylose, was dehydrated with toluene as azeotropic dehydration agent and dried in vacuum (80 °C, 100 Pa) for 48 h. *N*-Methyl-imidazole was dried over CaH_2 for 2 days and distilled. Stannous octoate was distilled in vacuum and dissolved in freshly dried toluene. PCL was purchased from Nature Works LLC (Minneapolis, MN, USA). All the other reagents were of analytical grade and used as received.

2.2. Measurements

FT-IR spectra were recorded as pellets with potassium bromide. ^1H and ^{13}C NMR spectra were recorded on a MercuryVX-300 spectrometer (Varian, Palo Alto, USA) using tetramethysilane as an internal standard and $CDCl_3$ and DMSO-d_6 as solvents.

Differential scanning calorimetry (DSC) measurement was carried out on a DSC apparatus (DSC822^e, Mettler Toledo, USA) under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} from 30 to 200 °C. Wide-angle X-ray powder diffraction was performed by XRD-6000 X-ray diffractometer (Shimadzu, Kyoto, Japan) using Ni-filtered CuK$_\alpha$ radiation (40 kV, 30 mA) with 4°/min scanning rate at room temperature.

SEM images were obtained with a Model XL 30 ESEM FEG (Micro FEI Philips, Oregon, USA) after the sputter coating of gold on the specimen surface. The photographs of the starch granules in [AMIM]Cl was measured by a polarizing light microscope (Olympus BX51, Olympus Optical Co., Japan).

M_w and the polydispersity index (M_w/M_n) of PCL were determined by gel permeation chromatography (GPC) on a Waters high-pressure liquid chromatographic system equipped with a model 2690D separation module, a model 2410 refractive-index detector, and a Shodex K803 column. Chloroform was used as an eluent at a flow rate of 1.0 ml/min. GPC data were calibrated by standard polystyrene.

2.3. Preparation of [AMIM]Cl

N-Methyl-imidazole (41.06 g, 0.50 mol) and 3-chloropropylene (45.92 g, 0.60 mol) were added into a three-necked flask equipped with a mechanical stirrer and a water condenser. The reaction was conducted at 60 °C for 6 h under the protection of argon atmosphere. The excess 3-chloropropylene was removed by distillation and the unreacted *N*-methyl-imidazole was extracted out with ether. The obtained light yellow viscous ionic liquid was dried in vacuum for 48 h and the yield was 98%.

2.4. Dissolving and regeneration of starch

Under the protection of argon atmosphere, a mixture of starch (1 g) and [AMIM]Cl (4 g) was stirred at 80 or 100 °C until a transparent solution was formed and the dissolving process was traced by a polarizing light microscope. The dissolved starch was regenerated by precipitating in ethanol.

2.5. Grafting reaction of starch in [AMIM]Cl

Typical procedure: The ROGP of ε-CL onto starch granules in [AMIM]Cl was carried out at 110 °C for 28 h under argon atmosphere and anhydrous conditions with 0.1% $Sn(Oct)_2$ as a catalyst. The fed ratio of ε-CL to starch in weight was 0.5:1, 1:1, 1.5:1, 2:1, respectively. The obtained reaction mixture was precipitated in ethanol to remove unreacted ε-CL, residual catalyst and [AMIM]Cl, the precipitate was a mixture of the grafted copolymer and homo-PCL (Starch-*g*-PCL/PCL).

Starch-*g*-PCL/PCL (1 g) was stirred with 50 ml of dichloromethane at room temperature for 72 h to dissolve homo-PCL. After filtration, the residue was washed several times with dichloromethane and dried in vacuum for 48 h before it was characterized by FT-IR, DSC, WAXD, ^{13}C NMR as well as SEM.

2.6. Recovery of [AMIM]Cl

To separate [AMIM]Cl from the waste liquid produced at the step of precipitation in the grafting of starch, ethanol was first eliminated by evaporation and the other impurities such as unreacted ε-CL and residual catalyst were extracted by acetone. The recovered [AMIM]Cl, which was re-characterized by ^{1}H and ^{13}C NMR, qualified for recycling in the ROGP.

2.7. Calculation of the grafting efficiency of PCL

The grafting efficiency (*G*%) is calculated as follows

$$G\% = \frac{m_{ST}}{m_{CL}} \times \frac{\text{PCL wt\%}}{1 - \text{PCL wt\%}} \qquad (1)$$

where m_{ST} is the weight of dried native starch and m_{CL} is the weight of feed ε-CL monomer. PCL wt% is the weight percentage of PCL in starch-*g*-PCL, which is estimated by the following equation

$$\text{PCLwt\%} = 6.41 + 0.95\Delta I \qquad (2)$$

where, ΔI is defined as the difference between the intensities of two FT-IR signals at 1730 cm^{-1} and 1645 cm^{-1}, which are characteristic peaks of PCL and starch segment in starch-*g*-PCL, respectively.

3. Results and discussion

3.1. Evaluation on the starch/[AMIM]Cl system

The evaluation of [AMIM]Cl as a homogeneous reaction media for the ROGP of ε-CL onto starch was conducted on the solubility and stability of starch in [AMIM]Cl and the recovery feasibility of [AMIM]Cl from waste liquid phase of the ROGP mixture.

The dissolution of starch in [AMIM]Cl at different temperature was investigated. At room temperature, [AMIM]Cl only swelled starch but could not dissolve it. With increasing temperature, starch dissolved more rapidly, dissolving readily at 60 °C with stirring. At 80 °C, the starch granules in [AMIM]Cl (15 wt%) decreased with time and disappeared almost completely after 40 min (Fig. 1). The results of dissolving process show that a solution of starch in [AMIM]Cl was formed as expected. What is more, a complete dissolution of 20 wt% starch in [AMIM]Cl was observed at 15 min under argon anhydrous atmosphere without any pretreatment or activation at 100 °C, by which the substantial degradation of starch upon dissolution was prevented. In addition, a viscous solution of 50 wt% starch in [AMIM]Cl was also obtained, which still kept clear and transparent after cooling to room temperature. It was thus concluded that [AMIM]Cl was an efficient solvent for starch.

Studies on the state of dissolution of starch in [AMIM]Cl were carried out by ^{13}C NMR spectra (Fig. 2). The six signals of the unmodified anhydroglucose unit appeared at 100.6 (C-1), 79.3 (C-4), 73.8 (C-3, 5), 72.5

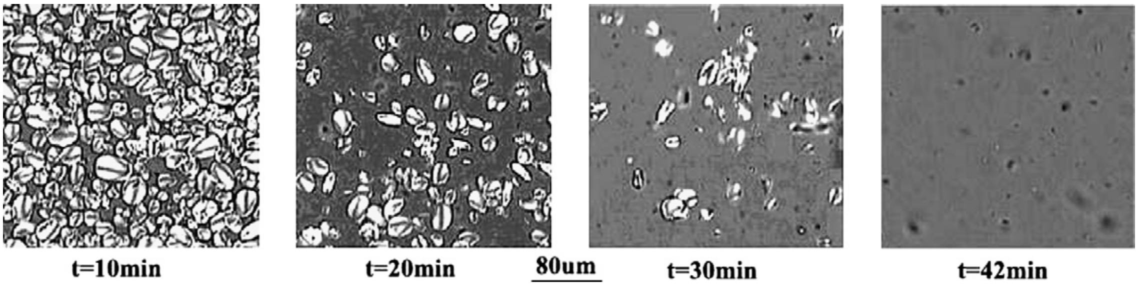

Fig. 1. Dissolving process of starch in [AMIM]Cl at 80 °C traced by a polarizing light microscope.

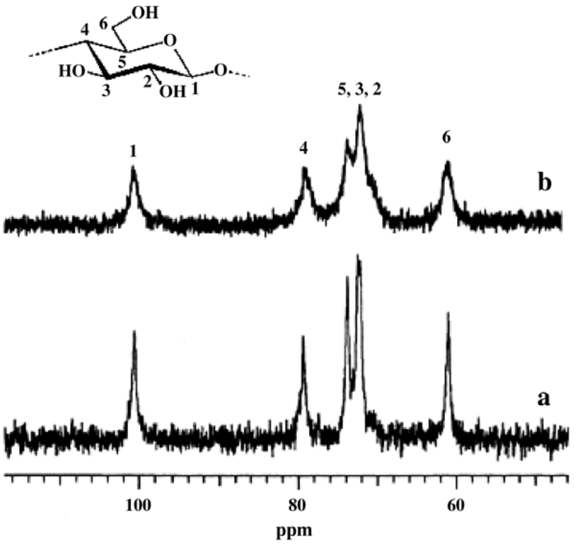

Fig. 2. ^{13}C NMR spectra of starch in [AMIM]Cl solution (b) and DMSO (a).

(C-2) and at 60.9 ppm (C-6), which were well-resolved and very similar to those dissolved in DMSO. This indicates that this IL can be classified as a so-called non-derivatizing starch solvent, in which starch could be molecularly dispersed.

The ^{1}H and ^{13}C NMR spectra of unused and recovered [AMIM]Cl are shown and compared in Fig. 3. The recycling procedure includes the washing of the used [AMIM]Cl, hence the ethanol and acetone are removed and the recycled [AMIM]Cl is pure. The consistency of the two kinds of [AMIM]Cl in their NMR properties depicts that there was no by-product left in the recovered [AMIM]Cl and the reusing of [AMIM]Cl was feasible.

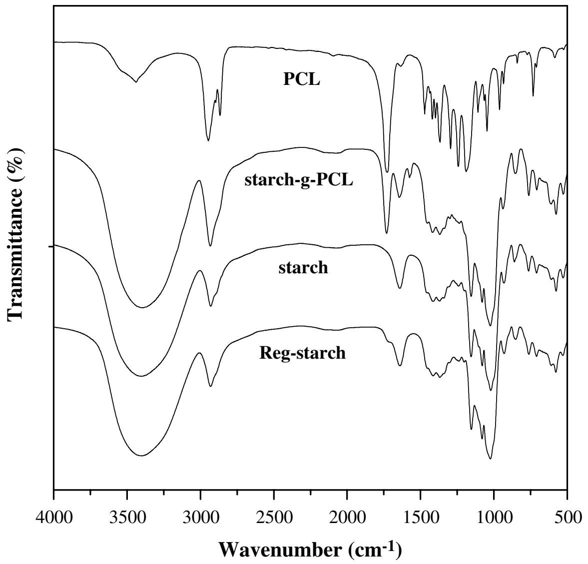

Fig. 4. FT-IR spectra of PCL, starch-*g*-PCL (G% = 20%), native starch and Reg-starch.

3.2. Characterization of starch-*g*-PCL

Starch-*g*-PCL was purified *via* dichloromethane extraction to remove homo-PCL from the reaction mixture, which was inevitably formed during the graft polymerization. The thus obtained starch-*g*-PCL was characterized

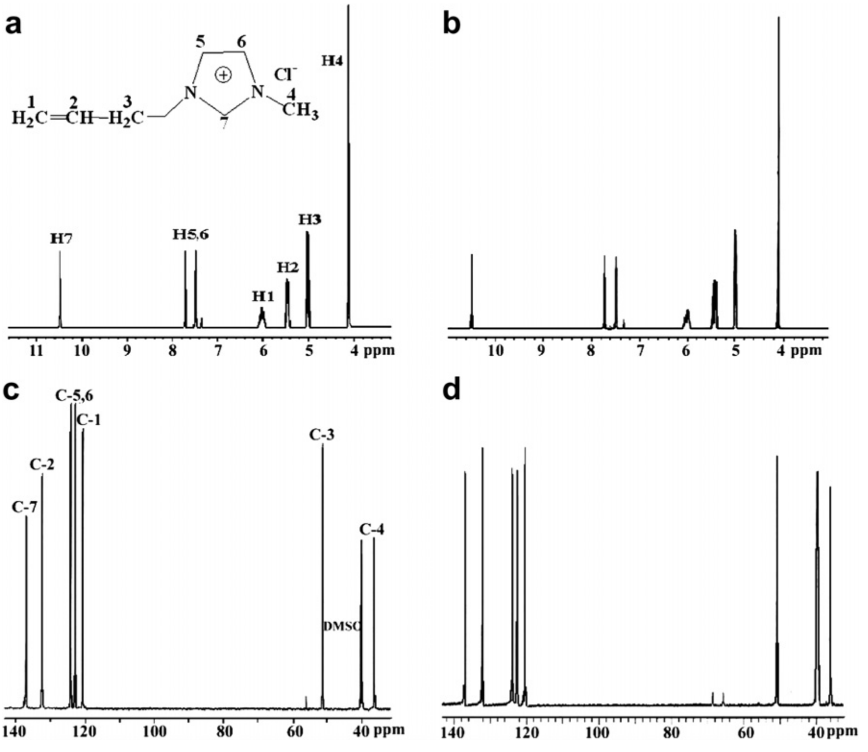

Fig. 3. Typical ^{1}H and ^{13}C NMR spectra of unused (a and c) and recovered [AMIM]Cl (b and d).

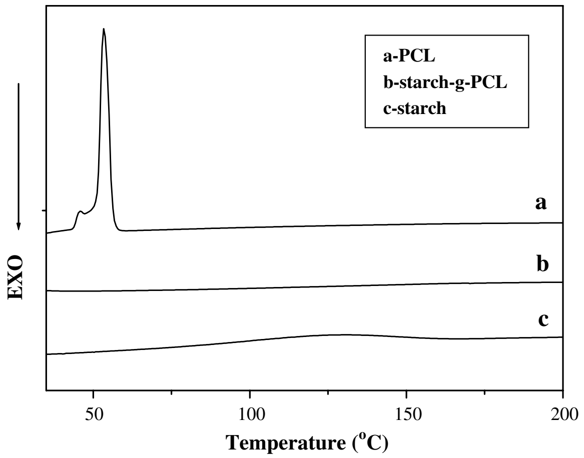

Fig. 5. Second heat DSC curves of native starch, starch-*g*-PCL (G% = 20%) and PCL (M_n = 10,000, from GPC).

by various methods such as FT-IR, DSC, WAXD, ^{13}C NMR as well as SEM. The specimens of pure PCL and native starch were also measured as a contrast.

The notable difference between the FT-IR spectra of starch and PCL was that the strongest peak for starch appeared at 3400 cm^{-1} (s, OH) but that for PCL at 1730 cm^{-1} (Fig. 4), which was assigned to the carbonyl group in PCL. However, both the peaks were recorded in the spectra of purified starch-*g*-PCL. To attest that the signal at 1730 cm^{-1} was just from the PCL grafted on starch but not homo-PCL mixed with native starch, a sample of regenerated starch (Reg-starch) was prepared by stirring a mixture of starch and pure PCL in [AMIM]Cl at 110 °C for 28 h and then extracting PCL with dichloromethane. The FT-IR spectrum of Reg-starch and the lowest *G*% (0.16%) show that almost all mixed homo-PCL was removed by dichloromethane extraction. It is reasonable to deduce that the ROGP of ε-CL onto starch chains took place.

The DSC thermogram of starch-*g*-PCL, native starch and pure PCL are compared in Fig. 5. It is noticeable that neither the melting peak (115.9 °C) of native starch nor the step-like glass transition (46.0 °C) and melting peak (53.4 °C) of pure PCL was observed from the thermogram of starch-*g*-PCL. No crystallization and melting peak appeared in the thermogram. The results show that PCL was grafted onto starch, and that the physical properties of the grafted PCL in starch-*g*-PCL were really different from those of homo-PCL.

The crystallinity of starch, starch-*g*-PCL, PCL and starch/PCL are discussed on the basis of WAXD patterns (Fig. 6). PCL shows two main diffraction peaks at $2\theta = 21.5$ and 23.9°, whereas starch shows three peaks at $2\theta = 15.2$, 17.1 and 23.1°. However, in the case of starch-*g*-PCL neither the crystallization peak of PCL nor that of starch was observed but a dispersive broad peak around $2\theta = 21.2°$. The pattern was totally different from that of starch/PCL, in which both the diffraction peaks of crystal PCL and starch were determined. The variety indicated that starch-*g*-PCL was amorphous and the conclusion was accordant with that obtained by DSC measurement.

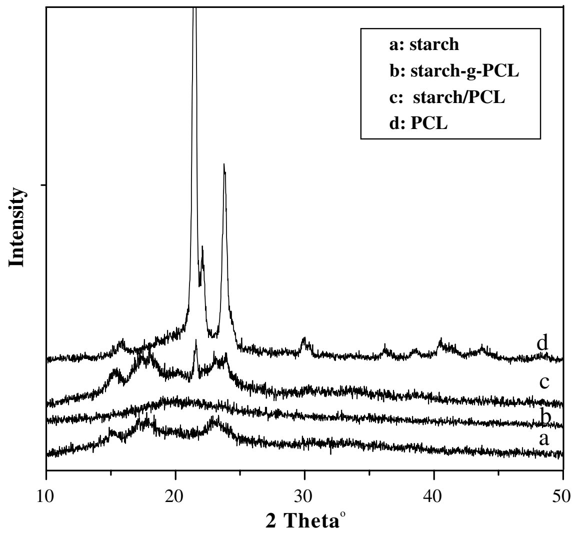

Fig. 6. WAXD spectra of starch, starch-*g*-PCL (G% = 20%), PCL (M_n = 10,000, from GPC) and starch/PCL with the same PCL wt% as in starch-*g*-PCL.

The grafting of PCL onto starch was also confirmed by ^{13}C NMR spectroscopy as starch-*g*-PCL dissolved well in DMSO. In addition to the ^{13}C signals of starch, group (g′ and h′) and (g–l) of PCL peaks were recorded (Fig. 7A), which indicated that the PCL chains were linked with starch segments as the absorption peaks of group (g–l) in the grafted PCL chains shifted to high-field in contrast to those of group (1–6) in homo-PCL chains (Fig. 7B) and the grafted PCL peaks kept independent without any increase in the intensity after the addition of pure PCL (Fig. 7C). Signals g′ and h′ were cleaved from signal g and h by the strain of starch annulus.

The scanning electron microscopy (SEM) images of native starch (A and B) and starch-*g*-PCL (C and D) attest to the good interfacial adhesion between the starch and the PCL chains (Fig. 8). The clear connections and smooth surfaces were obtained after starch was grafted by PCL, which may be helpful to the improvement of the mechanical properties of the modified composites.

3.3. Estimation of PCL wt% in starch-*g*-PCL

As is known, the peaks at 1730 cm^{-1} and 1645 cm^{-1} are characteristic signals of PCL and starch segments in the FT-IR spectra of starch-*g*-PCL (Fig. 4); their intensities were enhanced by the addition of pure PCL and native starch, respectively. Furthermore, the addition of native starch or pure PCL to starch-*g*-PCL showed no influence on the independence of the two peaks, which kept independent also for the mixture of starch and PCL (Fig. 9). So, PCL wt% in starch-*g*-PCL could be estimated by the

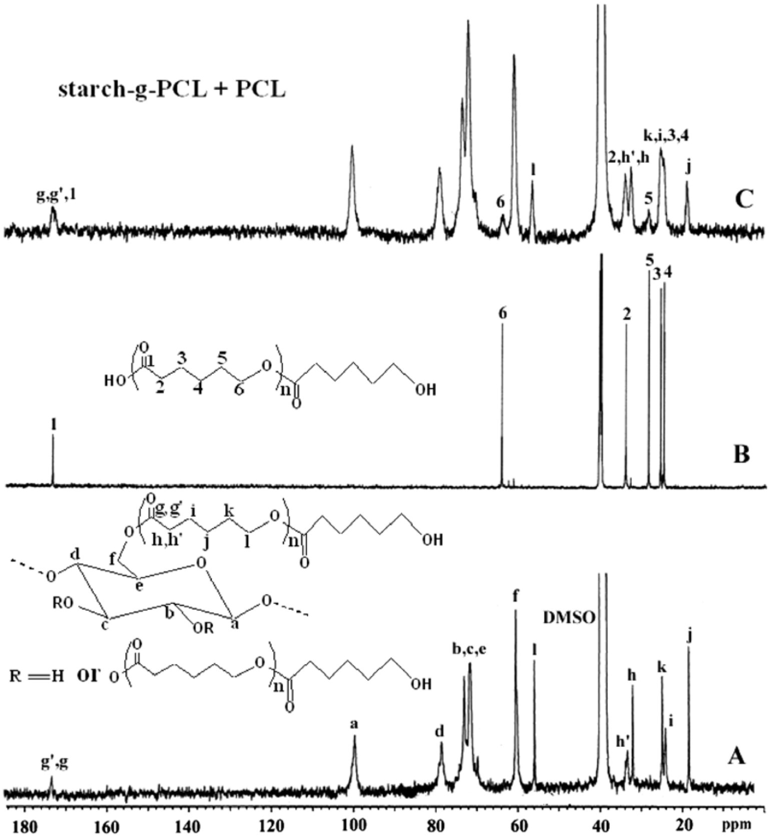

Fig. 7. Typical ^{13}C NMR (DMSO-d_6) spectra of starch-*g*-PCL (G% = 20%) (A), pure PCL (B) and starch-*g*-PCL + PCL (M_n = 10,000 from GPC) (C).

difference between the intensities (ΔI) of the signals 1730 cm^{-1} (PCL) and 1645 cm^{-1}(starch segment) using a linear regression equation (Fig. 10), which was created from the starch/PCL system (Fig. 11).

3.4. Ring opening graft polymerization of ε-caprolactone onto starch

The factors that influence the grafting reaction, including the catalyst concentration, the reaction time, the ε-CL/starch mass ratio, and the reaction temperature, were investigated. The ROGP of ε-CL onto starch was conducted with a solution of 25 wt% starch in [AMIM]Cl.

The *G*% and PCL wt% with varied catalyst concentration are shown in Fig. 12. When the polymerization was carried out without Sn(Oct)$_2$ (ε-CL/starch (wt) = 1:1, 110 °C, 28 h), the values of *G*% and PCL wt% were as low as 0.16, which was considered as the residue of PCL physically adsorbed by starch. The results demonstrate that the catalyst was necessary. However, the decline of PCL wt% and *G*% was observed with catalyst concentration increasing from 0.1% to 0.5%, and the value for PCL wt% ranged as 19.63, 19.05, 17.06, 13.94 and 13.20 but that for *G*% was 24.42, 23.53, 20.57, 16.20 and 15.21. It seems that the competitive homo-polymerization of ε-CL was enhanced with the higher catalyst concentration.

The results of the ROGP with various reaction times conducted at 110 °C (ε-CL/starch (wt) = 1:1, 0.1% Sn(Oct)$_2$) are compared in Fig. 13. It was observed that *G*% increased within 28 h (110 °C) and 26 h (120 °C) but decreased afterwards, which demonstrated that the grafting reaction is very efficient at first; however, homopolymer is almost exclusively formed at longer reaction times. The maximums of *G*% reached 24.42% and 23.67% at 28 h (110 °C) and 26 h (120 °C), respectively.

Fig. 14 shows the PCL wt% and *G*% with varied ε-CL/starch ratio (0:1, 0.5:1, 1:1, 1.5:1 and 2.0:1 in weight, 0.1% Sn(Oct)$_2$, 110 °C, 28 h). The highest grafting efficiency and PCL wt% were detected at 1:1, which indicated that the excess ε-CL was also favorable to the homo-polymerization of ε-CL.

The temperature also took an important role in the ROGP (Fig. 15). When the reaction time was 28 h, the highest grafting efficiency was detected at 110 °C, but the increasing in *G*% (20.37%) was broken at 120 °C if the reaction time was shortened to 22 h, which indicated that the high *G*% could be obtained by appropriate reaction temperature and time.

4. Conclusions

In summary, [AMIM]Cl was found to be a powerful, non-derivitizing and single-component solvent for starch, which can be easily prepared and recovered. By using

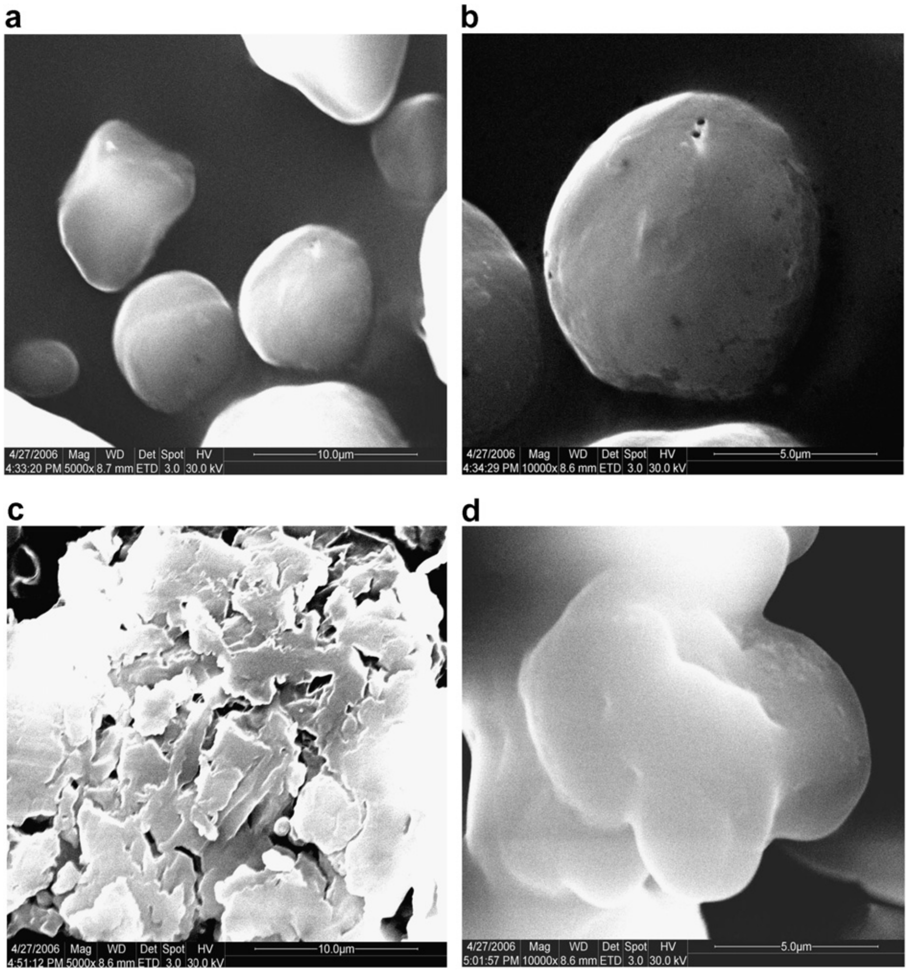

Fig. 8. SEM images of native starch (a and b), starch-*g*-PCL (G% = 20%) (c and d).

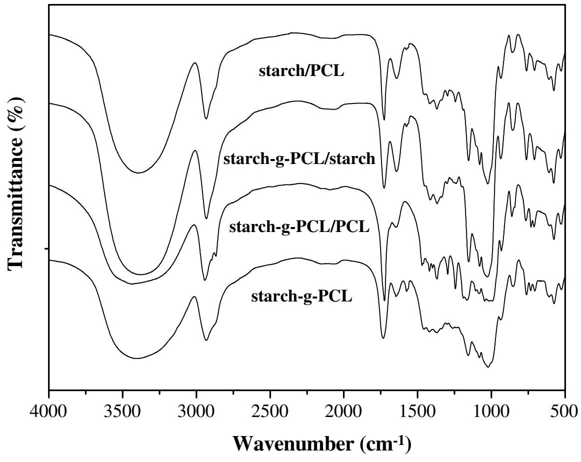

Fig. 9. FT-IR spectra of starch-*g*-PCL (G% = 23%), starch-*g*-PCL + PCL, starch-*g*-PCL + starch and starch/PCL with the same PCL wt% as in starch-*g*-PCL.

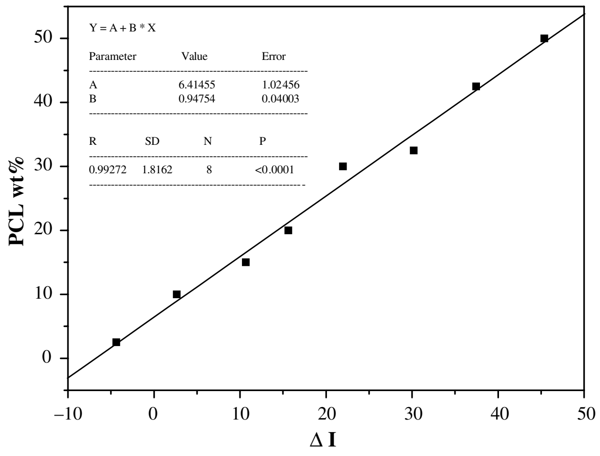

Fig. 10. Standard curve of PCL wt% to the difference between the intensities of the FT-IR signal of PCL (1730 cm^{-1}) and starch segment (1645 cm^{-1}) (ΔI).

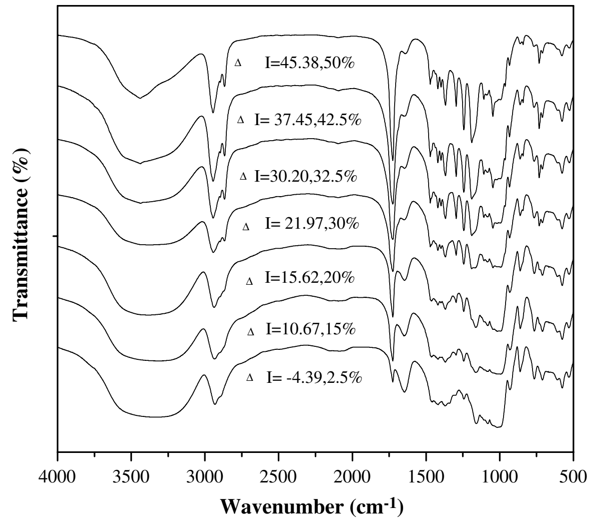

Fig. 11. FT-IR spectra of starch/PCL with varied PCL wt%.

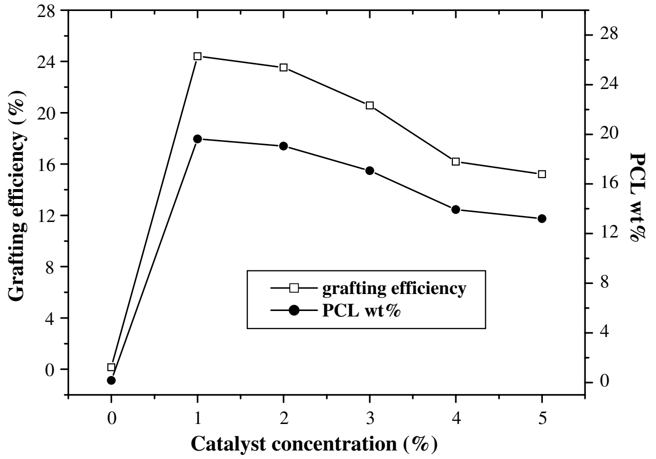

Fig. 12. Influence of catalyst concentration on the graft polymerization [110 °C, 28 h, ε-CL/starch (wt) = 1:1].

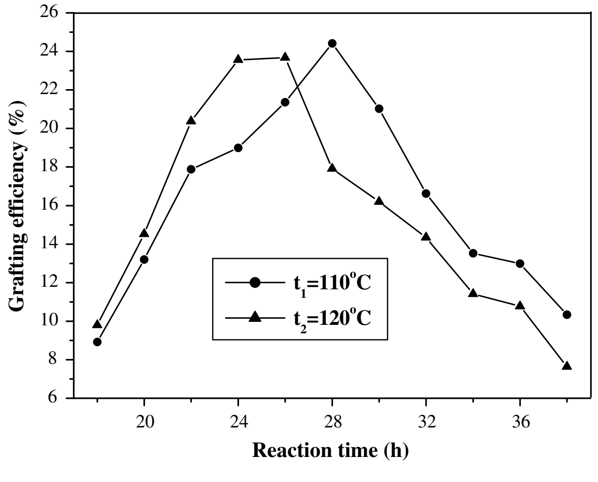

Fig. 13. Effect of reaction time on the graft polymerization [ε-CL/starch (wt) = 1:1, 0.1% Sn(Oct)2].

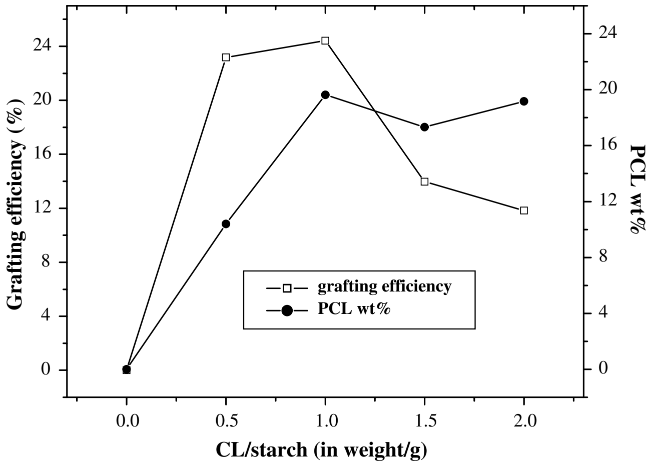

Fig. 14. Effect of ε-CL/starch (in weight) on the graft polymerization [0.1% Sn(Oct)2, 110 °C, 28 h].

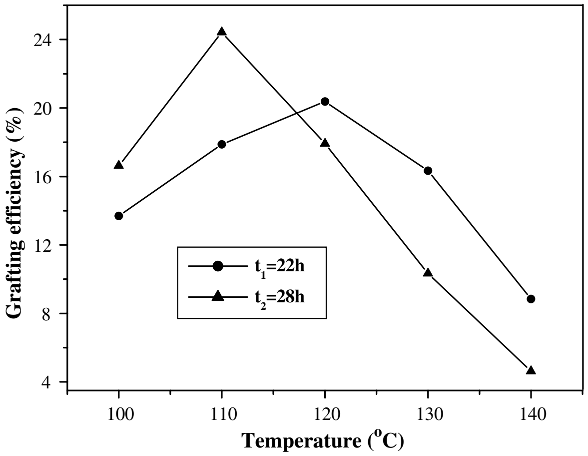

Fig. 15. Influence of reaction temperature on the graft polymerization [ε-CL/starch (wt) = 1:1, 0.1% Sn(Oct)2].

[AMIM]Cl as a reaction media, the ring opening graft polymerization of ε-caprolactone onto starch was carried out smoothly and the grafting efficiency of PCL reached 24.42%, which was calculated according to a standard curve created by FT-IR method.

Acknowledgements

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