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Preparation of corn starch-*g*-polystyrene copolymer in ionic liquid: 1-Ethyl-3-methylimidazolium acetate

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ABSTRACT

The copolymer of starch grafted with polystyrene (starch-*g*-PS) was synthesized with high grafting percentage by utilizing the ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac) as solvent and potassium persulfate as initiator. The effect of various parameters upon the polymerization were studied including: initiator concentration, styrene:starch weight ratio, the reaction time and temperature. Grafting percentages were calculated using an FT-IR calibration method, with values up to 114%. The resulting copolymer was characterized using FT-IR, SEM, WAXD and TGA, which demonstrated that polystyrene side chains were evenly distributed on the starch backbone. Our results indicate that ionic liquid dissolution of starch, prior to polystyrene grafting, is a versatile methodology for the synthesis of amphiphilic, polysaccharide-based graft copolymers, having high grafting percent.

1. Introduction

Starch is one of the most cost-effective renewable materials that is used industrially in the production of paper, textiles and food additives, as well being a commonly used biotemplate and carbon precursor in materials research (BeMiller & Whistler, 2009; Brun, Wohlgemuth, Osiceanu, & Titirici, 2013; Hu et al., 2010; Wang et al., 2014; Xia, Cui, He, & Li, 2012; Xia, He, & Li, 2013; Xia, Wang, He, Cui, & Li, 2012). Starch is nontoxic, biodegradable, and can be blended with plastics to prepare bioplastics (Janssen & Moscicki, 2010). However, the mechanical properties of thermoplastic polymer/starch blends are very poor due to the hydrophilic nature of starch. One way to improve the mechanical strength of such materials is by covalently combining the starch and polymer chains, which can be accomplished through graft copolymerization of a thermoplastic polymer onto starch. Various methods have been reported for the production of starch-based graft copolymers, such as reactive extrusion (de Graaf & Janssen, 2000), bulk polymerization (Chen et al., 2005), suspension polymerization (Kadokawa, Murakami, Takegawa, & Kaneko, 2009), emulsion polymerization (Cho & Lee, 2002), and atom transfer free radical polymerization (Liu & Su, 2005; Nurmi, Holappa, Mikkonen, & Seppala, 2007). Starch solubility remains an unresolved problem, when using common solvents, due to the presence of strong inter and intramolecular hydrogen bonding, resulting in poor control and yield in the grafting reaction. To overcome such difficulties a solvent is needed that can fully dissolve the starch, and act as an effective reaction medium.

Room temperature ionic liquids, have been utilized as 'green solvents' in a wide range of applications owing to their efficacious dissolution of polysaccharides (Dou & Liu, 2012; Esposito, Kirchhecker, & Antonietti, 2013; Fu & Liu, 2008; Li, Zhang, & Liu, 2006; Men, Kuzmicz, & Yuan, 2014; Men, Schlaad, & Yuan, 2013; Men, Siebenburger, Qiu, Antonietti, & Yuan, 2013; Wang & Liu, 2012, 2013; Zakrzewska, Bogel-Lukasik, & Bogel-Lukasik, 2010). Over the last decade, much research has been conducted into the application of ionic liquids as a solvent for cellulose, displaying good solubility (Swatloski, Spear, Holbrey, & Rogers, 2002), reactivity (Feng & Chen, 2008; Sui et al., 2008; Yan et al., 2009), and control over the resulting material (Amarasekara & Owereh, 2009). Recently, it has been found that starch can also be dissolved in ionic liquids. For example, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) can dissolve corn starch at 15 wt% when heated to 80 °C (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2006), although a decrease in molecular weight was observed (Stevenson, Biswas, Jane, & Inglett, 2007). 1-Ethyl-3-methylimidazolium acetate ([EMIM]Ac) is another well-known solvent for starch. Interestingly, water is capable of acting as a good co-solvent, alongside [EMIM]Ac, to further improve the dissolution of starch, whereas the opposite is observed when using cellulose.

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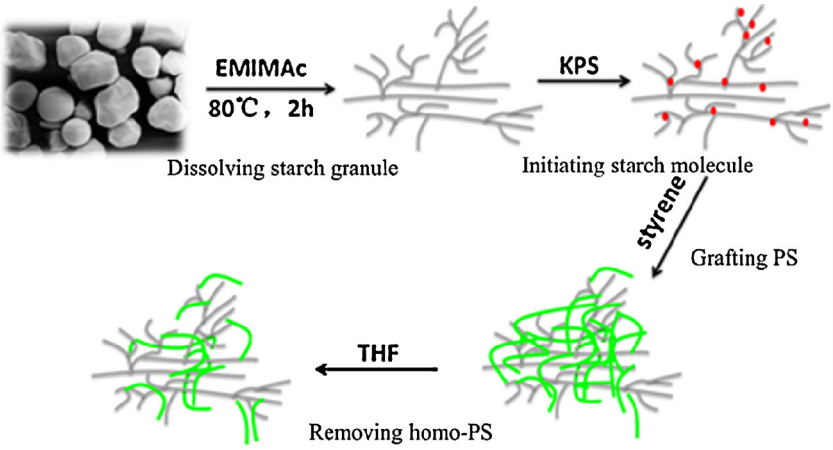

Scheme 1. Synthesis procedure of starch-*g*-PS.

(Komulainen, Verlackt, Pursiainen, & Lajunen, 2013; Lappalainen, Kärkkäinen, & Lajunen, 2013; Liu & Budtova, 2013; Mateyawa et al., 2013).

Using ionic liquids as a reaction media to modify native starch was first reported by Biswas et al. (2006), who prepared acetylated starch with degree of substitution (DS) from 0.3 to 2.6 in 1-butyl-3-methylimidazolium dicyanimide ([BMIM]dca). It was also found that the acetylation substitution preferred at C2 position to C3 and C6 positions when using [BMIM]dca, while there was a more uniform distribution between at C2, C3 and C6 positions when using [BMIM]Ac (Shogren & Biswas, 2010). Lehmann and Volkert (2009) demonstrated that the reactivity order of different hydroxyl groups towards esterification was C6 > C2 > C3 in [BMIM]Cl. Other modification reaction of starch, like esterification with succinic anhydride, acetic anhydride (Lu, Luo, Yu, & Fu, 2012; Luo & Zhou, 2012; Xie, Shao, & Liu, 2010) and phosphorylation (Xie & Shao, 2009) have also been studied in ionic liquids. Moreover, biodegradable starch-*g*-polylactic acid and starch-*g*-polycaprolactone have been prepared through ring opening graft polymerization in 1-allyl-3-methylimidazolium chloride ([AMIM]Cl), with grafting efficiencies up to 30.0% and 24.4%, respectively; marked improvements over the equivalent reactions in common (poor) solvents (Xu, Kennedy, & Liu, 2008; Xu, Wang, & Liu, 2008). However, reports describing the utilization of ionic liquids for grafting of hydrophobic polymers onto starch are scarce in the literature. Moreover, all available protocols suffer from low grafting efficiencies, the graft percentage of starch-*g*-PS was hardly over 46% (Cho & Lee, 2002), likely due to inhomogeneity in the reaction mixture.

In the present work, we demonstrate a method to disperse starch at the molecular level using [EMIM]Ac, followed by grafting with polystyrene to generate starch-*g*-polystyrene (starch-*g*-PS). The effect of a number of factors upon the grafting efficiency are presented, including: initiator concentration, styrene:starch weight ratio, the reaction time and temperature. The structure, composition and physical characteristics of the reaction mixture and resulting graft copolymer have been characterized using FT-IR, SEM, WAXD and TGA.

2. Material and methods

2.1. Material

Corn starch (from Aladdin; 25 wt% amylose, AR) was used after drying in vacuum (60 °C, 100 Pa) for 48 h. Styrene and bromoethane were purchased from Beijing Chemical Engineering Plant, and were distilled under reduced pressure before usage. 1-Methylimidazole was used after drying over CaH_2 for 2 days, and then was distilled under reduced pressure. Other reagents were purchased from Aladdin, and were used as received.

2.2. Preparation of [EMIM]Ac

The two steps synthesis of [EMIM]Ac was modified from literature (Bonhote, Dias, Papageorgiou, Kalyanasundaram, & Gratzel, 1996). The first step was preparation of 1-ethyl-3-methylimidazolium bromide [EMIM]Br. 1-Methylimidazole (41.06 g, 0.50 mol) and bromoethane (65.35 g, 0.60 mol) were added into a three-neck flask fitted with reflux condenser and stirrer for 8 h at 60 °C under an argon atmosphere. After washing with diethyl ether, the obtained yellow liquid was transferred to a crystallizing dish filled with ethanol/acetone (2/1 v/v). Transparent crystal ([EMIM]Br) was obtained after 3 days followed by drying in a vacuum oven at 60 °C for 12 h.

The second stage was conversion to the acetate salt: [EMIM]Br (0.50 mol) was dissolved in water (150 mL) and added slowly into $Ag(CH_3COO)$ aqueous solution (0.50 mol in 250 mL). The mixture was stirred at room temperature for 6 h, followed by filtration to remove AgBr. Charcoal was added to the filtrate in order to remove any impurities (indicated by color), then refrigerated overnight. After filtering off the charcoal, water was removed from the filtrate through rotary evaporation under vacuum at 70 °C. The obtained light yellow liquid was dried in a vacuum oven for 48 h at 80 °C. The synthesized [EMIM]Ac (100 mg) dissolved in D_2O (0.5 mL) for ^1H NMR measurement. Multiplicities are reported as s (singlet), d (doublet), t (triplet) and m (multiplet). ^1H NMR (400 MHz, D_2O, δ ppm): 1.38 (t, 3*H*, $-CH_3$), 1.77 (s, 3*H*, $-CH_2CH_3$), 3.78 (s, 3*H*, $OOCH_2CH_3$), 4.13 (m, 2*H*, $OOCH_2CH_3$), 7.33 (s, 1*H*, —N—CH = CH—), 7.39 (s, 1*H*, —N—CH = CH—), 8.63 (s, 1*H*, —N = CH—N—).

2.3. Starch dispersion in [EMIM], Ac

Starch (0.25 g) was dispersed in [EMIM]Ac (4 g) with stirring at 80 °C until a transparent solution was formed. The dissolving procedure was observed in-situ through polarized light microscope (PLM) equipped with a heating stage. The heating rate was set as 20 °C/min, and the final temperature was maintained until 95% of starch granules disappeared from the view-window.

Regenerated starch was precipitated out using 100% ethanol, collected by filtration and then dried in a vacuum oven for 24 h at 50 °C. The final products were characterized by scanning electron microscope (SEM) and nuclear magnetic resonance (NMR).

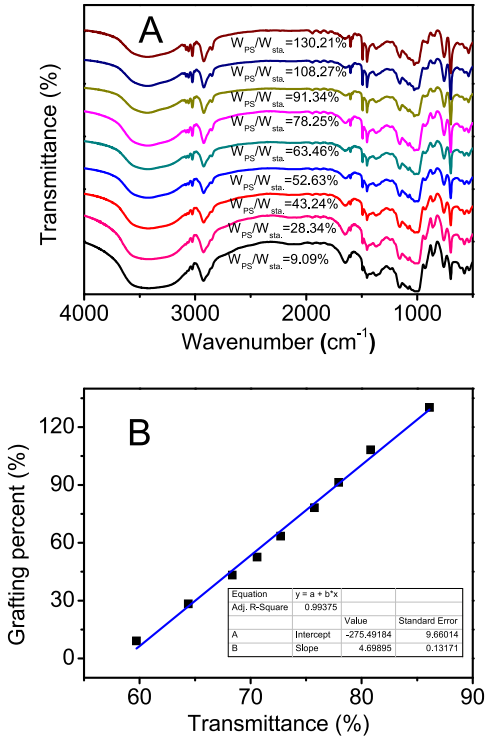

Fig. 1. (A) FT-IR spectra of various ratios of PS to starch, (B) standard curve of GP % to the adjusted intensities of signals of PS (1600 cm^{-1}).

2.4. Grafting procedure

Starch-*g*-PS was synthesized according to the procedure of Scheme 1. Starch (0.25 g) was dissolved in [EMIM]Ac (4 g) in a 10 mL three-neck flask under argon and stirred at 80 °C for 2 h. The initiator, potassium peroxydisulfate (KPS, 0.03 g, 4 wt%), was added into the flask and stirred for 10 min before the styrene was added into reaction, which was heated to the desired temperature and stirred under argon. Although the specific weight ratio of styrene to starch varied, the total weight of reactant was maintained at 0.75 g.

Reaction products were precipitated by the addition of 50 mL methanol/H_2O (3/2 v/v). The precipitate was washed for 3 times, and then dried under vacuum at 60 °C for 12 h. The obtained product was a mixture of the grafted copolymer (starch-*g*-PS), and polystyrene homopolymer (homo-PS). Homo-PS was isolated from the products by Soxhlet extraction with tetrahydrofuran (THF) for 24 h. The residue was starch-*g*-PS, which was dried in vacuum at 60 °C for 12 h before characterization.

2.5. Measurements

Fourier transform infrared (FT-IR) spectra were obtained with an Avatar 360 spectrometer made by Nicolet Instruments Corp. (Madison, WI) in transmittance mode using pressed KBr discs. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution using tetramethylsilane as an internal standard on a Bruker Advance DRX-400 NMR spectrometer.

Polarized light microscope (PLM) observation of starch dissolution in [EMIM]Ac was performed on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage.

Scan electron microscope (SEM) images were obtained using a Hitachi S-4800 SEM (Tokyo, Japan) after the sputter coating of gold on the specimen surface.

Wide-angle X-ray diffraction (WAXD) patterns were performed on an X'Pert PRO MPD diffractometer with Cu $K\alpha$ radiation (λ = 1.5418 Å) at 25 °C (scan range: 10–40°).

Thermal gravimetric analysis (TGA) measurement was performed on METTLER TOLEDO TGA-SDA 851e analyzer with a heating rate of 10 °C/min from 50 to 600 °C under nitrogen with Al_2O_3 crucible.

2.6. Calculation of the grafting percent of PS

The grafting percent was defined by following equation (Xu et al., 2008b):

$$\text{grafting percent (GP)} = \frac{\text{weight of grafting PS}}{\text{weight of total starch}} \times 100\% \quad (1)$$

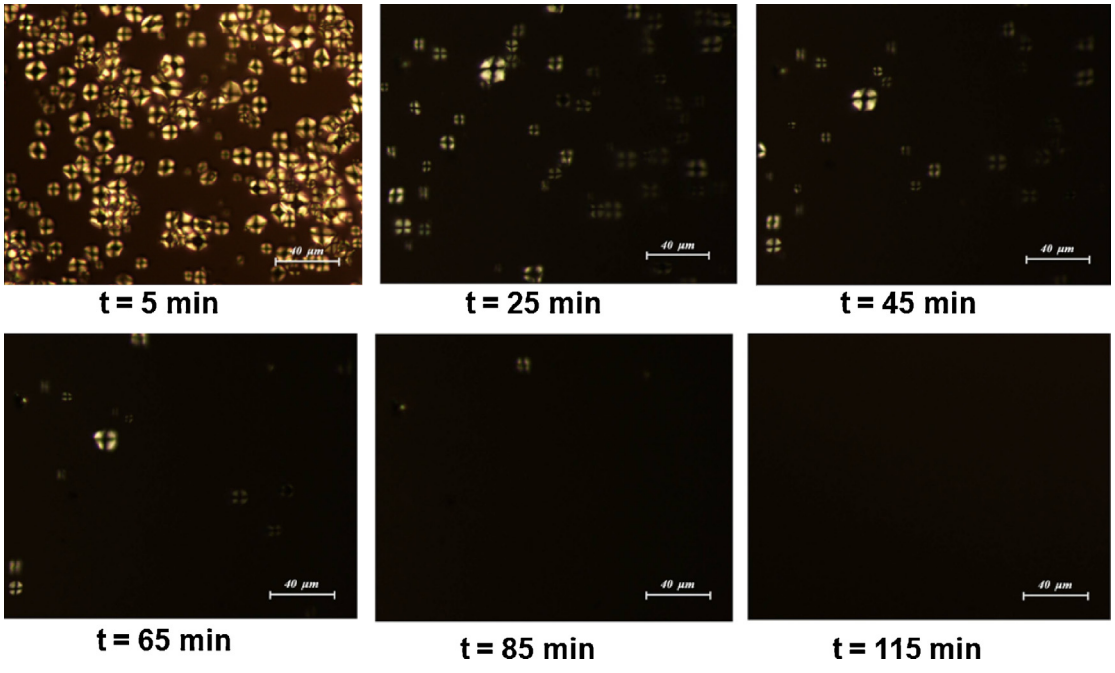

Fig. 2. Dissolving process of starch in [EMIM]Ac at 80 °C in-situ traced by a PLM.

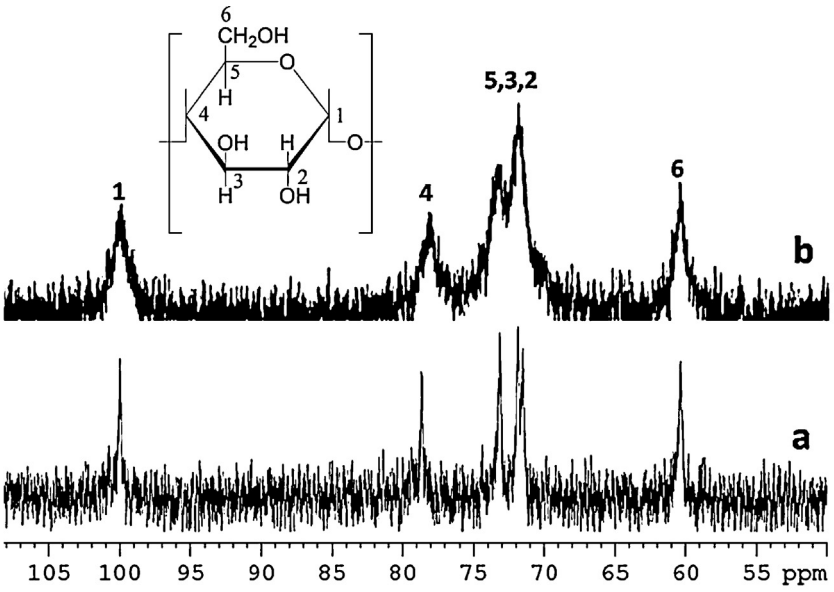

Fig. 3. ^{13}C NMR spectra of recovered starch from DMSO (a) and [EMIM]Ac (b) in DMSO-d_6.

A series of FT-IR spectra (Fig. 1A) were obtained using a fixed amount of KBr and different weight ratios of starch and polystyrene (5 mg) in the pellet. After baseline correction, keeping the intensities of signal at 1648 cm^{-1} (starch) as a constant, the adjusted intensities of the signal at 1600 cm^{-1} (PS) was obtained. A graph was plotted of the weight ratios of starch and polystyrene against adjusted intensities (T) of the signal at 1600 cm^{-1} (Fig. 1B) from which, a regression equation was obtained.

$$GP = 4.67T - 275.49 \quad (2)$$

3. Results and discussion

3.1. Dissolution of starch in [EMIM]Ac

The dissolution of starch in [EMIM]Ac (6.25 wt%) at different temperatures was monitored in real via PLM equipped with a heating stage. When the temperature was below 60 °C, starch granules could not be dissolved by [EMIM]Ac without applying a shearing force. At 70 °C, however, slow dissolution occurred, taking 12 h. With increasing temperature, the starch was dissolved more rapidly. At 80, 90, 100, and 120 °C, the dissolution rate greatly

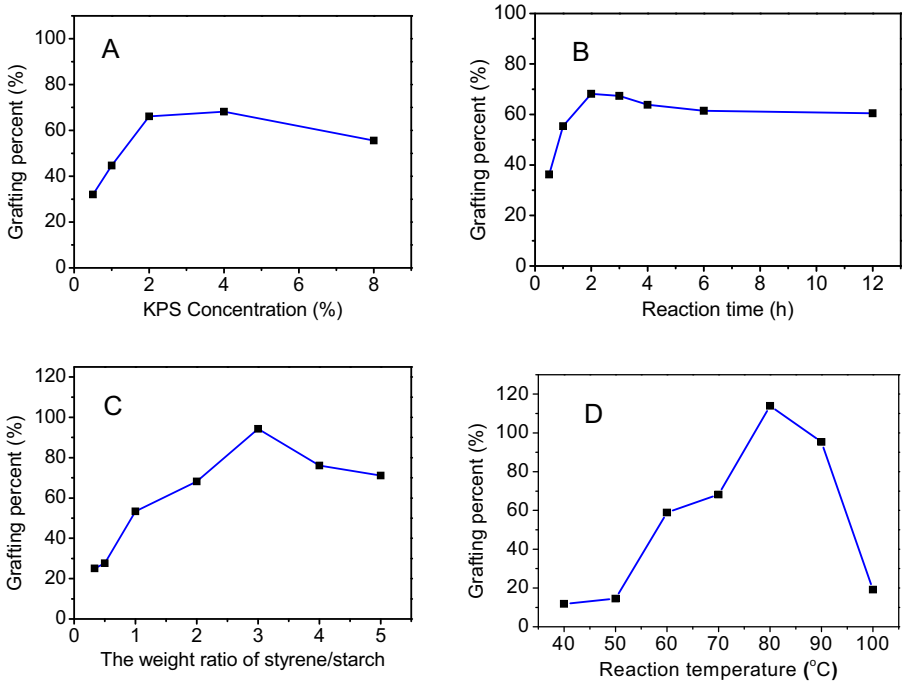

Fig. 4. Influence of (A) initiator concentration, (B) reaction time, (C) the weight ratio of styrene to starch, and (D) reaction temperature on the grafting polymerization [KPS 4 wt%, 70 °C, 2 h, styrene/starch (wt/wt) = 2:1, when changing one infector, other variables as constants].

Table 1
Dissolving time of starch in [EMIM]Ac at different temperatures.

Temp. (°C)	60	70	80	90	100	120
Time (min)	–	720	115	24	7	3

increased and the corresponding dissolution times were 115, 24, 7 and 3 min, respectively (Table 1). A temperature of 80 °C was chosen for further investigation, being a good compromise between speed and cost. As shown in Fig. 2, PLM was effective in identifying semi-crystalline starch granules by the presence of characteristic Maltese cross patterns due to the birefringence of particles with a high degree of molecular orientation. In the first 25 min about half of the starch granules disappeared from view-window, whilst the sizes of any remaining starch particles decreased with time. Such observations indicate that the dissolving process starts from outlayer of starch to the inside, which is different from gelatinization of starch in water that is associated with a swelling process.

^{13}C NMR was employed here to study on the chemical structure changes of corn starch after dissolution in [EMIM]Ac (Fig. 3). The six characteristic signals of the unmodified anhydroglucose units appeared clearly at 99.99 (C-1), 78.7 (C-4), 73.1 (C-5), 71.8 (C-3), 71.5 (C-2), and 60.4 ppm (C-6), in accordance with starch dissolved in DMSO and [AMIM]Cl (Xu et al., 2008a). These results demonstrate that [EMIM]Ac is a non-derivatizing and efficient solvent for starch.

3.2. Grafting of polystyrene onto starch in [EMIM]Ac at molecular level

Knowing that corn starch can be homogenously dispersed in [EMIM]Ac, a high graft percent with polystyrene was expected to be obtained due to the increased surface area of starch. A systematic investigation was conducted into the effect of initiator concentration, the reaction time styrene:starch weight ratio, and the reaction temperature upon the GP. The influence of initiator concentration on grafting percent is presented in Fig. 4A, which shows that the GP increased sharply from 32% to 62% when [KPS] ≤ 2 wt% and then decreased slightly when the KPS concentration was over 4 wt%. The increase of GP may be ascribed to greater number of free radicals generated on the glucose unit of starch by increasing levels of KPS (Cho & Lee, 2002). Decrease in the GP when the KPS concentration was over 4 wt% was due to the concentration of persulfate radicals being too high, causing a high chance of quenching between adjacent free radicals and a large amount of homo-PS.

Fig. 4B displays the effect of reaction time on GP. It was observed that GP increased gradually in the first 2 h, but leveled off afterwards, which demonstrates that the grafting reaction was very efficient during the first 2 h but ceased thereafter. The reaction leveled off after 2 h due to the reduction in the concentration of monomers and free radicals in the reaction system.

Fig. 4C shows the effect of the styrene:starch weight ratio on the grafting reaction, which was varied from 1/3 to 5, while keeping other reaction variables constant. It was observed that the GP increases as the weight ratio of styrene is increased up to a maximum at styrene:starch = 3, with further increase in the ratio resulting in a reduction of GP. The increase in GP was ascribed to higher local concentration of styrene monomers around the starch backbone, giving rise to an increased reaction probability. However, when the concentration of monomer was too high it presumably became more favorable to form homo-PS, which are 0.012 g, 0.048 g, 0.128 g, 0.185 g, 0.283 g, 0.372 g and 0.401 g, respectively, corresponding to the styrene:starch = 1/3 to 5, leading to a decreased GP.

The influence of temperature on grafting parameters is shown in Fig. 4D, which presents a gradual increase of the GP as the temperature was increased from 40 °C to 80 °C and a sharp reduction

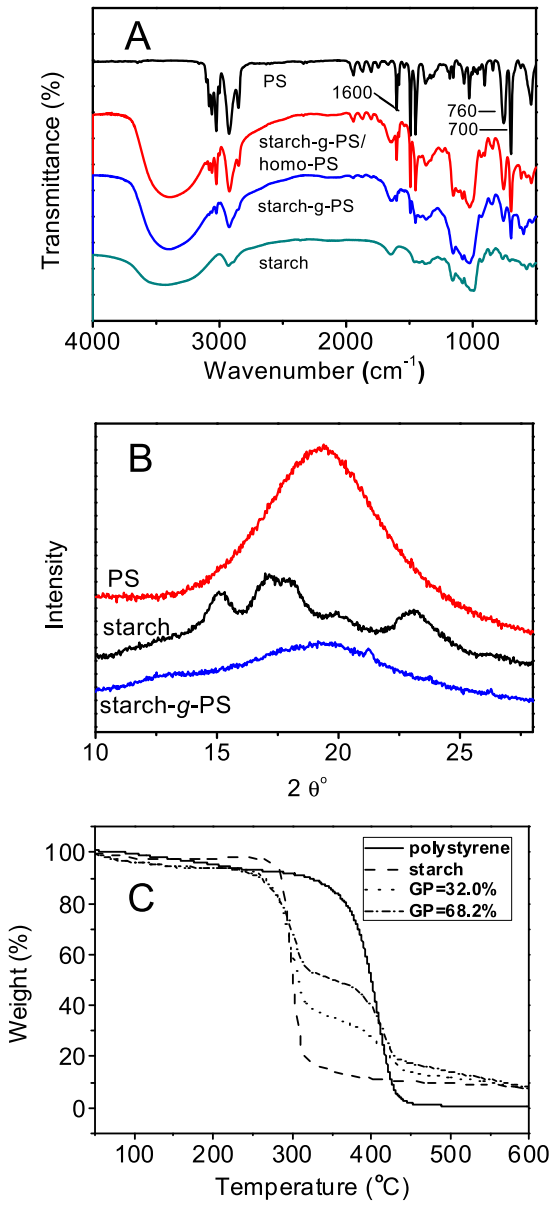

Fig. 5. (A) FT-IR spectra of PS, starch, starch-g-PS and starch-*g*-PS composed homo-PS, (B) WAXD patterns of PS, starch and starch-*g*-PS, (C) TGA curves of PS, starch, starch-*g*-PS.

at elevated temperature. At lower temperatures, generally below 60 °C, KPS did not decompose at a short induction time, thus no enough free radicals were generated to react with the hydroxyl groups of starch, whereas at elevated temperature KPS radicals could react with the starch to generate increasing amounts of macroradicals to initiate the graft copolymerization of PS. However, when temperature was increased above 90 °C the reaction seemed to become unstable, which was observed in the color changing of the solution, from yellow to crimson, and lead to a sharp reduction of GP.

3.3. Characterization of starch-g-PS

FT-IR spectra of starch, PS and starch-*g*-PS products before and after removing homo-PS are represented in Fig. 5A. The characteristic peaks of corn starch at 980–1250 cm^{-1} were attribute to the C—O stretching vibration. After grafting copolymerization, the peaks from PS (1600, 760, 700 cm^{-1}), due to the C—H stretching of

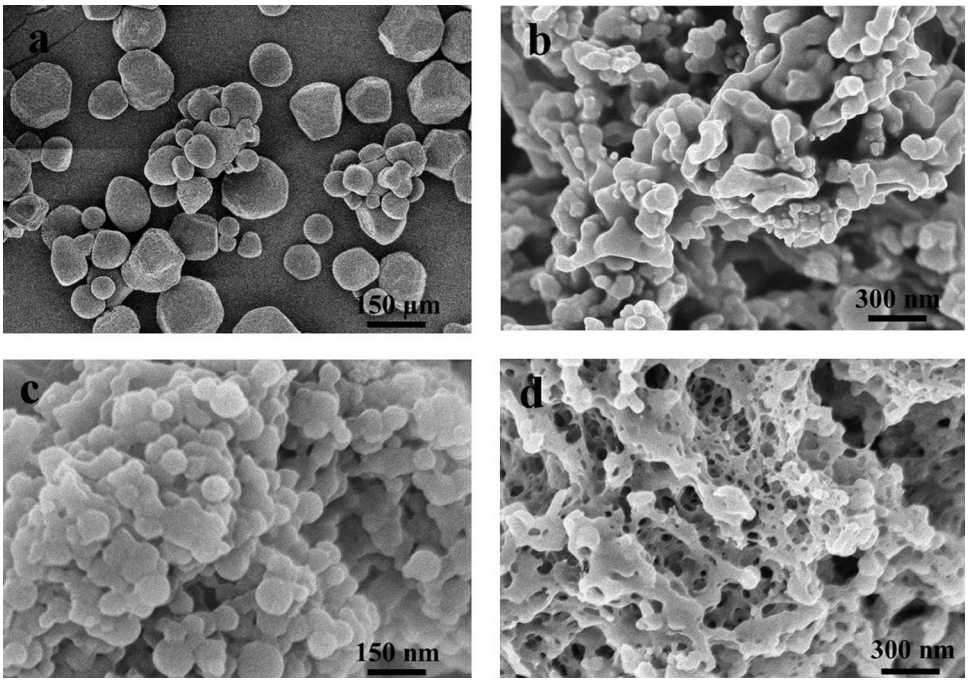

Fig. 6. Scanning electron micrographs of native corn starch (a), starch dispersion in [EMIM]Ac (b) starch-*g*-PS (GP = 32.0%) before (c) and after extraction (d).

aromatic ring, appeared in the spectra. The intensities of PS peaks are diminished, but still existed after removing of homo-PS by Soxhlet extraction, which demonstrated that PS was successfully grafted onto starch.

The WXAD patterns illustrate the changes in crystallinity of starch, PS, starch-*g*-PS (Fig. 5B). For comparison, PS was synthesized in [EMIM]Ac using the same conditions as starch-*g*-PS. No sharp peaks were observed in the diffractogram of PS, indicative of a low crystallinity in the synthesized mono-PS. Native starch has five peaks at $2\theta = 15.1$, 17.2, 17.9, 19.8 and 23.1°, according to literature. After the grafting reaction, only a broad dispersive peak around $2\theta = 19.5°$ existed in the starch-*g*-PS pattern, which demonstrated that the prepared starch-*g*-PS was amorphous, and also indicated [EMIM]Ac could effectively disrupt the crystalline structure of starch.

TGA thermograms of polymers are shown in Fig. 5C. Starch exhibited a lower thermal stability than PS; the degradation temperature of corn starch is about 300 °C, 100 °C lower than that of PS. Grafted starch presented two-step degradation, including the characteristics of both starch and PS. The grafting percent was also be calculated from TGA curves, yielding 34% and 72%, which was similar to the values obtained by FT-IR spectra (32%, 68%).

SEM was also used to compare the structure and morphological changes in the polymer before and after PS grafting. The diameters of native starch granules were more than 10 μm (Fig. 6a). After dispersion in [EMIM]Ac, starch granules were dispersed into small particles with sizes less than 500 nm (Fig. 6b). The grafted starch (GP = 32%) before Soxhlet extraction was covered by spherical particles of PS with diameters about 100 nm (Fig. 6c). After Soxhlet extraction, however, the homo-PS molecules and particles were removed by hot THF, leaving numerous cavities in starch-*g*-PS (Fig. 6d).

4. Conclusion

In summary, [EMIM]Ac was found to be an effective solvent for starch, which could disperse starch granules to molecular level without derivatization. Starch-*g*-PS was successfully prepared by homogeneous grafting copolymerization in [EMIM]Ac. The GP of PS, which was calculated according to a standard curve created by FT-IR method, reached to 114%, when the weight concentration of KPS was 4% and the weight ratio of styrene to starch was 2:1 at 80 °C for 2 h. The results obtained from WAXD, TGA and SEM demonstrated that the morphology and crystallinity of native starch were significantly altered after grafting reaction. This method is expected to be used commonly to prepare starch graft hydrophobic monomers with high GP.

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