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Controlled graft copolymerization of lactic acid onto starch in a supercritical carbon dioxide medium

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ABSTRACT

This work presents a new approach for the synthesis of a starch-*g*-poly L-lactic acid (St-*g*-PLA) copolymer via the graft copolymerization of LA onto starch using stannous 2-ethyl hexanoate ($Sn(Oct)_2$) as a catalyst in a supercritical carbon dioxide ($scCO_2$) medium. The effects of several process parameters, including the pressure, temperature, $scCO_2$ flow rate and reaction time, on the polymerization yield and grafting degree were studied. Amorphous graft St-*g*-PLA copolymers with increased thermal stability and processability were produced with a high efficiency. The maximum grafting degree (i.e., 52% PLA) was achieved with the following reaction conditions: 6 h, 100 °C, 200 bar and a 1:3 (w/w) ratio of St/LA. It was concluded that these low cost biobased graft biopolymers are potential candidates for several environment-friendly applications.

1. Introduction

Conventional polymers/plastics are indispensable materials of modern life, but in a short time, the after-use fates of these products has led to a waste disposal problem (Bertuzzi, Armada, & Gottifredi, 2007). The development of environment-friendly materials based on natural and renewable resources (i.e., biobased) have arisen as the most attractive and popular approach to overcome this problem (Petersen et al., 1999). Starch is the most abundant renewable biopolymer in the world, and it is relatively inexpensive (Lawal, Lechner, Hartmann, & Kulicke, 2007; Xie, Zhang, & Liu, 2011). Commercial granular starch has been used in polyolefins as a filling agent and blended with synthetic polymers to produce biodegradable materials with desired properties (Otey & Westhoff, 1982). Earlier publications (Bhattacharya, Vaidya, Zhang, & Narayan, 1995; Vaidya, Bhattacharya, & Zhang, 1995) have indicated that blends of functional anhydride polymers and starch could lead to products with useful end properties. Research on blending polysaccharides (e.g., starch and cellulose) and synthetic polymers (e.g., polyolefins) has a long history, but poor compatibility limits the production of these blends. To improve the poor compatibility, many approaches have been proposed, such as the chemical modification of both starch (Kiatkamjornwong, Thakeow, & Sonsuk, 2001; Thakore, Desai, Sarawade, & Devi, 2001) and polyolefins (LDPE) (Chandra & Rustgi, 1997) and/or the introduction of compatibilizer (Bikiaris, Prinos, & Panayiotou, 1997; Yoo et al., 2002) into the blends of starch and polyethylene (PE). Grafting hydrophobic thermoplastic polymers with more hydrophilic monomers (e.g., maleic anhydride (MA) and dioctyl maleate (DOM)) has been presented as an effective approach to fabricate compatible and biodegradable polymer materials (Rzayev, 2010, 2011). Zhang and Sun (2004) have used MA as a nontoxic reactive compatibilizer to improve the compatibility and properties of poly(lactic acid) (PLA)/starch blends for extrusion. According to Heinze and Liebert, starch in a granular state was modified by chemical deviation grafting processes that improve the properties of the starch (Heinze & Liebert, 2001). In the starch modification by grafting, acrylic monomers (e.g., methyl acrylate) were grafted onto the starch backbone leading to modified starch that can be injected or extruded into films (Willett, Jasberg, & Swanson, 1994).

In the conventional methods, to produce grafted starch materials, organic solvents such as dimethylsulfoxide (DMSO) and pyridine have been employed, and that is a major drawback of these materials, especially when they are used as food packaging. Moreover, this bottleneck creates environmental problems and obstructs the industrialization and commercialization of the production method (Harris, Jureller, Kerschner, Trzasko, & Humphreys, 1999). Well-known techniques utilize highly toxic organic solvents as mediums in polymerization reactions. This problematic issue forced researchers to propose alternative approaches and

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Table 1
Effects of reaction parameters on grafting degree.

St/LA feed ratio (w/w)	T (°C)	P (bar)	Time (h)	$scCO_2$ flow rate (g/min)	Grafted LA (mol%)
Effect of St/LA ratio					
1:0.5	100	200	6	10	32 ± 1.5
1:1	100	200	6	10	41 ± 2
1:3	100	200	6	10	52 ± 2.3
1:5	100	200	6	10	43 ± 2.1
Effect of temperature					
1:3	70	200	6	10	32 ± 1.2
1:3	90	200	6	10	49 ± 2.2
1:3	100	200	6	10	52 ± 2.3
1:3	110	200	6	10	41 ± 1.9
Effect of $scCO_2$ flow rate					
1:3	100	200	6	1	28 ± 1.2
1:3	100	200	6	5	36 ± 1.6
1:3	100	200	6	10	52 ± 2.3
1:3	100	200	6	15	40 ± 1.8
Effect of pressure					
1:3	100	70	6	10	21 ± 1.1
1:3	100	100	6	10	43 ± 1.8
1:3	100	200	6	10	52 ± 2.3
1:3	100	300	6	10	52 ± 2.4
Effect of reaction time					
1:3	100	200	1.5	10	26 ± 1.3
1:3	100	200	3	10	48 ± 2.3
1:3	100	200	6	10	52 ± 2.3
1:3	100	200	9	10	52 ± 2.4

reaction mediums. Supercritical carbon dioxide ($scCO_2$), with its high abundance, inexpensive cost and chemically inert nature, has emerged as a suitable reaction medium instead of toxic organic solvents in the last two decades (Cooper, 2000; Woods, Silva, Nouvel, Shakesheff, & Howdle, 2004). Furthermore, recently $scCO_2$ has become a green solvent for polymer synthesis without requiring the use of any conventional solvents, especially in the processing of the products for biomaterial applications and biodegradable polymers, such as the production of drug delivery systems and highly porous scaffolds for tissue engineering, which would be very difficult to achieve using the traditional system (Aydin, 2011; Davies et al., 2008; Gencer, Odabas, Sasmazel, & Piskin, 2012). Additionally, Condo, Paul, and Johnston (1994) reported the effect of compressed $scCO_2$ fluid acting as a plasticizing agent on the T_g behaviour of polymers. $scCO_2$ has proven to be an ideal solvent for polymerization reactions, especially in the chemical or physical modification of polysaccharides (Harris et al., 1999; Kemmere & Meyer, 2006; Muljana, Picchioni, Heeres, & Janssen, 2008; Yin et al., 2007). Moreover, $scCO_2$ has a clear advantage over traditional solvents in that it acts as a plasticizer for crystalline polymer derivatives of starch. Recently, the utilization of $scCO_2$ in condensation without any organic solvents led to removal of small molecules from the condensate (e.g., water, MeOH and phenol) and an increase in the degree of polycondensation (Cooper, 2000; Inodot, Pi, & Scedil, 2011; Yılmaz, Eğri, Yıldız, Çalımlı, & Pişkin, 2011).

Considering all of the benefits of $scCO_2$ mentioned above, in the context of this study, we propose the graft copolymerization of lactic acid (LA) onto a starch backbone over the C-2, C-3 and C-6 carbon atoms of starch macromolecules. The effects of several reaction parameters, including the temperature, pressure, $scCO_2$ flow rate, reaction time, and polymer/monomer ratio, on the grafting degree and copolymer properties are presented here.

2. Experimental procedure

2.1. Materials

Corn starch (22–28% amylose and 72–78% amylopectin) was supplied by Cargill (USA). L-Lactic acid (20 wt% aqueous solution) was purchased from Purac (The Netherlands). Sodium hydroxide and stannous 2-ethyl hexanoate $Sn(Oct)_2$) were purchased from Sigma-Aldrich (Germany). High purity $scCO_2$ (99.9%) was obtained from Linde (Germany).

2.2. Graft copolymerization

Graft copolymerization was conducted by the following two steps: (1) gelatinization of the starch according to a related study (Sivam, Waterhouse, Zujovic, Perera, & Sun-Waterhouse, 2013) and (2) grafting in the $scCO_2$ reactor. For the gelatinisation, 5 g of starch was dispersed in 30 mL of 0.40 M NaOH in a three-necked reactor at 70 °C for 1 h. The gelatinized starch was transferred into a 250 mL high pressure stainless reactor (Thar R100, USA) consisting of two sapphire windows on both sides with a high-pressure pump (Thar, P series) to pressurize CO_2, an automated back pressure regulator (Thar, ABPR 200), a temperature controller (Thar, CN6), a mechanic mixer (Minarik Corporation, MM23101C) with four blades and a computer control system. The graft copolymerization was initiated with an excess amount of LA and catalyst ($Sn(oct)_2$) under different reaction conditions (70–110 °C, 70–300 bar, 1.5–9 h and 1–15 g/min, see Table 1) under mechanical stirring (700 rpm). The reactor was cooled to room temperature to terminate the reaction, and the product was isolated by venting with CO_2. The product was then washed twice with methanol to remove the unreacted LA and oligo(lactic acid), and it was dried under vacuum at 70 °C. Additionally, to eliminate the presence of PLA in the product, an extraction procedure was applied as a further purification step for 12 h using methanol as an extraction solvent in a Soxhlet system. Finally, the extracted polymer was dried at 70 °C under vacuum.

2.3. Characterization

2.3.1. Chemical structure

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analysis was employed by using an ATR-equipped spectrophotometer (FTIR-SMART-IR, THERMO Scientific, USA) throughout the wavenumber range of 4000 to 500 cm^{-1}.

The ^{13}C NMR analysis was carried out using a Bruker AVANCE 300 (Germany) spectrometer operating at a 300.13 MHz proton frequency with a 4-mm Bruker spinning probe and zirconia rotors.

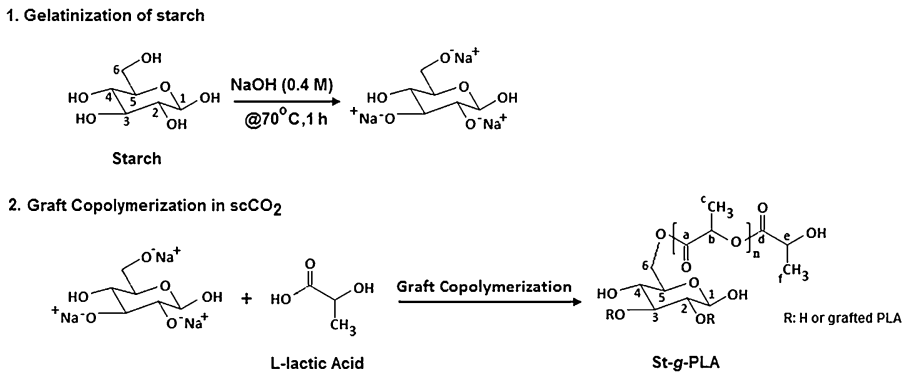

Fig. 1. The synthetic pathway of the St-*g*-PLA copolymer.

Spectra were obtained using the standard CP/MAS (cross polarization magic angle spinning) technique with 1400 scans. The magic angle was adjusted by maximizing the side bands of the ^{79}Br signal of a KBr sample. The samples were rotated at 4000 ± 1 Hz. The compositions of the graft copolymers were determined by ^{1}H-nuclear magnetic resonance spectroscopy (Bruker Spectrospin Avance Ultrashield 400, Germany). ^{1}H NMR analysis was performed at 400 MHz. The samples were prepared by dissolving them in $CHCl_3$ (4 mg/mL). All of the chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as the internal reference.

The grafted copolymer removed from the reactor was precipitated in methanol. The number of COOH end groups coming from the lactic acid grafts were determined by titrating the polymer solution (0.4 g polymer), which included 1–3% (w/w) of indicator (phenolphthalein), with KOH–methanol (0.05 N KOH solution). The titration was conducted until the colour of the solution turned purple and was terminated when no change was observed in the colour of the solution for at least for 12 s.

2.3.2. Physical structure

The crystalline structures of starch and the graft copolymer were analysed by XRD diffractometry (Bruker AXS 5000 X-ray Diffractometer operated at 10 kV, Germany). Scans were conducted in the 2θ range of 0–50° at a speed of 2°/min.

The surface morphologies of samples were investigated via scanning electron microscopy (SEM, FEI Nova NanoSEM 430, USA). The dried samples were coated onto Au/Pd with a thickness of 80 Å using a PECS 682 (USA) coating system.

2.3.3. Thermal behaviours

To investigate the thermal stability of the starch and graft copolymer, thermogravimetric analysis (Perkin Elmer Diamond, USA) was performed at a heating rate of 10 °C/min in the range of 25 to 600 °C under a nitrogen atmosphere.

3. Results and discussion

3.1. Graft copolymerization

The synthetic pathway for the preparation of the St-*g*-PLA graft copolymer in a $scCO_2$ medium includes a two-step reaction schematically demonstrated as follows (Fig. 1):

Synthesis of the graft copolymer was performed by gelatinization of the starch (first step) and graft copolymerization of LA monomer onto the starch in a $scCO_2$ medium (second step). To optimize the operational parameters of the reaction (St/LA feed ratio, temperature, pressure, $scCO_2$ flow rate and reaction time) and evaluate their effects on the grafting degree, graft copolymerizations were investigated in detail, and the results are summarized in Table 1. We observed that these operational parameters significantly influenced the graft copolymerization and thus the grafting degree (content of branched PLA). It was found that St-*g*-PLA with a maximum grafting degree (52 mol%) is formed using the following reaction conditions: a St/LA feed ratio of 1:3, 100 °C, 200 bar, a $scCO_2$ flow rate of 10 g/min and a reaction time of 6 h.

The grafted LA mole fraction (in mol%) of monomers (m_1 and m_2) in the St-*g*-PLA copolymer was calculated by using FTIR absorption bands from St and grafted PLA with the following equations (Pekel, Şahiner, Güven, & Rzaev, 2001):

$$m_1 = \frac{A^{1336}/M_1}{A^{1336}/M_1 + A^{1735}/M_2} \times 100 \quad (1)$$

$$m_2 = \frac{A^{1735}/M_2}{A^{1336}/M_1 + A^{1735}/M_2} \times 100 \quad (2)$$

where A^i donates the absorption area for the characteristic peaks and M_1 and M_2 are the molecular weights of the repeating St and LA units, respectively.

The results are summarized in Fig. 2. To determine the contents of the starch and LA units in the copolymer, absorption band value ratios between the characteristic bands of 1735 cm^{-1} (for the LA C=O ester peak) and 1336 cm^{-1} (for the St–CH_2 peak) were employed.

The effects of the graft copolymerization parameters, i.e., temperature, reaction time, $scCO_2$ flow rate and pressure, are shown in Fig. 2, and related data are summarized in Table 1. The effect of the temperature on the graft copolymerization is shown in Fig. 2A. There is an inverse relationship between the temperature and the grafted LA mole fraction; at temperatures above 100 °C, the grafted LA mole fraction decreased due to the breaking of grafted LA. It is obvious that over the starch gelatinization point, the starch structure puffed up, and this led to the partial separation of the amylose and amylopectin, which resulted in an increase in the activated groups (especially OH groups) available to react with the excess lactic acid in the polymerization media (Muljana, Picchioni, Heeres, & Janssen, 2009). Especially of note is that at extremely high temperatures, the tendency of the lactic acid to homo-polymerize increased remarkably, which adversely caused a clear fall in the grafted PLA mole percent.

Fig. 2B depicts the effect of time on graft copolymerization. It is clear that increasing the reaction time from 1.5 h to 6 h changed the grafted PLA mole percent significantly, and the maximum amount of grafted PLA (52%) was achieved after 6 h of reaction time. A further increase in the polymerization time had almost no effect on the grafted percentage.

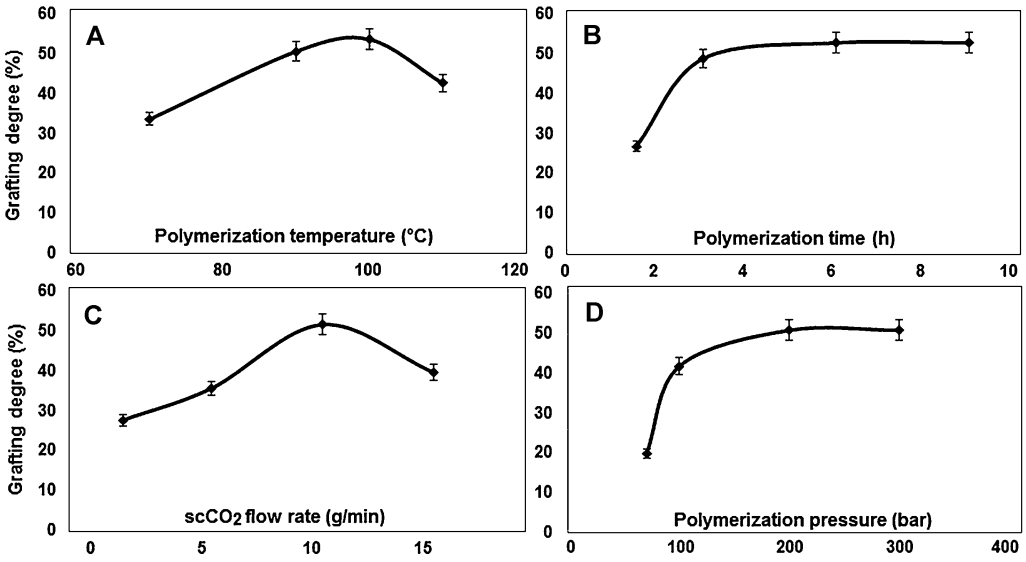

Fig. 2. Influence of variable conditions on the grafted LA mole percent: (A) polymerization temperature, (B) polymerization time, (C) $scCO_2$ flow rate and (D) polymerization pressure.

The effects of the $scCO_2$ flow rate and the polymerization pressure on the graft copolymerization are shown in Fig. 2C and D, respectively. The maximum grafted PLA mol percent (52%) was attained by increasing the $scCO_2$ flow rate to 10 g/min and the polymerization pressure to 200 bar.

Furthermore, to demonstrate the reproducibility of our proposed system, we performed 10 consecutive trials at maximum grafting degree conditions (6 h, 100 °C, 200 bar, 10 g/min $scCO_2$ flow rate and a 1:3 (w/w) ratio of St/LA). Relative standard deviation (RSD) analysis via Microsoft-Excel-2013 resulted in quite acceptable RSD value (4%) for the related data which is a strong proof of the proposed graft copolymerization procedure.

3.2. Chemical structure

The FTIR spectra of starch and St-*g*-PLA are shown in Fig. 3. Two characteristic peaks appear at 1000 and 1200 cm^{-1} in the FTIR spectra of corn starch (Fig. 3A), which are associated with the C—O band stretching of ether groups (Ma, Yu, & Wang, 2007). The characteristic peak at 1642 cm^{-1} is related to the bending of the OH group of absorbed water. The observed shift of this peak indicated that the gelatinization of the starch prior to copolymerization led to a decrease in the hydrogen bonding in the starch backbone. In the case of St-*g*-PLA, a decrease in the OH groups as a result of the gelatinization process and graft copolymerization reaction resulted in a broad band being observed at 3320 cm^{-1} that was related to hydrogen bonded hydroxyl groups (Fig. 3B).

In addition, in the spectra of the graft copolymer the appearance of a peak at 2993 cm^{-1} associated with C—H (aliphatic) stretching indicated the occurrence of PLA grafting. A new strong characteristic C=O stretching band at 1735 cm^{-1} in the spectra of St-*g*-PLA (Fig. 3B), which is not detected in the spectra of starch (Fig. 3A), can be attributed to the ester carbonyl group (Chang et al., 2009). From these FTIR analysis results, it was concluded that an efficient graft polymerization of LA monomer onto a starch backbone was achieved.

The chemical structure of the graft copolymer was also confirmed by NMR analysis. Fig. 4 shows the ^{13}C/CPMAS NMR spectra of the starch and St-*g*-PLA copolymer made using a 1:3 starch-to-LA monomer ratio under the following polymerization conditions: 10 g/min $scCO_2$ flow rate at 100 °C, 200 bar and 6 h. The chemical shifts (ppm) of the major peaks are presented on the insets of Fig. 4(A and B). The signals at 26.1 and 27 ppm are attributed to the aliphatic group (CH_3) of the poly(L-lactic acid) chain. Additionally, the signals at 57.68 and 67.85 ppm are assigned to C-6 (CH_2—OH) and the C-2, 3 and 5 groups of the starch chain, respectively. The broad peak at 77.28 ppm corresponds to the C-4 group of the starch chain while the peak between 94.73 and 98.21 ppm corresponds to the C-1 group. The presence of peaks at 172 and 178.3 ppm is of great importance. These peaks indicate the grafting of lactic acid to the starch and correspond to the ester carbonyl (C=O) peaks of the poly(L-lactic acid) chain.

^1H NMR analysis was also applied to determine the composition of the graft copolymers synthesized with different feed ratios of M_1:M_2 ranging from 1 to 0.2 (see Table S1). In this approach, the integrated peak areas (Am_i) of the proton from the —(CH)— [$1H^+$] group of the m_2 unit (LA) and the —(CH_2)— [$2H^+$] group of the m_1 unit (St) (Fig. S1) in the spectra of the polymers were calculated using the following equations (Cameron, Cowie, Ferguson, & McEwan, 2000):

$$\frac{A_{m_1}(\mathrm{CH})}{A_{\mathrm{total}}} = \frac{n_1 m_1}{(a_1 m_1 + b_2 m_2)} \quad (3)$$

$$\frac{A_{m_2}(\mathrm{CH_2})}{A_{\mathrm{total}}} = \frac{n_2 m_2}{(a_2 m_2 + b_2 m_2)} \quad (4)$$

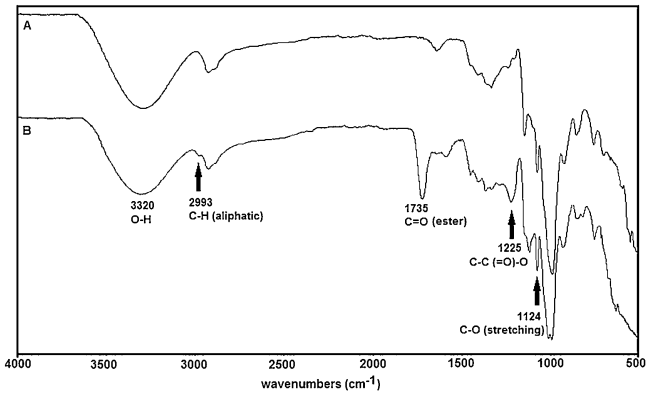

Fig. 3. FTIR spectra of (A) starch and (B) St-*g*-PLA copolymer using the following reaction conditions: 1:3 polymer/monomer ratio, 100 °C, 200 bar and 6 h (see Table 1).

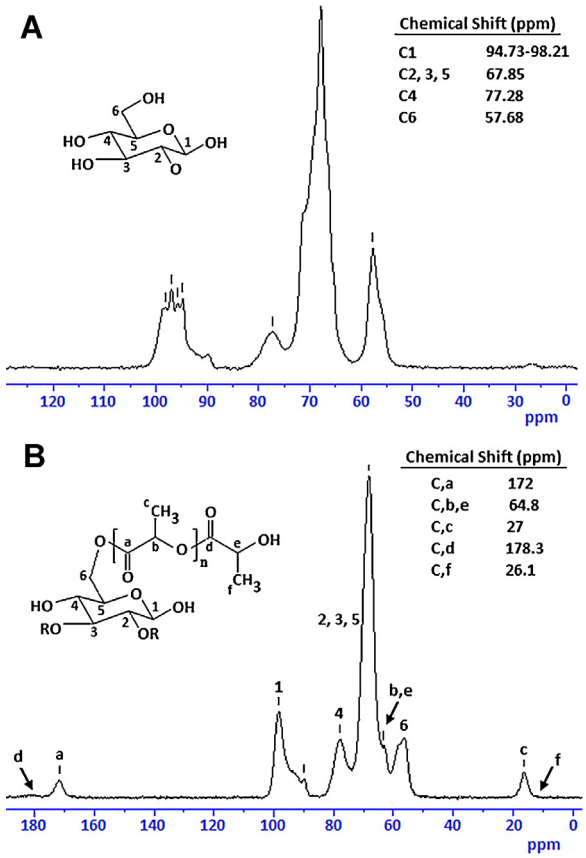

Fig. 4. ^{13}C CP/MAS NMR spectra of (A) starch and (B) St-*g*-PLA copolymer prepared at 100 °C and 200 bar for 6 h with a 1:3 St/LA feed ratio.

where A_{m_1} and A_{m_2} are the normalized peak areas per H from the corresponding functional groups of the monomer unit; A_{total} is the total peak area of the protons in the copolymer; n_1 and n_2 are the integer number of protons in the functional groups of the monomer; and a and b are the integer number of protons in the monomer units (m_1 and m_2) in the case of ($m_1 + m_2$) = 1. Monomer unit ratios can be calculated from Eqs. (1) and (2) using the following equation:

$$\frac{m_1}{m_2} = f = \frac{n_2 A_{m_1}(\text{CH})}{n_1 A_{m_2}(\text{CH}_2)} \tag{5}$$

where $n_1 = 1$ and $n_2 = 2$ are the number of protons in the chosen analytical groups from each monomer unit with integrated areas.

From Eq. (3) the molar monomer unit ratio in samples was found to be m_1(LA): m_2(St) = 60:40 for a 1:3 monomer ratio (Gong, Wang, & Tu, 2006). These values have reasonable agreement with the FTIR results and are supported by the data of the grafted PLA mol% (see Table 1).

To obtain the grafting degree, we utilized the standard alkali titration method for determining the acid number (AN) of the precipitated phase. The AN (in mg KOH/g) was calculated using Eq. (6) as follows:

$$AN = \frac{\left[Mw_{(\text{KOH})} \times V_{(\text{KOH})} \times N_{(\text{KOH})}\right]}{m} \tag{6}$$

where $Mw_{(\text{KOH})} = 56.1$ g/mol; $V_{(\text{KOH})}$ = consumed titrant; $m = 0.4$ g polymer; $N_{(\text{KOH})} = 0.05$ and the —COOH end group concentration ($C_{(\text{COOH})}$) was determined via Eq. (7).

$$C_{(\text{COOH})} = \frac{\left[(AN) \times (Mw_{(\text{COOH})}\right]}{Mw_{(\text{KOH})}} \tag{7}$$

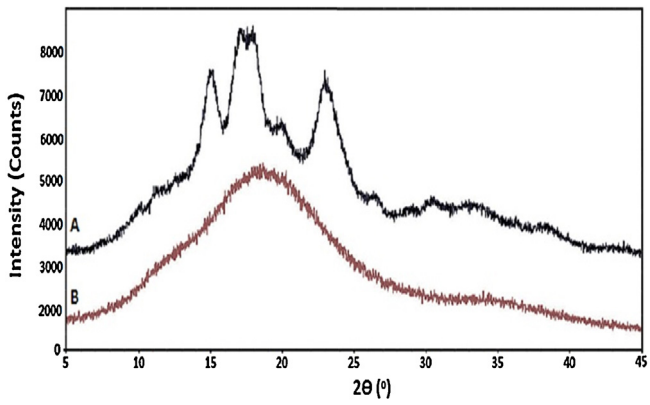

Fig. 5. X-ray diffraction patterns of (A) starch and (B) St-*g*-PLA copolymer prepared using the following optimized reaction conditions: 1:3 St/LA ratio, 200 bar, 100 °C and 6 h.

The acid number and —COOH end group concentration of the unreacted LA monomer and oligomers soluble in methanol was calculated and is summarized in Table S2. All of the precipitated phases with acid numbers more than 20 indicate that as the lactic acid monomer (from a 1:1 ratio to 1:3 and 1:5 ratios) increases, the —COOH groups increase, and the consumed volume of KOH increases as well. This results is well in accordance with the grafted PLA (mol%) data from Table 1, which indicates that lactic acid monomers and lactic acid oligomers have reacted with hydroxyl groups of the starch backbone under the $scCO_2$ pressure.

3.3. Physical structure

A wide angle powder X-ray diffraction (XRD) method was employed to determine the crystalline and amorphous structures in St-*g*-PLA. The XRD patterns are illustrated in Fig. 5. A significant change was observed in the crystallinity of native starch after being grafted with LA in a $scCO_2$ medium. The diffraction peaks present at $2\theta = 14.98$, 17.08 and 23.04° are associated with crystalline structures of starch (Chang et al., 2009). The crystallinity of the graft copolymer essentially disappeared as evidenced by the emergence of a broad peak at $2\theta = 19.12°$. This observation indicates the formation of a predominantly amorphous structure of the St-*g*-PLA copolymer. The partial gelatinization of starch crystalline regions at high pressure as well as the diffusion of $scCO_2$ solvent into St-*g*-PLA structures led to the disappearance of the characteristic crystalline peaks after graft polymerization.

3.4. Reaction parameters-morphology relationships

To determine the effect of $scCO_2$ on the morphology of starch granules under different reaction conditions, scanning electron microscopy (SEM) micrographs were taken, and representative SEM images are shown in Fig. 6. According to the SEM images (Fig. 6A), it is obvious that starch granules exhibit a regular shape and a smooth surface morphology. The grafting of LA onto the starch backbone resulted in a dramatic change in the morphology of the product. These notable changes in the St-*g*-PLA morphology can be attributed to the interaction of the inner part of the starch structure with LA units under the high pressure of $scCO_2$ fluid, which is easily observed in the structures of the granules (Fig. 6B–D). The effect of the LA/St ratio on the morphology of the graft copolymer was also easily detected. Increasing the LA/St ratio in the $scCO_2$ medium led to the degradation of macroscopic starch structures. Due to the low amount of LA, a poor interfacial adhesion was observed between LA and starch functional groups (Fig. 6B). A further increase in the ratio of LA/St increased the hydrophilic groups of LA in the polymerization medium with a high compatibility of the two phases, and the

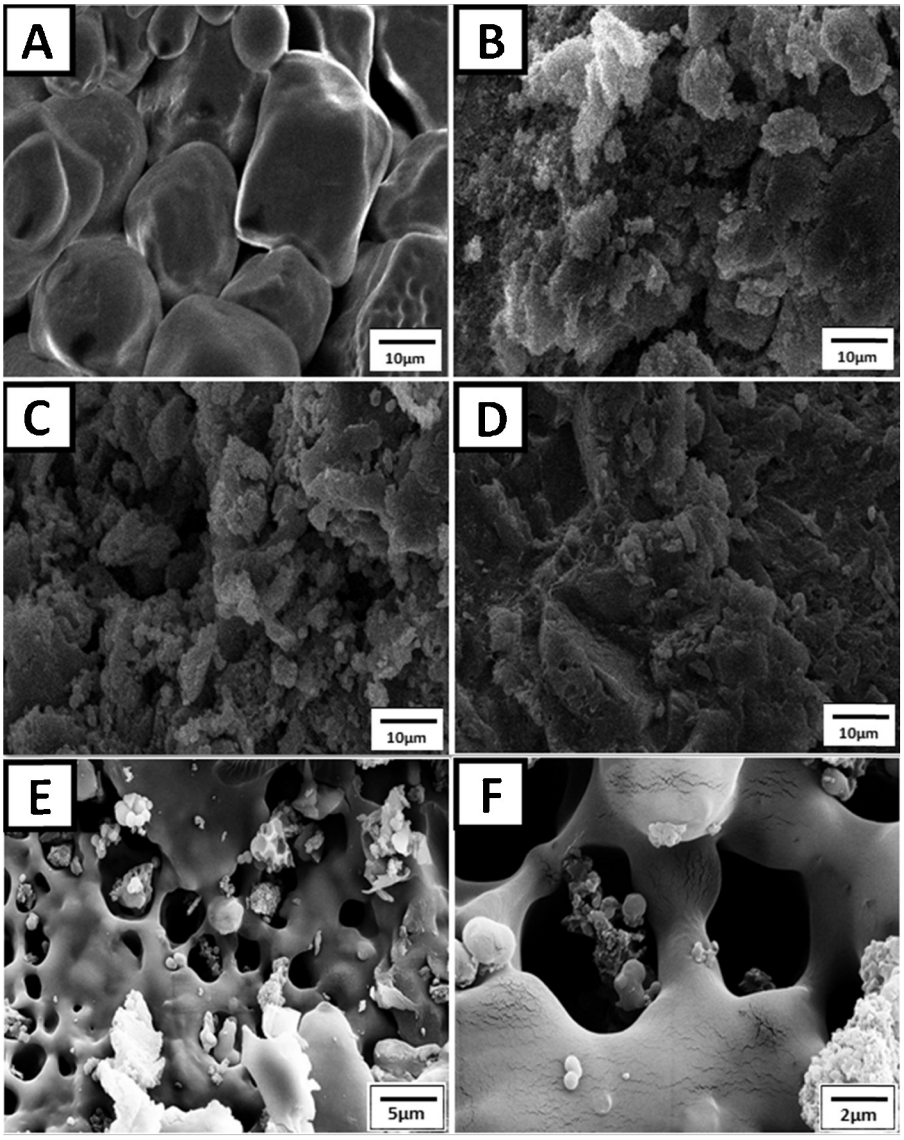

Fig. 6. SEM images of (A) starch and St-*g*-PLA copolymers at (B) 1:1, (C, E and F) 1:3 and (D) 1:5 St/LA feed ratios. All of the polymerizations were performed at 100 °C and 200 bar for 6 h.

degassing of supercritical fluid from the reaction medium led to the formation of a microporous morphology in St-*g*-PLA (Fig. 6C and D).

The detailed SEM images with higher magnification (Fig. 6E and F) indicated that a St/LA feed ratio of 1:3 caused the formation of micropores with sizes ranging from 1 μm to 5 μm. In addition to micropores, nano-sized cracks on the starch backbone in the St-*g*-PLA copolymer were also observed due to the effect of $scCO_2$ on the morphology.

Thus, we can conclude that SEM images are in good agreement with the XRD spectra in the context of the polymer morphology. Both micropores and nanocracks in the products make the copolymer a potent candidate as a biomaterial for micro-sized fibres in wound closure materials and as scaffolds for tissue engineering applications due to the high biocompatibility of the grafted poly(lactic acid) (Meshram, Patil, Mhaske, & Thorat, 2009).

3.5. Thermal behaviours

The thermal stabilities of the St-*g*-PLA copolymers prepared in different LA/St ratios were investigated via TGA and DTG techniques (Fig. 7). The TGA curves showed that the degradation of the graft copolymers occurs at ~300 °C (Fig. 7a), which is remarkably higher than unprocessed starch (270 °C) (Muljana et al., 2010). This may be due to the effect of supercritical carbon dioxide on the intermolecular interactions of several hydrogen bonds in the starch chain during the graft copolymerization with lactic acid (Muljana et al., 2009). TGA curves depicted two indicative mass loss events that occurred in the copolymer structure. The first mass loss (6%) in the range of 50 to 110 °C can be related to the elimination of absorbed water molecules during the copolymerization procedure. Starch degradation was easily detected by the thermal degradation of the copolymer over a broad temperature range of approximately 190–360 °C. From the DTG curves (Fig. 7b), it could be concluded that the copolymers decomposed at 290 °C, and the rapid and maximum of weight loss was observed at approximately 260–360 °C with 60% chain degradation for second stage. Furthermore, the degradation was also reported for native starch, and it was lower than 65% and in the same temperature range. It is clear that the graft copolymerization led to enhancement of the thermal stability of the starch, which was essentially consistent with related literature. According to Xie et al. (2011), a reduction in the amount of hydroxyl groups in the backbone of starch, which was

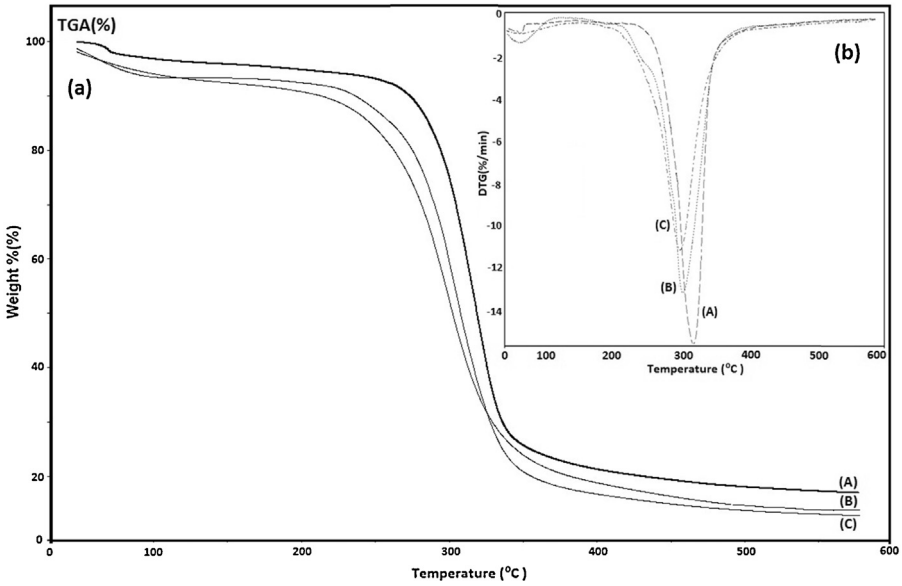

Fig. 7. (a) TGA and (b) DTG thermograms of St-*g*-PLA copolymers prepared with the following different St/LA feed ratios: (A) 1:1, (B) 1:3 and (C) 1:5.

confirmed by FTIR spectra, results in an increase in the thermal stability.

4. Conclusion

In this study, to increase thermal stability and processability of the starch-based products, we have developed a new approach for the synthesis of St-*g*-PLA copolymers by the catalytic graft copolymerization of an LA monomer onto starch in an $scCO_2$ medium. It was found that the St/LA feed ratio, temperature and pressure significantly affected the grafting degree, thermal stability and morphology of St-*g*-PLA. It was observed that higher pressure and temperature values, as well as an increase in the $scCO_2$ flow rate, led to decrease in the number of grafted LA units and a degradation of the granular starch morphology. An increase in the polymerization temperature is suitable for PLA chain length growth at a relatively low flow rate value. The chemical and physical structures, surface morphologies and thermal analyses reasonably confirmed the above-mentioned evaluated effects. The structures and compositions of the St-*g*-PLA copolymers were quantitatively confirmed by FTIR, ^1H (^{13}C CP/MAS) NMR and alkali titration. The XRD results indicated the disappearance of characteristic crystalline peaks of starch after grafting LA onto starch chains and the formation of amorphous structures in the St-*g*-PLA copolymer. SEM images demonstrated the microporous morphology of St-*g*-PLA with a pore size of approximately 1–5 μm and nano-sized cracks on the starch backbone due to the effect of $scCO_2$. Degradation of St-*g*-PLA copolymers has occurred in the temperature range of 260 to 360 °C by a one-step chain degradation mechanism. The thermal stability of St-*g*-PLA depends on the St/LA feed ratio and decreases with an increasing amount of LA monomer in the reaction mixture. We concluded that the synthesized St-*g*-PLA copolymers with controllable amounts of PLA branches were the major products of this study. We suggest that fabricated graft copolymers, which have an expected improvement in their processability and biocompatibility due to PLA branches, can be utilized in a wide range of engineering, bioengineering and medical application areas, which will be the subject of our future investigations.

Electronic supplementary information (ESI)

^1H NMR (400 MHz) spectra of St-*g*-PLA copolymers are illustrated in Fig. S1. ^1H NMR analysis data and end group analysis data are shown in Tables S1 and S2, respectively.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.07.077.

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