

Microwave-assisted green approach for graft copolymerization of L-lactic acid onto starch

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ABSTRACT: Poly L-lactic acid grafted starch (St-g-PLA) copolymers were directly synthesized under microwave irradiation by using sodium hydroxide (NaOH) and stannous 2-ethyl hexanoate acting as a catalyst, without the use of toxic solvents. The product were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (¹³C CP/MAS NMR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA-DTG). SEM analysis indicated that microwave heating had a considerable effect on the interfacial adhesion between PLA and starch. Thermogravimetric analysis (TGA-DTG) revealed that copolymers exhibited better thermal stability. Maximum PLA grafting was achieved with the following reaction conditions: 450W microwave power, monomer ratio of 1:5 and 0.4M of NaOH. This study demonstrates that it is possible to obtain St-g-PLA copolymers with better processing characteristics and smaller sizes via microwave-assisted synthesis. The applied procedure is an interesting “green” synthesis method for the production of biodegradable materials used in a diverse range of applications. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42937.

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INTRODUCTION

Environmental concerns have raised significant international interest in the using carbohydrate polymers to produce biodegradable plastics.¹ Among these, starch is a natural polysaccharide, which consists of a mixture of two components: amylose (mainly a linear (1→4)- α -D-glucopyranan units) and amylopectin (highly ordered semi-crystalline, contains (1→4)- α -D-glucopyranan units).^{2–4} In its granular structure, starch comprises of hydrogen bonds (intermolecular and intramolecular) abundantly. These bonds can be destroyed with temperature and plasticizers (water, glycerin, urea, sorbitol, and acrylamide) and acid hydrolysis which leads to obtaining thermoplastic products and semi-crystalline nanoparticles from starch for use in biocompatible macromolecular matrices.^{4,5} However, and in contrast to most conventional polymers, the water solubility of starch causes poor mechanical properties which limits its applications.^{6,7} This important problem has been overcome by

improving the compatibility by blending and/or chemical modification (acetylation, esterification, or etherification) and enzymatic hydrolysis of starch.^{8–10} Among these, conventional grafting is a chemical modification method that has carries several problems such as decreasing the yield of copolymerization, degradation of the polysaccharide backbone and limited control over the graft molecular weight distribution.^{11–13} PLA, with a linear aliphatic polyester structure, is one of the most important bio-based polymers that is derived from renewable sources and which exhibits a combination of physical properties and features that make PLA an alternative replacement for petrochemical resources.¹⁴ The poor mechanical and thermal properties found with most natural polymers limit the processing capabilities associated with them and thus precluding the production of environmentally friendly products. There are several studies in relevant literature related to the blending of starch with natural and commodity polymers.^{15,16} However, the hydrophilic

structure of starch leads to a weak interfacial interaction between hydrophobic polymers such as PLA, poly caprolactone (PCL) and polybutylene adipate-co-terephthalate (PBAT), resulting in poor mechanical properties of the final blend.¹⁷

To overcome the immiscibility between starch and PLA, two main approaches have been reported: the use of compatibilizers as a bridge to binding (chemical or physical) between the PLA and starch rigid structure; or the plasticizing of starch granules to perform the penetration of L-lactic acid functional groups and/or PLA chains into the amylose and amylopectin complex.^{18–23} These conventional modification methods, however, have been found to lead to some undesirable effects on final product properties such as causing full biodegradation, all of these conventional modification methods made some undesirable effects on the final product properties such as full biodegradation.¹⁴

Recently, new methods have improved the synthesis process of grafted polysaccharide copolymers, and they involve free radical initiators, gamma rays, UV radiation and electron beam and microwave irradiation.^{24–32} Using microwave energy in organic reactions has found widespread applications in polymer laboratories for developing novel materials. Microwave-assisted heating has been performed in various polymerization techniques, such as radical polymerization, step-growth polymerization and ring opening polymerization (ROPs), thanks to more efficient energy transfer than conventional heating.^{33,34} In microwave-assisted polymerization methods, microwave reactors allow fast and accurate monitoring of important process parameters, such as temperature and pressure, for the production of materials in different forms and with high purity.³³

Grafting onto polysaccharides by microwave irradiation has been performed in different conditions (i) in completely homogeneous solutions where all the reaction contents are fully miscible with no phase separation; (ii) in suspension where the reactants are not fully miscible; either the polysaccharide and/or monomer/catalyst are immiscible; (iii) in solid phase where the polysaccharide monomers and initiator are impregnated on neutral solid support. These materials have diverse applications in the fields of science and technology such as flocculant for wastewater treatment and controlled drug delivery.^{35–39}

In recent decades, microwave irradiation has been used actively as a “green” approach for the chemical modification of starch. Chang *et al.* reported the microwave irradiation for one-pot grafting of ϵ -caprolactone (ϵ -CL) onto starch via ROP at 255W for 3 min in the presence of tin octanoate [Sn(oct)₂] as a catalyst.³⁰ Singh and coworkers modified starch by acrylonitrile grafting using peroxodisulfate as an initiator, at 1200W in a domestic microwave oven.³¹ Mishra and coworkers prepared polyacrylamide grafted starch (St-g-PAM) by performing microwave radiation in the presence of a free radical initiator (ceric ammonium nitrate).³⁷ Zheng *et al.* grafted sodium acrylate on cornstarch by using polyethylene glycol diacrylate (PEGD) as a crosslinker and potassium persulfate (KPS) as a catalyst, at 85–90W for 10 min in a microwave oven. In these studies, microwave power was accepted as a significant factor affecting the swelling ratio and solubility of the product.⁴⁰ Alfaifi *et al.* also

reported the microwave assisted graft copolymerization of the amino-acid based monomers onto starch as method of introducing a stationary phase involved in the immobilization of drugs in drug delivery systems.⁴¹

The objective of this study was to apply microwave irradiation as a “green” approach for graft copolymerization of L-lactic acid onto starch backbone by using sodium hydroxide (NaOH) and stannous 2-ethyl hexanoate [Sn(oct)₂] as catalysts. The effects of the reaction variables, such as power of radiation (W), monomer ratio (w/w) and NaOH concentration (M) on grafting efficiency have been investigated. Moreover, the microwave-assisted graft copolymerization was confirmed by structural analysis (FTIR, ¹³C CP/MAS NMR), crystallinity (XRD), morphological examination (SEM) and thermal analysis (TGA-DTG).

EXPERIMENTAL

Materials

Cornstarch (23–28% amylose) was supplied from Cargill (USA) and L-lactic acid (20 wt % aqueous solution) was purchased from Purac (Netherlands). The sodium hydroxide and stannous 2-ethyl hexanoate [Sn(Oct)₂] were obtained from Sigma-Aldrich (Germany).

Graft Copolymerization of Poly L-Lactic Acid onto Starch by Microwave Irradiation

The microwave-assisted graft copolymerization was carried out in a microwave oven (Milestone Microsynth, USA) using two different methods. An optical fiber temperature probe (FISO Technologies, Québec, Canada) was employed to measure the temperature of the slurry during the heating process. The details of the synthesis procedure with each of the variables and synthesis parameters are summarized in Table I. Graft copolymerization was performed in two stages. During the first stage, 5 g cornstarch was dispersed in 30 mL of 0.40M NaOH solution in a three-necked reactor. The gelatinization of starch was carried out by increasing the temperature to 70°C and holding the system at this temperature for 1 h.⁴² During the second stage, the as-prepared slurry was transferred into a three-necked round bottom flask using a vacuum system (–600 mmHg) to remove the water from the reaction media. The microwave irradiation was optimized with the following process: an excess amount of L-lactic acid and stannous octoate (0.3 wt % of LA amount) were mixed with a magnetic stirrer. Reaction parameters such as power, duration of radiation, concentration of LA and NaOH, (Table I) were modified to achieve LA grafting on starch. The mixture was heated to 100°C by increasing the power outputs from 150 W to 750 W. Since the maximum grafted PLA (mol %) was achieved at 450 W irradiation, the optimal irradiation power was determined as 450 W. During the synthesis procedure, microwave irradiation was periodically paused before the mixture reached boiling point (not exceeding 100°C) and kept for a while at this point, as a method by which the mixture was allowed to collapse thereby both preventing the non-uptake of the slurry by the vacuum system and also ensuring the production of vapor containing a mixture of LA and starch. This process was repeated until a highly viscous polymer (light brown) was obtained. After completion, the irradiation time was recorded and the sample was left undisturbed for 12 h to

Table I. Synthesis Parameters of Starch-g-PLA Copolymers under Different Conditions

Copolymers	Amount of LA (g)	NaOH Concentration (M)	MW Power (W)	Duration of Radiation (sec)	Grafted PLA (mole %)
Optimized effect of NaOH concentration (M) @ constant temperature (100°C) in microwave-assisted synthesis (amount of starch = 1 g)					
	5	0.1	-	360	32 (±1.64)
	5	0.2	-	290	41 (±2.05)
St-g-PLA	5	0.3	-	205	45 (±2.21)
	5	0.4	-	335	51 (±2.55)
	5	0.5	-	220	48 (±2.34)
Optimized effect of power of radiation in microwave-assisted synthesis (amount of starch = 1 g)					
	5	0.4	150	556	40 (±2.03)
	5	0.4	300	540	57 (±2.83)
St-g-PLA	5	0.4	450	337	62 (±3.12)
	5	0.4	600	305	49 (±2.45)
	5	0.4	750	195	49 (±2.42)
Optimized effect of monomer ratio in microwave-assisted synthesis (amount of starch = 1 g)					
	0.5	0.4	450	89	38 (±1.91)
	1	0.4	450	110	41 (±2.04)
St-g-PLA	3	0.4	450	200	46 (±2.33)
	5	0.4	450	336	62 (±3.16)
	7	0.4	450	448	50 (±2.53)

complete the grafting reaction. After the specified conditions were fulfilled, the product was washed with excess methanol to remove the unreacted lactic acid and polylactic acid (PLA) homopolymers, and dried under vacuum at 70°C. To remove the unreacted PLA in the final product, an extraction procedure was carried out for 12 h by using methanol as the extraction solvent in a Soxhlet system. Finally, the extracted polymer was dried at 70°C under vacuum.

Characterization

Characterization of the chemical structure, morphology and thermal properties of graft copolymers have been performed by various instrumental techniques.

Fourier transform infrared spectroscopy (FTIR) analysis was carried out in the wave number range of 4000–400 cm⁻¹ (FTIR-SMART-IR, Thermo Scientific, USA). The chemical structure of the polymers was studied with Nuclear Magnetic Resonance Spectroscopy (Bruker Spectrospin Avance Ultrashield 400, Germany).

The ¹³C-Nuclear Magnetic Resonance spectra were acquired on a Bruker AVANCE 300 (Germany) spectrometer operating at a 300.13 MHz proton frequency with a 4-mm Bruker spinning probe and using the standard CP/MAS (Cross Polarization Magic Angle Spinning) technique with 1400 scans. Thermogravimetric analysis (TGA, Perkin Elmer Diamond, USA) was carried out to investigate the weight loss in samples as a function of temperature at a heating rate of 10°C/min between 25–550°C and under a nitrogen atmosphere with a 20 mL/min flow rate.

X-ray diffraction analysis was performed using a XRD diffractometer (Bruker AXS 5000 X-ray Diffractometer operated at 10 KV, Germany) to investigate the crystal structure of starch and copolymer in the range between 2θ = 5–45° with a selected speed of 2 degrees per minute.

Surface morphology of samples was investigated via scanning electron microscopy (FEI Nova NanoSEM 430, USA). Using a coating system (PECS 682, USA), the dried samples were coated with Au/Pd with a thickness of 80 Å.

RESULTS AND DISCUSSION

Characterization of Starch-g-PLA Copolymers

Figure 1 shows the FTIR spectra for starch (A) and St-g-PLA copolymers (B–D). From the FTIR spectrum of starch [Figure 1(A)], it is clear that the absorption peak at 3351 cm⁻¹ can be attributed to the stretching vibration of O–H groups, a peak at 2883 cm⁻¹ is due to C–H stretching and the bands between 900 and 1200 cm⁻¹ are assigned to C–O–C stretching vibration of starch, respectively. The band at 1648 cm⁻¹ is due to tightly bound water present in starch.⁴³

To aid the visualization of the graft reaction, the FTIR spectra of graft copolymers are illustrated in Figure 1(B–D). As can be seen, the sharp and strong peak at 1732 cm⁻¹ corresponds to the carbonyl group of ester, which confirms the grafting of PLA chains onto the backbone of starch. The absorption peaks in the region of 3500 and 3000–2800 cm⁻¹ are related to the O–H stretching vibration and the C–H stretching vibration of PLA, respectively. Compared to the starch spectra, the

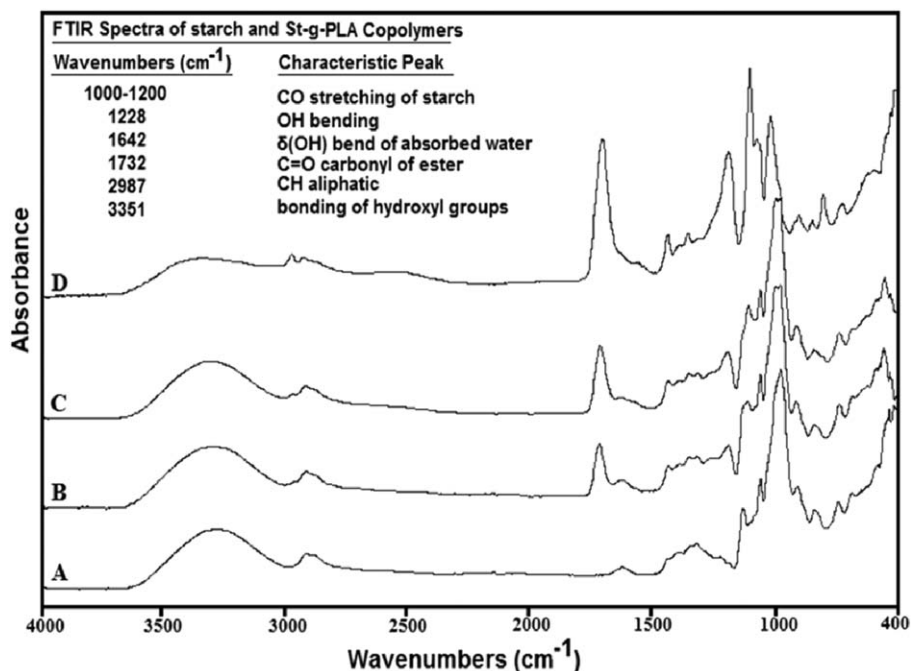


Figure 1. FTIR spectra of (A) starch, (B) St-g-PLA at 150W, (C) St-g-PLA at 300 W and (D) St-g-PLA at 450W microwave irradiation.

appearance of both two group absorption peaks between 1200–900 and 1600–1250 cm⁻¹ are related to the C–O–C stretching vibration of starch and –COO⁻ stretching vibration of PLA chain, respectively.⁴⁴ Furthermore, the appearance of two peaks at 1228 and 2987 cm⁻¹ due to the OH bending and C–H aliphatic groups of the PLA chain compared to starch, clearly indicates that the grafting of PLA chains onto the backbone of starch has successfully taken place by the microwave-assisted copolymerization method.

To analyze the chemical structure of starch and St-g-PLA copolymer, ¹³C CP/MAS NMR spectroscopy was used (Figure 2). In Figure 2(A), the region between 55 to 105 ppm is mostly assigned to the carbons of starch backbone (C-1 to C-6). The peaks between 94.73 and 98.21 ppm are attributed to the C-1 carbons. The peak at 57.68 ppm is related to the C-6 and the peak at 77.28 ppm belongs to the C-4 carbon of starch, respectively. In this region there was also a broad and sharp peak at 67.85 ppm which is assigned to C-2, C-3, and C-5. On the other hand, in Figure 2(B), the presence of two peaks at 173.8 and 19.6 ppm are related to the carbonyl group of ester (C=O) and methyl group (CH₃) of the PLA chain which indicated that the graft copolymerization reaction of PLA had successfully occurred on the starch backbone. In addition, the graft copolymerization reaction led to the decrease of the intensity of C-6 and C-2, 3, 5 peaks [Figure 2(B)], which was because of the degradation of the granular shape of starch under microwave irradiation and the grafting of PLA from C-2, C-3 and C-6 hydroxyl groups. These results are consistent with FTIR, XRD, and SEM data. Finally, the hydroxyl groups in C-6 should be attacked first by the carboxyl groups of L-lactic acid. This relates to the isomerism of functional groups (hydroxyl), which is proven by the decreasing intensity of C-6 resonances.

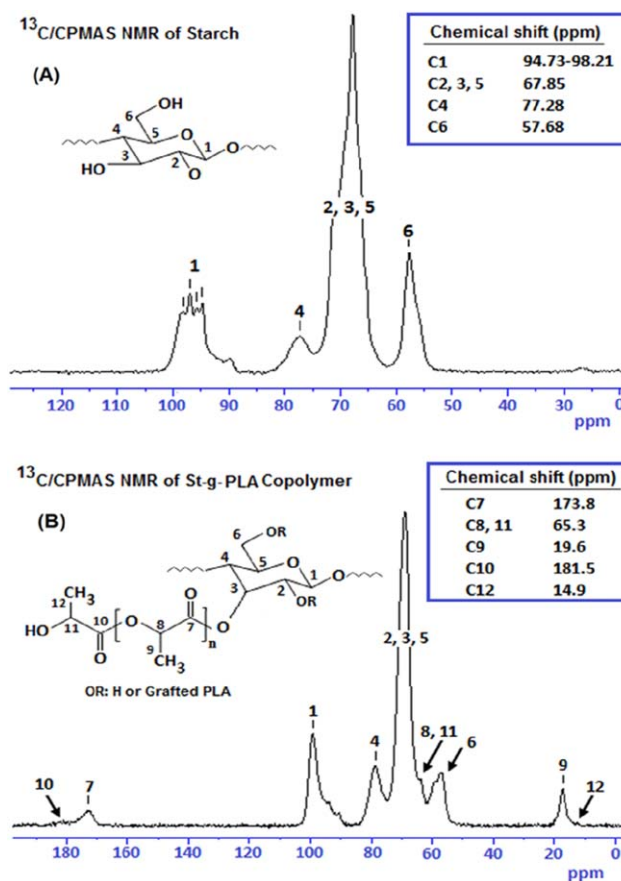


Figure 2. ¹³C CP/MAS NMR spectra of (A) starch and (B) St-g-PLA at 450W microwave irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

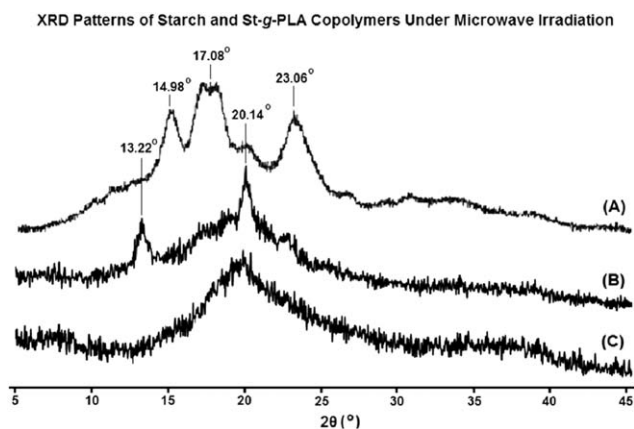


Figure 3. X-ray diffraction patterns of (A) starch, (B) St-g-PLA at 300W and (C) St-g-PLA at 450 W microwave irradiation.

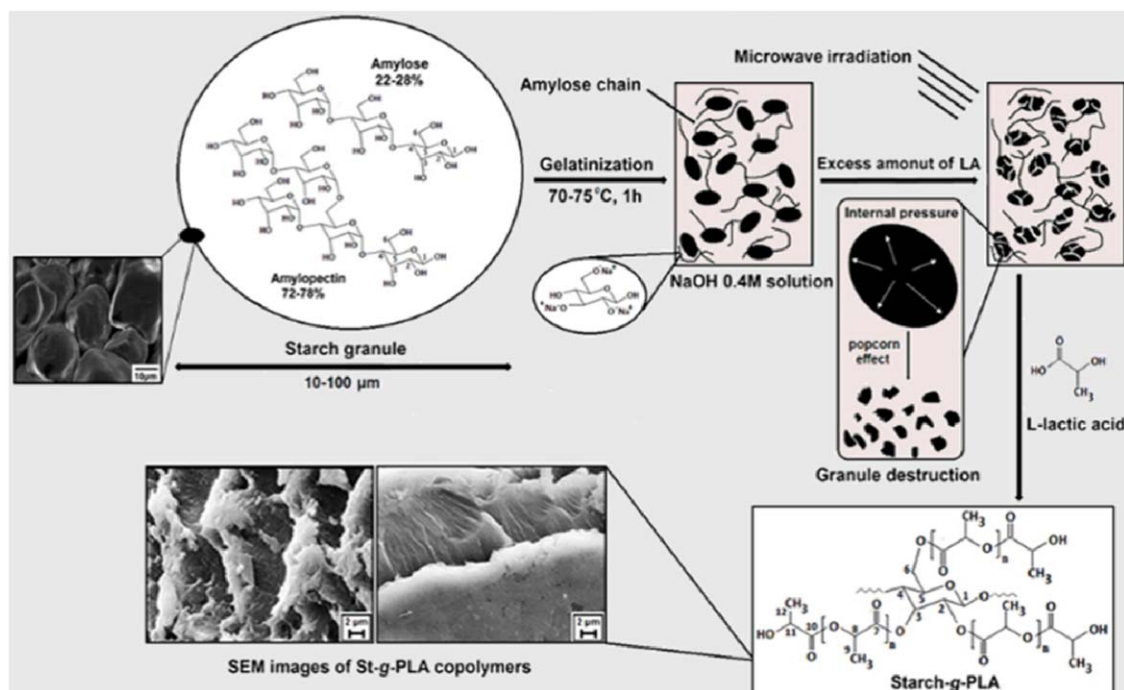
Wide angle powder X-ray diffraction method (XRD) was used to determine the crystalline and amorphous structures in starch and St-g-PLA copolymers. Figure 3 depicts the XRD patterns of unreacted starch [Fig. 3(A)] and St-g-PLA copolymers [Figure 3(B,C)]. In Figure 3(A), starch shows a crystalline structure with three diffraction peaks at 14.98° , 17.08° , and 23.06° of 2θ .

Absorption of microwave energy and transfer of this energy to heat led to the molecular friction of starch (Scheme 1), so, excitation by radiation frequencies resulted in the disruption of the starch polar crystalline structure. However, PLA chains in the polymerization medium spoiled the excited starch functional groups and caused the loss of crystallinity. Elimination of starch crystalline peaks in St-g-PLA copolymers (from Figure 3, diffraction patterns B to C) is assigned to the grafting of PLA

chains and the appearance of a wide broad peak at $2\theta = 20.14^\circ$ proved that the St-g-PLA copolymers were existed in amorphous structure.

Figure 4 shows the morphological analysis of St-g-PLA copolymers under different microwave irradiation that was performed by SEM. The changes in the surface morphology of the copolymers as an effect of PLA grafting with increasing of microwave energy is clearly revealed in the SEM micrographs. As can be seen, from Figure 4(A–D), an increase in the microwave energy led to the formation of a continuous layer between St and PLA chains corresponding to successful graft copolymerization of LA which in turn affects the regular structural arrangement of starch.

The thermogravimetric (TGA-DTG) curves of St-g-PLA copolymers prepared under different microwave irradiations are shown in Figure 5. The maximum thermal degradation of starch occurred at about 270°C with a total weight loss of 84% until 500°C while this value for PLA is higher than starch ($\sim 365^\circ\text{C}$) with total weight loss nearly 100% at $\sim 390^\circ\text{C}$.⁴⁵ The TGA curves showed that the decomposition temperature of the St-g-PLA copolymers [Figure 5(A–D)] begins at a higher temperature than starch ($\sim 330^\circ\text{C}$) and the completion of decomposition occurs at temperature near that of PLA. This demonstrates that the addition of LA and microwave irradiation causes a gradual thermal enhancement of St-g-PLA copolymers that can be attributed mainly to good starch-lactic acid interactions and the thermal destruction of starch granules. As shown in Figure 5, there was two significant mass losses in the TGA curves. The first range ($50\text{--}160^\circ\text{C}$) is assigned to the removal of adsorbed water molecules presented in starch and corresponds to the first step of the starch thermal degradation-dehydration process.



Scheme 1. Schematic representation of starch-g-PLA synthesis by microwave irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

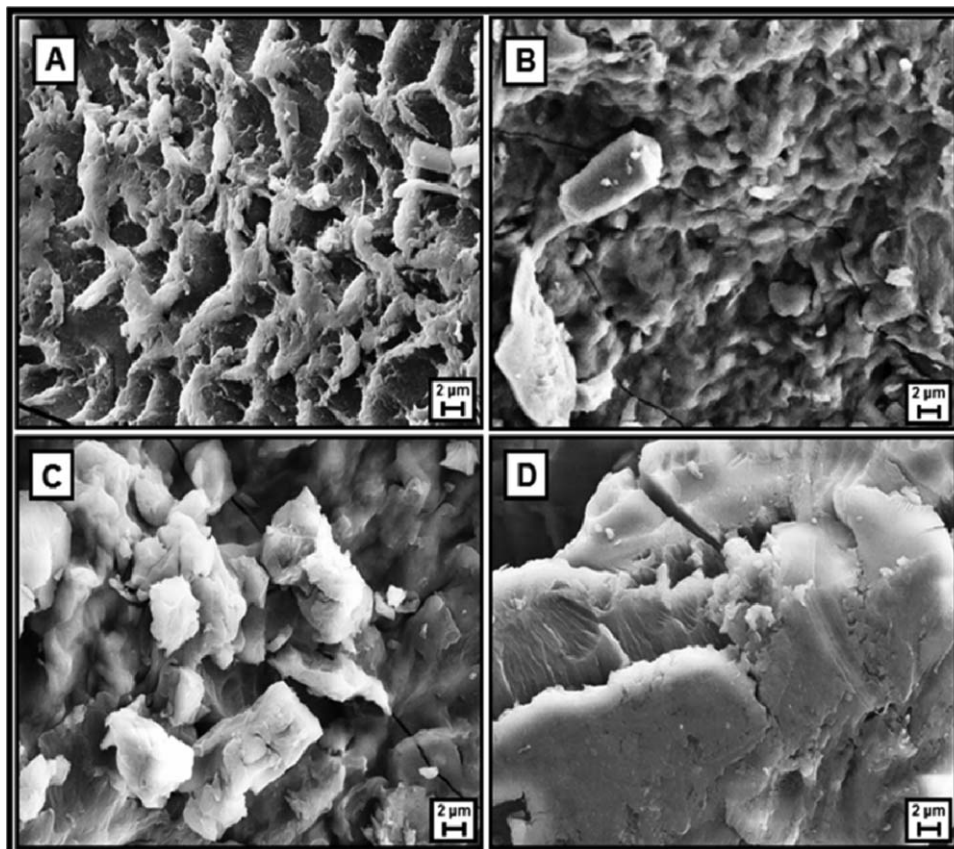


Figure 4. SEM images of (A) St-g-PLA at 300W, (B) St-g-PLA at 450W, (C) St-g-PLA at 600W and (D) St-g-PLA at 750W microwave irradiation.

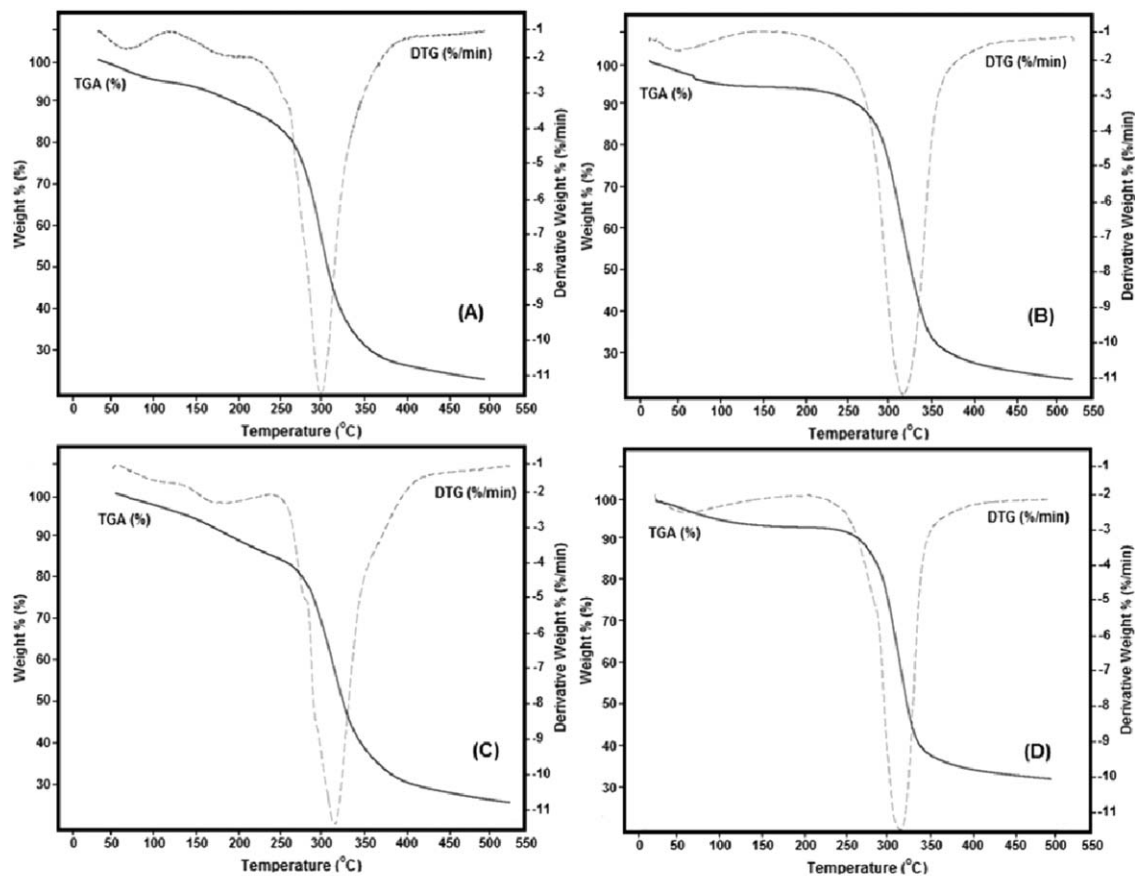


Figure 5. TGA and DTG diagrams of St-g-PLA Copolymers. (A) at 150 W, (B) at 300 W, (C) at 450 W, and (D) at 600 W microwave irradiation.

At the second stage of thermal degradation (190–450°C), according to Liu *et al.*, heating of St-g-PLA copolymer above 300°C produced volatile products (CO, CO₂, H₂O etc.) which caused the breakdown of strong bonds of the starch backbone and PLA polyester chains. Furthermore, it is clear that in the presence of microwave energy, 20% aqueous solution of LA and NaOH solution in polymerization media caused the irreversible gelatinization of starch granules and changes included the swelling of starch polar molecule granules and, finally, there was an appearance of an amorphous copolymer with the grafting of LA on the starch backbone. However, this hypothesis indicates an increase in the thermal stability of St-g-PLA copolymers and is in agreement with SEM and XRD data.

Effect of Reaction Conditions on Graft Copolymerization

The effect of variable reaction parameters on grafting PLA mole percent was observed by changing the NaOH concentration (0.1–0.5M), power of radiation (150–750 W) and monomer ratio (0.5–7 w/w) and summarized in Table I and Figure 6. According to Pekel *et al.*, the grafted PLA mole fraction (in mol %) of monomers (starch and lactic acid) in St-g-PLA copolymer was calculated using the absorption bands from the starch and LA units in the copolymer, and the band absorption value ratios between characteristic bands of 1732 cm⁻¹ (for LA C=O ester peak) and 1336 cm⁻¹ (for St —CH₂ peak) were employed.⁴⁶

To optimize the effect of NaOH concentration as co-catalyst in reaction media, a constant temperature regime (100°C) was applied and the duration of radiation (sec) was determined by observing the formation of a brownish viscous product. It was found that grafted PLA (mol %) increased with the decrease of the duration of radiation up to 0.4M and, after this point, both of them decreased (Table I). This may be due to the large number of active radical groups (ONa⁺) on the C-2, 3, 6 carbons of starch during gelatinization of starch and the presence of excess amounts of LA resulting in a higher grafted PLA mole (%) at 0.4M. On the other hand, grafting values over 0.4M tend to reduce this phenomenon. It is believed that the accumulation of high amounts of NaOH on the starch backbone causes PLA chain scission leading to the formation of oligo and homopolymers of LA.

In Figure 6(A), the increase in the power of radiation from 150 to 750 W at fixed concentration of NaOH (0.4M) and monomer ratio (amount of LA: 5g) showed that the gelatinized polar structure of starch excited with microwave power and the amylose-amylopectin separation occurred is evidence of the formation of more excited groups (free radicals) and resulted in grafting of PLA. The first increase in the grafted PLA value 450 W and then a decrease may be due to the disruption of starch macromolecule structure and some depolymerization of the PLA chain.

Figure 6(B) shows the effect of monomer ratio in the range of 0.5–7 g (amount of LA) on the optimized concentration of NaOH (0.4M) and radiation power (450 W). The increase in monomer ratio led to increasing grafted PLA mole fraction and absorption of more microwave energy. However, the decrease in grafted PLA value may be due to the tendency of LA toward homopolymerization because of the excess amount of LA suitable

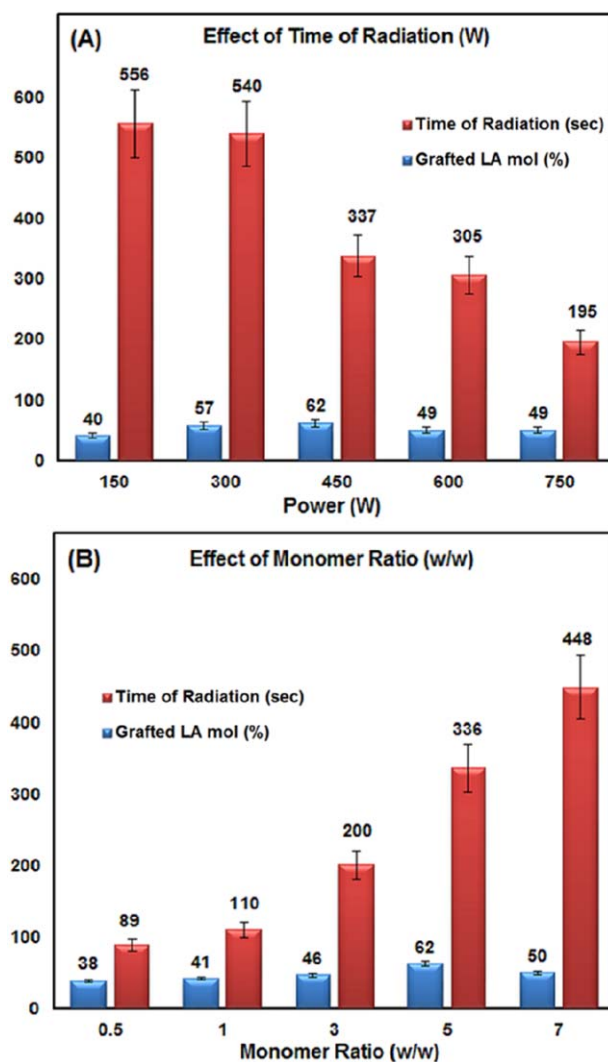


Figure 6. The effect of power of radiation (A) and monomer ratio (B) on duration of radiation and grafted PLA mole fraction (%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ble for homopolymerization. Thus, the maximum grafted PLA mole fraction of 62% was obtained at a 0.4 M concentration of NaOH, 450 W power of radiation and 5g of LA.

CONCLUSIONS

This study describes an alternative method to the conventional thermal heating process in the synthesis of starch-g-PLA copolymers. The occurrence of graft copolymerization of PLA on the starch macromolecule backbone was confirmed by FTIR, ¹³C CP/MAS NMR and XRD. This analyses that verified the presence of chemically bound PLA chains. Thermal and SEM analyses indicate that there is faster energy transfer by microwave heating and finally that the popcorn effect in starch macromolecule structure caused an increase of thermal stability in final amorphous graft copolymers. Furthermore, absorption of more microwave energy up to 450W by many activated radical groups from two main monomers (starch and LA) resulted in the maximum grafted PLA (62%) indicating that the higher the

microwave power, higher the grafted PLA value. This study represents that microwave dielectric heating is not only a “green” approach to graft copolymerization on starch, but also demonstrates the possibility of eco-friendly and economically feasible mass production for packaging, biomedical materials, filtration materials and industrial applications.

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