Polym. Bull. (2012) 68:2009–2019
DOI 10.1007/s00289-012-0701-6

ORIGINAL PAPER

Preparation of poly(lactic acid) and modified starch composites

Chunping Ouyang · Yu Wang · Naipeng Zhao · Xiaogang Liu · Shizhong Li · Zhengpu Zhang

Received: 10 June 2011 / Revised: 13 December 2011 / Accepted: 2 January 2012 /

Abstract In this article, the pretreatment before extrusion between the PLA and the modified starch was researched. The research on the composites of PLA and the modified starch focused on improving its compatibility and mechanical properties. The pretreatment samples were characterized by solid ^{13}C-NMR and the chemical titration of the carboxyl end (–COOH) groups in PLA. The results illuminated that the pretreatment reaction was successful and the –COOH in PLA had reacted with the –OH in modified starch. The compatibility of the composites was determined by differential scanning calorimetry and scanning electron microscopy. The results showed that pretreatment could improve the compatibility of the composites. The mechanical properties of the composites were also enhanced. This approach is identified as a reasonable method to produce commercial PLA/modified starch composites with economical feasibility.

Keywords Poly(lactic acid) · Modified starch · Pretreatment · Composites · Compatibility

Introduction

As biodegradable materials, the excellent mechanical properties and biocompatibility of PLA [1, 2] have a wide range of research and applications, especially in biomedical fields, such as controlled drug release [3–5], surgical suture [6],

---

C. Ouyang · Y. Wang · N. Zhao · Z. Zhang (✉)
Key Laboratory of Functional Polymer Materials, Ministry of Education, and Institute of Polymer Chemistry, Nankai University, Tianjin 300071, People's Republic of China
e-mail: zhangzp@nankai.edu.cn

X. Liu · S. Li
Institute of New Energy Technology, Tsinghua University, Beijing 100084,
People's Republic of China

orthopedic fixation [7, 8], and tissue engineering [9–11], etc. Since its price is higher than general purpose plastics, PLA has not been widely used as packaging materials and mulch film. As yet, several studies on the modification of PLA including copolymer [12, 13] and blend [14–18] have been reported, and other composites have been researched [19–22].

Starch [23] is a nature biodegradable polymer. Because of its abundant output and low cost, starch is the preferred material for the modification of other polymers. PLA mixed with the starch, on one hand, can reduce the cost of materials [24]; On the other hand, it can improve the toughness of materials. However, PLA and starch has the poor compatibility by mixing directly. In order to improve the compatibility, we usually mix them into a compatibilizer [17, 25–27], or modify PLA and starch [28–32]. These methods will not only increase production cost, but also affect its biodegradability and security of using as the medical or food packaging materials.

Recently, we had reported the research on the composites of the PLA and the etherified starch (EST), and it showed good results [33]. In this article, we processed pretreatment between the PLA and the acetylated starch (AST) before extrusion and improved the compatibility of the composites. In addition, the pretreatment samples were characterized by solid ^{13}C-NMR and the chemical titration of the carboxyl end (–COOH) groups in PLA. The acetylated modified starch would have better effect because the forming of the ester bond increases its hydrophobicity. Experimental results showed this method could improve the mechanical properties of composites of PLA/AST and have better results than the composites of PLA/EST.

Experimental

Materials

PLA with a viscosity average molecular weight of 45,359 g/mol [34] was purchased from Nantong Jiuding Biological Engineering Co., Ltd. (Jiangsu, China). The PLA particles were grinded by a high-speed herbal medicine grinder machine (FW135, Tianjin Test Instrument Co. Ltd., China) into powder (the particle size was 60 mesh). Hydroxypropyl EST was purchased from the peak starch Development Co., Ltd., in Tianjin, the etherified degree of substitution (DS) was 0.01, the particle size was 120 mesh. Acetylated modified starch (AST) was prepared from the corn starch in our lab, the acetylated DS was 1.85–2.00, and the particle size was 100 mesh [35]. All of above raw materials were vacuum-dried at 60 °C for 24 h before use.

Dichloromethane and ethanol were purchased from the chemical reagents sixth factory (Tianjin, China) and redistilled before use. Sodium hydroxide was purchased from the chemical reagents factory (Tianjin, China), and was used without further purification. All of them were analytical reagent grade.

Pretreated mixing of the composites

The composites composition was listed in Table 1. Sample was added into a 1-L flask and then the flask was connected to a rotary vacuum evaporator (Model

Table 1 The composites composition and the method of processing

Samples	PLA	Modified starch	Method of processing blends
E80	24 g (80%)	Etherified starch 6 g	Extruding after pretreatment
E70	21 g (70%)	Etherified starch 9 g	
E60	18 g (60%)	Etherified starch 12 g	
A80	24 g (80%)	Acetylated starch 6 g	
A70	21 g (70%)	Acetylated starch 9 g	
A60	18 g (60%)	Acetylated starch 12 g	
$E_0$70	21 g (70%)	Etherified starch 9 g	Extruding without pretreatment
$A_0$70	21 g (70%)	Acetylated starch 9 g	

Laborota 4000, Heidolph, Germany) with a mechanical stirrer. The temperature of the sample was kept at 80 °C for 1 h, and then enhanced to 135 °C with a heat rate of 10 °C/h and maintained for a desired time. All processes were kept in vacuum (1–2 mmHg). After the pretreatment, the sample was restored in dryer.

Preparation of PLA and modified starch composites by extrusion and uniaxial orientation processing

The composites were produced by extrusion using a lab-scale, PEL330 single-screw extruder (Germany Bra bender) for extrusion. The processing temperature was set at 100, 160, 160, and 120 °C from feed inlet to the die, and the rotation speed was maintained at 25 rpm.

The extrudate sheets were produced by a 3-mm thickness die nozzle and oriented at 90 °C by an affiliated tension roller. The final sheets were cut into tensile bars following ASTM D 1708 and then cooled to the room temperature. All moulded tensile bars were preconditioned at 25 °C and 30% RH for 1 week to relax internal stresses prior any mechanical tests.

Characterization of the composites

Solid ^{13}C-NMR spectra

The measurements of the ^{13}C-NMR spectra were performed on a VARIAN UNITY-plus 400 MHz NMR spectrometer (Varian, USA) with $CDCl_3$ as the solvent. Weight about 0.5 g samples without extrusion and wrap with filter paper and placed in Soxhlet extractor, and extracted with CH_2Cl_2 for 10 h to remove the unreacted PLA. The dichloromethane-insoluble products were vacuum-dried at 50 °C for 24 h.

The titration analysis of the carboxyl end (–COOH) groups in PLA of the composites

About 0.15 g of samples was weighed without extrusion and soaked in 10 mL CH_2Cl_2 for 3 h, the solution was filtered after completely dissolved, leaching three times using 5 mL CH_2Cl_2 each time. The filtrate was titrated with 0.02 mol/L $NaOH/C_2H_5OH$ solution for the content of the –COOH groups in the dissolved PLA, and 1% ethanol phenolphthalein solution was used as an indicator. The insoluble samples were vacuum-dried at 50 °C for 24 h, weighed, and calculated the mass of dissolved PLA and the percentage mass of the PLA in the composites.

DSC analysis

The extrude samples were cut to chippings with a blade, vacuum-dried at 50 °C for 24 h. 2–3 mg samples was taken and NETZSCH differential scanning calorimetry (DSC) was used to analyse. DSC scans were carried out over the temperature range from room temperature to +200 °C at a heating rate of 10 °C/min and isothermed for 2 min; cooled rapidly back to −10 °C, and again DSC scans were carried out over the temperature range from −10 °C to +190 °C, keep down the data in the second scan.

SEM

The fracture surfaces of the samples were performed with SS-550 scanning electron microscopy (SEM) (SHIMADZU, Japan), operating at an acceleration voltage of 20 kV. The samples of extruding and then drawing were cooled in liquid nitrogen, and then broken. The fracture surfaces were vacuum coated with gold for SEM testing.

Mechanical testing

A mechanical testing machine, AX-M500-10KN all-purpose material testing (Testometric company, Britain) was used to measure the mechanical properties according to ASTM D 1708 standard and the tensile testing rate of 1.0 cm/min. All results presented are the average values of five parallel samples.

Results and discussion

The solid ^{13}C-NMR spectra

The solid ^{13}C-NMR results of the samples E_070 and E70 are shown in Fig. 1a, b, respectively. As can be seen from these figures, the chemical shifts at C_1: 101.5 ppm, C_4: 82.4 ppm, $C_{2,3,5}$: 72.7 ppm, C_6: 62.4 ppm were assigned to the carbon of six-membered ring in the glucose. However, C_7: 170.4 ppm, C_8: 19.6 ppm were assigned to the C (C=O) and ($-CH_3$) in the PLA, respectively, which are shown in Fig. 1b. These results also proved that there may be a reaction between the PLA and the modified starch.

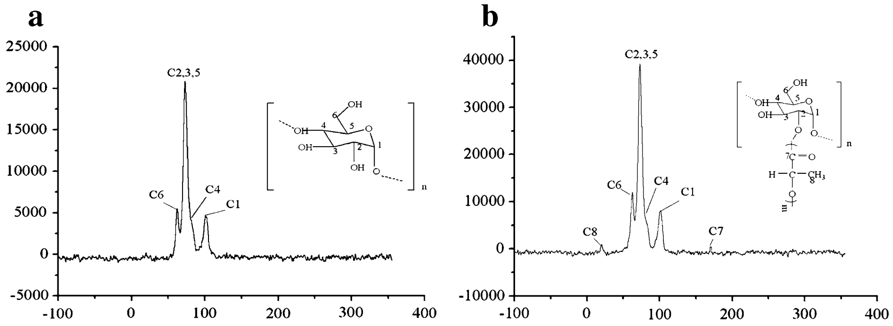

Fig. 1 The Solid ^{13}C-NMR of composites: **a** samples $E_0$70 and **b** E70 after extraction

Results of titration of the carboxyl end (–COOH) groups in PLA of the composites

The samples in Table 1 were dissolved in CH_2Cl_2 and the mass of the dissolved PLA were calculated. The contents of the –COOH groups in the dissolved PLA of the four samples were titrated, and the results were listed in Table 2. As displayed in Table 2, the content of the –COOH groups in the dissolved PLA was significantly decreased in the sample E70 compared with the sample $E_0$70. The content of the –COOH groups in the dissolved PLA of the sample E70 was about half of the sample $E_0$70, which was not suffered pretreatment. The obvious decrease of the –COOH groups in the PLA was indicated that the reaction may process between the PLA and EST. In addition, the mass of dissolved PLA was lower than that of the PLA added to the composites, and this may afford the information that a small amount of the PLA was grafted on the starch. The comparison between the sample A70 and the sample $A_0$70 showed the same trends.

DSC analysis

DSC curves of the samples E70 and $E_0$70 are shown in Fig. 2a, b, respectively. From Fig. 2b, it was seen that the glass transition temperature (T_g) of the sample $E_0$70 was 50.2 °C, while the T_g of the sample E70 was 43.2 °C, shown in Fig. 2a.

Table 2 Titration of the carboxyl end groups and mass of PLA dissolved in CH_2Cl_2

Sample	Composites weight (g)	Weight of PLA dissolved (g)	Weight of PLA added in composites (g)	Content of carboxyl end groups in PLA (mmol/g)
E70	0.1522	0.1043	0.1066	0.20
$E_0$70	0.1495	0.1046	0.1047	0.40
A70	0.1558	0.1067	0.1091	0.22
$A_0$70	0.1544	0.1079	0.1081	0.42

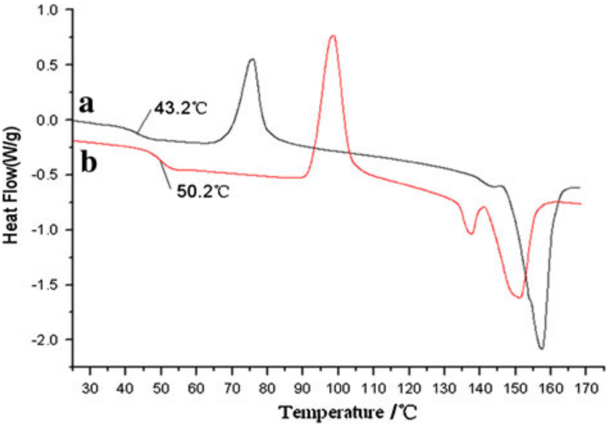

Fig. 2 DSC curves of samples: **a** E70 and **b** $E_0$70

The decrease in T_g demonstrated that the compatibility of composites had been obviously improved. The reinforcement of the compatibility of composites was ascribed to the pretreatment. It improved the compatibility of composites of PLA/EST and the plastic character of melting extrusion materials. In addition, after pretreatment, the movement of the cold crystallization peak to the lower temperature that also showed a chain segment movement had strengthened, and the more regular crystal structure of the PLA made the melting peak move to the higher temperature. DSC curves of the samples A70 and $A_0$70 are shown in Fig. 3a, b, respectively. They showed the same change with Fig. 2a, b, and could have the same explanation. The results above demonstrated whatever PLA mixed with EST or AST, the pretreatment had increased the compatibility of the composites.

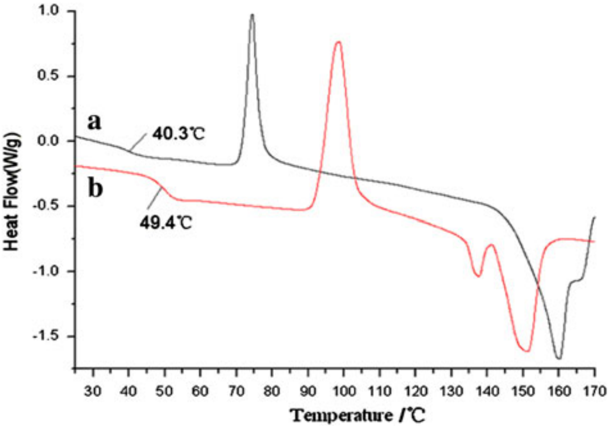

Fig. 3 DSC curves of samples: **a** A70 and **b** $A_0$70

Morphology of the composites

The SEM images of the samples E70 and $E_0$70 without drawing are shown in Fig. 4a, b, respectively. From Fig. 4b, we could observe that the fracture structure was evidently displayed a large number of holes and grooves, which were formed by brushing of the starch particles. The surface of the starch particles and the PLA was very clear, and the combining force between them was small due to the poor compatibility. The morphology of the sample E70 with the pretreatment is shown in Fig. 4a. The fracture structure was continuous and smooth, the starch particles were significantly smaller than that of the sample $E_0$70. Moreover, the starch particles were closely wrapped by the PLA particles, without falling and clear interface. The distinct morphology of the two samples proved the enhancement of compatibility of the composites.

The SEM images of the fracture structure of the samples E70 and $E_0$70 with drawing are shown in Fig. 5a, b, respectively. From Fig. 5b, the starch particles gathered in the tensile fracture structure, when EST and PLA were directly mixed. Without the pretreatment, the starch particles were unevenly scattered and gathered in a large agglomeration in the process of the drawing. This method of mixing would generate the mechanical defects and reduce the properties of the composites. In contrast, EST particles were not only evenly dispersed in the PLA, but also

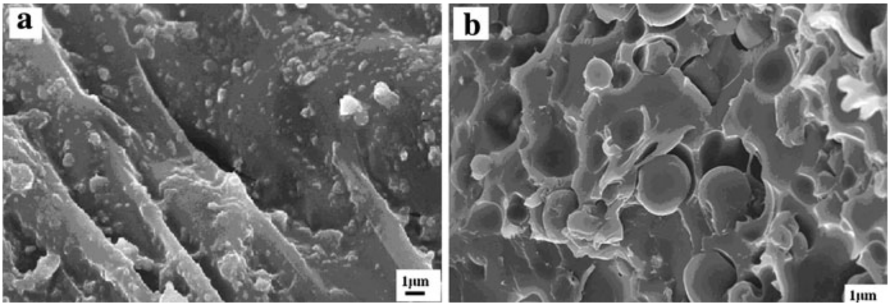

Fig. 4 SEM images of extruded composites bars without drawing: samples **a** E70 and **b** $E_0$70

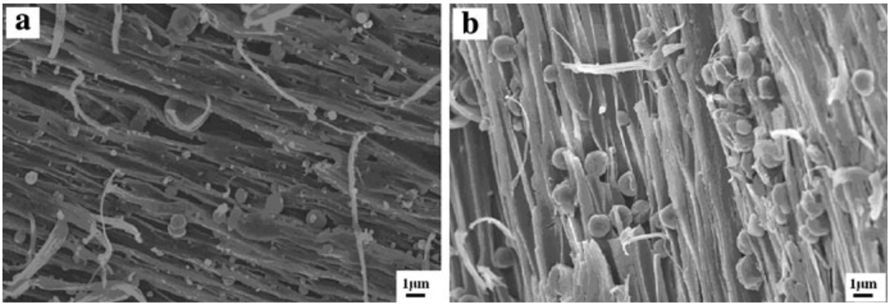

Fig. 5 SEM images of extruded composites bars with drawing: samples **a** E70 and **b** $E_0$70

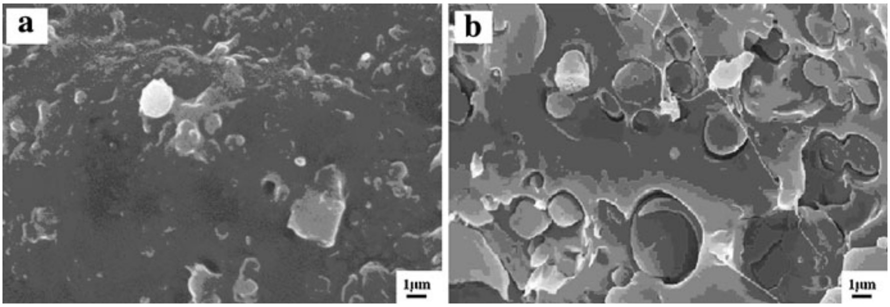

Fig. 6 SEM images of extruded composites bars without drawing: samples **a** A70 and **b** $A_0$70

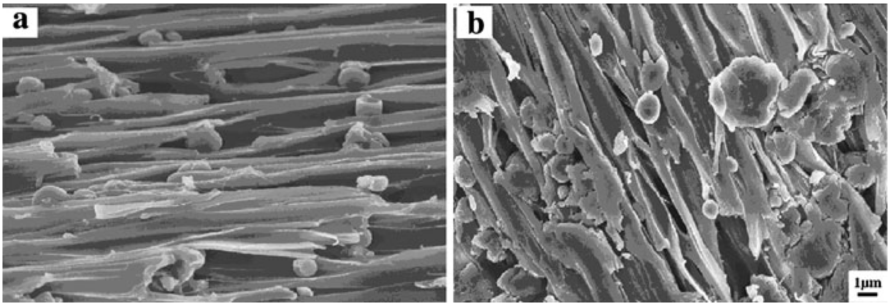

Fig. 7 SEM images of extruded composites bars with drawing: samples **a** A70 and **b** $A_0$70

closely integrated to the PLA, as shown in Fig. 5a. The pretreatment may generate the chemical binding between EST and PLA and enhance the compatibility of composites. The pretreatment had little influence on the material properties and the phenomenon matched the mechanical properties results. The comparison of the morphology could illustrate the excellent compatibility of composites because of the pretreatment of EST and PLA.

The SEM images of the fracture structure of the samples A70 and $A_0$70 without and with drawing are shown in Figs. 6a, b and 7a, b, respectively. They showed similar phenomenon with Figs. 4 and 5, and could have the same explanation.

The mechanical properties of the composites

The mechanical properties test results of the samples with drawing are shown in Table 3. When PLA simply mixed with 30% AST, the tensile strength of the sample $A_0$70 was 36.8 MPa, elongation at break was 17.4%. However, after the pretreatment, the mechanical properties of the composites had been greatly improved, the tensile strength of the sample A70 was 74.1 MPa and elongation at break was 54.1%. Meanwhile, the same trends happened on the samples A80 and $A_0$80, samples A60 and $A_0$60. The markedly improvement of tensile strength of samples with the pretreatment reflected that the system compatibility had been

Table 3 The mechanical properties of extruded composites bars after drawing

Samples	Rod diameter (mm)	Tensile strength (MPa)	Elongation at break (%)
E80	1.47 (±0.03)	72.6 (±3.5)	69.8 (±1.9)
E70	1.53 (±0.07)	69.0 (±0.3)	49.2 (±0.6)
E60	1.52 (±0.03)	53.1 (±0.5)	45.2 (±0.8)
A80	1.49 (±0.03)	80.8 (±1.0)	76.2 (±1.9)
A70	1.48 (±0.03)	74.1 (±2.0)	54.1 (±0.6)
A60	1.45 (±0.02)	61.3 (±0.4)	46.5 (±2.4)
$E_0$70	1.45 (±0.03)	38.4 (±7.1)	29.1 (±8.7)
$A_0$70	1.53 (±0.01)	36.8 (±1.6)	17.4 (±0.8)

improved. Comparison of the results of the sample A80, the tensile strength and elongation at break decreased as the content of AST in the composites increased in the samples A70 and A60. We noted that the content of AST in the composites should not be higher. Comparing to the results of Ref. [33], the pretreatment had more evident effect on the improved properties of composites of AST/PLA than EST/PLA. It may be the reasons that (1) EST had lower DS, while AST had higher DS and more hydrophobic; (2) the ester bond in AST could form the graft in the subsequent pretreatment. Table 3 could illuminate that the pretreatment would enhance the compatibility of composites, obviously improve the tensile strength and elongation at break, and reduce the negative effect on mechanical properties of the composites while adding AST to PLA.

Conclusions

In summary, the three different components of composites of the PLA and the AST with and without pretreatment were prepared for detailed comparison. From the analysis of FT-IR, solid ^{13}C-NMR, and the titration results, it is assumed that it may be related to the esterification reaction between the –COOH groups of the PLA and the –OH groups of the EST. From DSC and SEM results, we noted that the pretreatment not only improved the compatibility between the PLA and the AST, but also increased the connection ability of interface of the composites. The mechanical testing of the drawing bars expatiated that the mechanical properties of composites with the pretreatment were significantly better than those without the pretreatment.

Since starch is a compact solid particle, the pretreatment between the modified starch and PLA only happened at the surface of starch particles. With increasing content of modified starch in composites, starch particles started to congregate. The results of samples drawing showed the tensile strength and elongation at break became lower as the content of the modified starch in the composites increased. Considering the actual use of the material, the content of the modified starch in the composites should not be higher than 30%, if the viscosity average molecular weight of the PLA was 45,359 g/mol.

Acknowledgments We are grateful for the financial support of Tianjin Science and Technology Key Grants (05YFGPGX26200). We also thank Dr. Xiu-ping Lu and Dr. Su-hua Wu in Tianjin University of Science and Technology.

References

1. Ro AJ, Huang SJ, Weiss RA (2009) Synthesis and properties of random poly(lactic acid)-based ionomers. Polymer 50:1134–1143
2. Chognot D, Six JL, Leonard M, Bonneaux F, Vigneron C, Dellacherie E (2003) Physicochemical evaluation of PLA nanoparticles stabilized by water-soluble MPEO–PLA block copolymers. J Colloid Interface Sci 268:441–447
3. Allison SD (2008) Effect of structural relaxation on the preparation and drug release behavior of poly(lactic-co-glycolic) acid microparticle drug delivery systems. J Pharm Sci 97:2022–2035
4. Yang L, Wu XH, Liu F, Duan YR, Li SM (2009) Novel biodegradable polylactide/poly(ethylene glycol) micelles prepared by direct dissolution method for controlled delivery of anticancer drugs. Pharm Res 26:2332–2342
5. Miyajima M, Kiko A, Okada J, Ikeda M (1999) Mechanism of drug release from poly(L-lactic acid) matrix containing acidic or neutral drugs. J Control Release 60:199–209
6. Schmack G, Tändler B, Vogel R, Beyreuther R, Jacobsen S, Fritz HG (1999) Biodegradable fibers of poly(L-lactide) produced by high-speed melt spinning and spin drawing. J Appl Polym Sci 73:2785–2797
7. Winet H, Bao JY (1998) Fibroblast growth factor-2 alters the effect of eroding polylactide–polyglycolide on osteogenesis in the bone chamber. J Biomed Mater Res 40:567–576
8. Hu YS, Zhang ZP, Song D, Bai DR, Wang YM (2001) The Preparation and properties of high strength rods from L- and D,L-lactide copolymer. Chin J Polym Sci 19:351–357
9. Hu YS, Zhang ZP, Song D, Wang YM, Bai DR (2002) Preparation and properties of high strength sheets from L- and D,L-lactide copolymer. Int J Polym Mater 51:1071–1079
10. Leong MF, Rasheed MZ, Lim TC, Chian KS (2009) In vitro cell infiltration and in vivo cell infiltration an vascularization in a fibrous, highly porous poly(D,L-lactide) scaffold fabricated by cryogenic electrospinning technique. J Biomed Mater Res 91A:231–240
11. Ozkoc G, Kemaloglu S, Quaedflieg M (2009) Production of poly(lactic acid)/organoclay nanocomposite scaffolds by microcompounding and polymer/particle leaching. Polym Compos 31: 674–683
12. Bagheri S, Mohammadi-Rovshandeh J, Hassan A (2007) Synthesis and characterization of biodegradable random copolymers of L-lactide, glycolide and trimethylene carbonate. Iran Polym J 16: 489–494
13. George KA, Schue F, Chirila TV, Edeline WB (2009) Synthesis of four-arm star poly(L-lactide) oligomers using an in situ-generated calcium-based initiator. J Polym Sci A 47:4736–4748
14. Kim K, Yu M, Zong X, Chiu J, Fang D, Seo YS et al (2003) Control of degradation rate and hydrophilicity in electrospun non-woven poly(D, L-lactide) nanofiber scaffolds for biomedical applications. Biomaterials 24:4977–4985
15. Su ZZ, Li QY, Liu YJ, Hu GH, Wu CF (2009) Compatibility and phase structure of binary blends of poly(lactic acid) and glycidyl methacrylate grafted poly(ethylene octane). Eur Polym J 45:2428–2433
16. Ke T, Sun X (2001) Thermal and mechanical properties of poly (lactic acid) and starch blends with various plasticizers. Trans ASAE 44:945–953
17. Wang N, Yu JG, Ma XF (2007) Preparation and characterization of thermoplastic starch/PLA blends by one-step reactive extrusion. Polym Int 56:1440–1447
18. Zhang JF, Sun XZ (2004) Mechanical and thermal properties of poly (lactic acid)/starch blends with dioctyl maleate. J Appl Polym Sci 94:1697–1704
19. Raya SS, Yamada K, Okamoto M, Ueda K (2003) New polylactide-layered silicate nanocomposites. 2. Concurrent improvements of material properties, biodegradability and melt rheology. Polymer 44: 857–866
20. Bleach NC, Nazhat SN, Tanner KE, Kellomaki M, Tormala P (2002) Effect of filler content on mechanical and dynamic mechanical properties of particulate biphasic calcium phosphate–polylactide composites. Biomaterials 23:1579–1585

21. Xu L, Sun R, Zhang LF, Yang DJ, Tan YF, Xiong CD (2008) Studies on poly(D,L-lactic acid)/wollastonite composites as a biomaterial. Iran Polym J 17:407–418
22. Gu SY, Zou CY, Zhou K, Ren J (2009) Structure–rheology responses of polylactide/calcium carbonate composites. J Appl Polym Sci 114:1648–1655
23. Loisel C, Maache-Rezzoug Z, Esneault C, Doublier JL (2006) Effect of hydrothermal treatment on the physical and rheological properties of maize starches. J Food Eng 73:45–54
24. Wu CS, Liao HT (2005) A new biodegradable blends prepared from polylactide and hyaluronic acid. Polymer 46:10017–10026
25. Tu KH, Wang LQ, Wang YB (2002) The role of starch graft copolymers in starch and PLA blends. Polym Mater Sci Eng 18(108–110):114
26. Wang N, Yu JG, Chang PR, Ma XF (2008) Influence of formamide and water on the properties of thermo-plastic starch/poly(lactic acid) blends. Carbohydr Polym 71:109–118
27. Kozlowski M, Masirek R, Piorkowska E, GazickiLipman M (2007) Biodegradable blends of poly(L-lactide) and starch. J Appl Polym Sci 105:269–277
28. Ren J, Zhang ZW (2006) Application and development of reactive extrusion in synthesizing and modifying poly (lactic acid). Mater Rev 20:68–71
29. Chapleau N, Huneault MA, Li H (2007) Biaxial orientation of polylactide/thermoplastic starch blends. Int Polym Proc 22:402–409
30. Zhang JF, Sun XZ (2004) Physical characterization of coupled poly(lactic acid)/starch/maleic anhydride blends plasticized by acetyl triethyl citrate. Macromol Biosci 4:1053–1060
31. Gong QX, Tu KH, Wang LQ (2006) In situ graft copolymerization of starch with lactic acid. Acta Polym Sin 9:1045–1049
32. Zhang KY, Ran XH, Zhuang YG, Yao B, Dong LS (2009) Blends of poly(lactic acid) with thermoplastic acetylated starch. Chem Res Chin U 25:748–753
33. Liu XG, Zhao NP, Yang KK, Wang Y, Zheng C, Li SZ, Zhang ZZ (2008) Preparation of poly (lactic acid)/etherified starch composites. Iran Polym J 17:947–952
34. Schindler A, Harper D (1979) Polylactide. II. viscosity–molecular weight relationships and unperturbed chain dimensions. J Polym Sci A 17:2593–2599
35. Singha J, Kaurb L, McCarthy OJ (2007) Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications—a review. Food Hydrocoll 21:1–22