

# The starch grafted poly(L-lactide) and the physical properties of its blending composites

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## Abstract

A new method of the surface modified starch (SM-St) by grafting reaction of the hydroxyl groups on the starch with L-lactic acid was developed. A novel biodegradable starch grafted copolymer, starch-g-poly(L-lactide) (St-g-PLLA), was synthesized in situ by the ring-opening graft polymerization of a L-lactide (LLA) monomer onto the surface of the SM-St granules in the presence of Sn(Oct)<sub>2</sub> as a catalyst. The PLLA grafting efficiency could reach as high as 64 wt%. The structure of St-g-PLLA was characterized by IR, DSC and WAXD. The good adhesion between the two components had been evidenced by SEM observations. The medium-resistance of St-g-PLLA and the mechanical properties of the PLLA composite blending with St-g-PLLA were much better than that of the PLLA/starch blending composite. © 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Starch; Surface modification; Grafting polymerization

## 1. Introduction

The environmental pollution by non-degradable plastic wastes attracts more attention to the research and development on the biodegradable polymers of sustainable materials. However, many of the candidates for the biodegradable polymers have some limitation, especially the high cost that is one of the most serious factors restricting the application of biodegradable polymers.

Starch is a potentially useful material for biodegradable plastics because of its natural abundance and low cost. However, the starch-based materials produced by conventional melt-processing usually, such as the thermoplastic starch, with very poor mechanical properties, mainly due to the thermal decomposition of starch before melting, the strong water absorption and the poor interfacial adhesion

with other components. In order to solve these problems, various physical or chemical modifications of the starch granules have been considered, including the blending [1–7] and the chemical modification [8–11].

The starch graft copolymer is representative of the modification of the starch molecule by chemical method [12,13]. The starch graft copolymers such as starch-g-polystyrene [14] (St-g-PS), starch-g-methacrylonitrile [15], starch-g-polyvinyl alcohol [16] and starch-g-acrylonitrile [17], have been synthesized by generating free radicals on the surface of the starch granules and the copolymerization of these free radicals with the respective vinyl monomers. However, these copolymers with vinyl polymer branches have also limited the biodegradability because of the presence of their non-degradable part of the polymer, although their mechanical properties are acceptable for applications.

Another effort in chemical modification of starch is grafting starch with biodegradable polymers [18,19], such as PCL and PLA. The graft-copolymers of starch-g-PCL and starch-g-PLA can be completely biodegraded by bacteria or under natural conditions and have improved

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their mechanical performance. Therefore, the graft-copolymers can be used directly as thermoplastics or as compatibilizer in a starch-PCL or starch-PLA blend composites. The only problem of the application of the graft-copolymer is the cost of the production, so that it is very important to find a simple technology to reduce the cost.

The difficulty in the graft-polymerization is the existence of water in starch, because almost all catalysts for CL or LA copolymerization are sensitive to the moisture. Choi [20] have reported that the preparation of starch-*g*-PCL from highly purified CL monomer under careful protection with high purity N<sub>2</sub>. Our group [21] has synthesized starch-*g*-poly( $\epsilon$ -caprolactone) (St-*g*-PCL) by the ring-opening graft polymerization of a  $\epsilon$ -caprolactone (CL) monomer onto starch granules in the presence of Sn(Oct)<sub>2</sub>. Both of the CL monomer and amylose cornstarch are of industrial grade, without further purifications. The St-*g*-PCL compatible composites blending with starch and PCL have been proved efficiently to improve the interfacial adhesion and the mechanical properties of the thermoplastic with good water- and acid-resistance properties.

In this paper, we used L-lactic acid to modify the surface of the starch firstly, and then the surface modified starch was used as the macromolecular initiator for the ring-opening polymerization of L-lactide (LLA) to synthesis the starch grafted PLLA copolymer (St-*g*-PLLA). The chemical structure and physical properties of the St-*g*-PLLA composite blending with starch and PLLA were evaluated by modern analytical methods and discussed in detail.

## 2. Experiment

### 2.1. Materials and measurements

The corn starch was from Changchun Dacheng Corn Development Co. Ltd in Jilin province, China. The water content in the starch was about 12% in weight measured by water lost at high temperature. L-lactic acid (Purac) and Sn(Oct)<sub>2</sub> (Acros) were used without further purification. L-Lactide (LLA, Purac) was recrystallized from ethyl acetate under argon atmosphere. Ethyl acetate and tetrahydrofuran (THF) were dried by refluxing over CaH<sub>2</sub> and metal sodium, respectively.

The IR spectra were recorded on Bio-Rad FTS 135. The thermal analysis was carried out using Perkin–Elmer PYRIS 1 DSC under nitrogen flow (10 mL/min) at a heating or cooling rate of 10 °C/min. The wide angle X-ray diffraction (WAXD) analysis was conducted with a Philips apparatus using a Cu K $\alpha$  ( $\lambda=0.154$  nm) source. The dispersion of the starch granules grafted at the different PLLA chains in water was measured by the microscope (Nikon YS100) attached Nikon Digital Camera DXM1200F. The SEM images were obtained with a Model XL 30 ESEM FEG from Micro FEI Philips after the sputter coating of gold on the specimen

surface. The tensile tests were performed at room temperature by using a Lloyd apparatus with a constant deformation rate of 50 mm/min on dumbbell specimens cut in accordance to ASTM D638 V standard.

### 2.2. Polymerization procedure

#### 2.2.1. Surface modification of starch granules by L-lactic acid

First, 30 g raw starch was dispersed in 100 ml of THF. A certain amount of L-lactic acid was slowly dropped into the above stirred suspension and then the suspension was heated to 60 °C and maintained for 30 min. The THF solvent was removed by evaporation and 150 ml toluene was added into the suspension system. After that, the mixture was heated to 150 °C and maintained for 10 h, the water in the starch and formed by the reaction was removed by azeotropic dehydration with toluene. The mixture was washed five times by THF and ethyl acetate, respectively, to remove non-grafted L-lactic acid. Then the mixture was filtrated and dried in vacuum-oven at 60 °C for 24 h to remove the residual solvent, the surface modified starch (SM-St) were obtained. Three modified starch samples (SM-St<sub>1</sub>, SM-St<sub>2</sub>, SM-St<sub>3</sub>) with different grafting degrees were prepared by adding 15, 30, 60 g L-lactic acid as modifying reactant, respectively.

#### 2.2.2. Surface grafting of SM-St via in situ polymerization

The grafting polymerization of L-lactide onto the hydroxyl groups of the grafted L-lactic acid of the surface modified starch was carried out with 0.05 wt% Sn(Oct)<sub>2</sub> as catalyst at 130 °C under argon atmosphere and anhydrous condition for 48 h. The starch grafted PLLA product was washed fifth with ethanol to remove unreacted L-LA and residual catalyst. The feed ratio of SM-St to L-LA in weight is 50 to 50. The product directly obtained from the above method was the mixture of the grafted copolymer and the homopolymer of PLLA regarded as PLLA modified starch (St-*g*-PLLA/PLLA).

### 2.3. Separation of St-*g*-PLLA copolymer and PLLA homopolymer from PLLA modified starch

St-*g*-PLLA copolymer and PLLA homopolymer coexisting in the reaction product of PLLA modified starch (St-*g*-PLLA/PLLA) were separated by toluene extraction. Two grams of the PLLA modified starch were put into a 50 ml toluene in a bottle. The mixture was stirred at 20 °C for 24 h and then was filtrated. The remaining solids were washed with toluene for three times. The above process was repeated once again. The solids after toluene extraction were considered as St-*g*-PLLA which dried in vacuum and were characterized by IR, WAXD, DSC, microscope and SEM.

#### 2.4. Monomer conversion and grafting efficiency

The monomer conversion (%) is calculated as follows:

$$\text{Monomer conversion} = \frac{m_2 - m_1}{m} \quad (1)$$

Where  $m_1$  is weight of dried starch or the surface modification starch (SM-St),  $m_2$  is weight of the PLLA modified starch, and  $m$  is the weight of L-LA monomer in the feed.

The grafting efficiency is defined as:

$$\text{Grafting efficiency} = \frac{\text{grafted PLLA wt\%}}{\text{grafted PLLA wt\%} + \text{homo-PLLA wt\%}} \quad (2)$$

#### 2.5. Medium resistance measurements

The PLLA modified starch (St-g-PLLA/PLLA) was pressed into the thin films of 50–100  $\mu\text{m}$  in thickness. The films were immersed in a 0.5 mol/L HCl solution, a 0.5 mol/L NaOH solution and water at room temperature, respectively. After 24 h, the films were taken out and the liquid on the film surface was absorbed by filter papers. The films were maintained in the air at room temperature for 10 min to get rid of the surface water and then weighed to calculate the weight change percentage.

### 3. Results and discussion

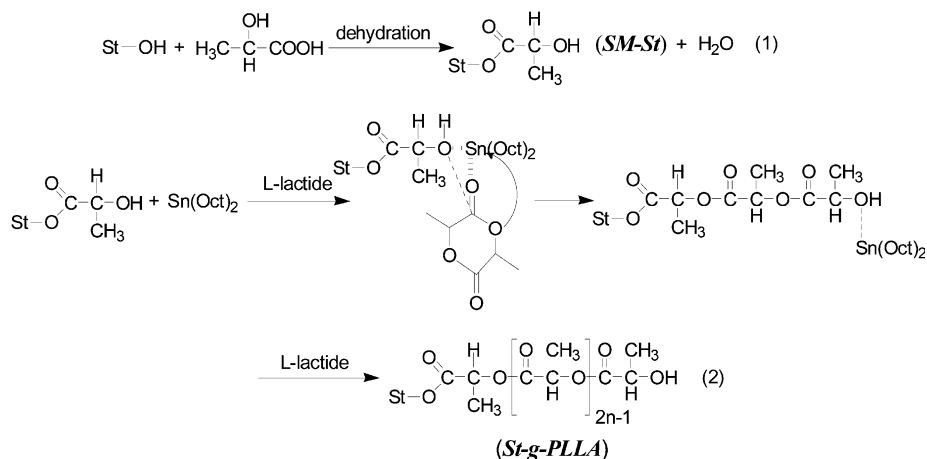
#### 3.1. The surface modification reaction and the polymerization

The surface modification reaction and the polymerization procedure are assumed to depict in Scheme 1. First, after azeotropic dehydration of the starch with toluene, the hydroxyl groups on the surface of the starch granules are

reacted with L-lactic acid and form a starch carboxylate bond (Eq. (1)). Then, the propagation reaction in the presence of  $\text{Sn}(\text{Oct})_2$  includes in succession the coordination of both the lactide and the hydroxyl group on the surface of starch with  $\text{Sn}(\text{Oct})_2$  followed by cleavage of the acyl-oxygen bond of the L-lactide by the Sn-coordinate insertion mechanism and thereby activated hydroxyl group as indicated in Eq. (2). Because the polymerization strategy is based on fixation of Sn–O functions onto the starch surface by in situ reaction of  $\text{Sn}(\text{Oct})_2$  with the hydroxyl groups on the surface of the modified starch, so the residual water and other impurity in the reaction system should have a strong influence on the ability to generate the active species at the modified starch surface. On the other hand, it is well known that  $\text{Sn}(\text{Oct})_2$  can readily react with the trace amount of water or other impurity molecules to form the active derivatives. This promotes the lactones polymerization directly with formation of non-grafted polyester chains as PLLA homopolymer.

The amounts of grafted L-lactic acid are measured by the weight increase of the starch after reacted with the lactic acid. Table 1 reports the lactic acid grafting efficiencies increase with the ratios of the lactic acid to starch in feed. The grafted lactic acid weight ratios can be controlled from 0 to 10 wt% by adjusting the feed ratio of L-lactic acid to starch.

The grafting products of starch or SM-St with PLLA could be separated into toluene-insoluble and soluble parts [8,9]. The former is considered mainly as graft-copolymer (St-g-PLLA) and the latter as homopolymer (homo-PLLA). As shown in Table 2, under the reaction conditions, the monomer conversion is usually 98–99% and the PLLA grafting efficiencies ranged from 12 to 64%. In the same reaction condition, the PLLA grafting efficiency of the surface modification starch (sample 2, 3 and 4) is much higher than that of the non-surface modification starch (sample 1). It can be attributed to the fact that after the surface modification, the hydroxyl group on the surface of



Scheme 1. The surface modification reaction of starch with L-lactic acid (1) and the  $\text{Sn}(\text{Oct})_2$  initiated polymerization mechanism of L-LA with the modified starch (2).

Table 1  
Grafting rate of the surface modified starch by the lactic acid

Sample	St/lactic acid (in weight (g))	Grafting rate <sup>a</sup> (%)
SM-St 1	2:1 (30:15)	2.9
SM-St 2	1:1 (30:30)	4.8
SM-St 3	1:2 (30:60)	6.2

<sup>a</sup> The grafting rate calculated by the weight increase of the starch after reacted with the lactic acid.

SM-St is more active than that on the starch, resulting in that more active sites are formed at the surface allowing the fixation of more polyester chains and thus a higher grafting efficiency. So with the increase of the lactic acid content in the SM-St, the PLLA grafting efficiency can reach to as high as 64% (sample 4). The effect of catalyst content on the grafting polymerization is also shown in Table 2. The samples 4, 6 and 7 are prepared by bulk process in 48 h but each with different catalyst concentrations. Among them, sample 4, the lowest catalyst content, has the highest grafting efficiency of 64%. It seems that the excess catalyst is favorable to the homo-polymerization of L-LA. On the other hand, sample 5 in Table 2 indicates that the longer reaction time over 48 h leads to lower grafting efficiency for the degradation of the grafted PLLA chains by the transesterification to form the homopolymer PLLA.

In order to attest that the PLLA are really grafted onto the surface of the starch by chemical link other than physical adsorption, 10 g SM-St3 were blended with 10 g PLLA ( $M_n = 14,900$ , from GPC) in toluene at 130 °C under argon atmosphere for 48 h without adding the catalyst. The mixtures were precipitated in ethanol and separated by toluene extraction as the description in Section 2.3. The increasing efficiency 2.3 wt% is the content of the physically adsorbed PLLA on the surface of the starch, while the increasing efficiency from 14 to 64 wt% (Table 2) much higher than 2.3 wt% are due to the chemical grafted PLLA.

### 3.2. Characterization of St-g-PLLA

The IR spectra of starch (a), the surface modified starch (SM-St) (b), and the starch grafted copolymer St-g-PLLA (c

and d) were shown in Fig. 1. Compared the spectrum of starch (a) with the surface modified starch (SM-St) (b and c), the new strong absorptions emerged at 1730  $\text{cm}^{-1}$  in the spectra of SM-St and St-g-PLLA, assigned to carbonyl (=CO) in lactic acid or in PLLA. The peak intensity of the hydroxyl groups in SM-St (3400  $\text{cm}^{-1}$ ) increased because the hydroxyl groups of lactic acid on the surface of the starch generated. At the same time, the peak intensity of the hydroxyl groups in 3400  $\text{cm}^{-1}$  decreased in the spectra (c) and (d), because the hydroxyl groups of the SM-St had initiated the ring open polymerization of the L-LA. Meanwhile, the new characteristic peaks at 1730  $\text{cm}^{-1}$  in the spectra (b), (c) and (d) illuminated that the surface of starch has been modified by the lactic acid and the surface of the modified starch has been grafted by L-LA to form St-g-PLL, respectively.

The typical DSC traces for starch, SM-St, St-g-PLLA, and PLLA ( $M_n = 17,800$ ) are collected in Fig. 2. The pure lactic acid is easy to crystal originally at room temperature, but when it is grafted and dispersed onto the surface of starch, it cannot crystallize anymore, just as shown in the Fig. 2(b). The PLLA homopolymer has a  $T_m$  at 156.1 °C and a  $T_c$  at 94.9 °C, while St-g-PLLA exhibits a  $T_m$  at 136.0 °C. This lower  $T_m$  indicates that the physical properties of the grafted PLLA in St-g-PLLA are really different from those of homo-PLLA. In the St-g-PLLA, the PLLA graft is still crystalline, but its crystalline parameters have changed much due to the restriction from the starch surfaces and the grafting efficiency of PLLA.

The crystallizability of the pure St-g-PLLA copolymer can be also confirmed on the basis of WAXD patterns shown in Fig. 3. The PLLA ( $M_n = 17,800$ , in Fig. 3(d)) shows two main diffraction peaks at  $2\theta = 16.74$  and  $19.12^\circ$ , respectively, whereas the starch show peaks at  $2\theta = 15.2$ ,  $17.1$ ,  $23.1^\circ$  (Fig. 3(a)). Comparing with the acute diffraction peaks of the starch, the surface modified starch (SM-St) only shows a broad dispersion peak at  $2\theta = 18.9^\circ$  in Fig. 3(b), which indicates that after the surface modified by the lactic acid, the crystal form of the raw starch has changed very much. In Fig. 3(c), in addition to the peaks associated with the starch, there appear narrow peaks at  $16.88$  and  $19.34^\circ$  attributed to the crystallization of the PLLA grafted on the starch surface in comparison with Fig. 3(a).

Table 2  
The grafting polymerization of starch or SM-St with the L-LA

St-g-PLLA	Starch	Catalyst (wt%)	Polymerisation time (h)	Monomer conversion (%)	Grafting efficiency (%)	( $\mu\text{m}$ ) <sup>a</sup>
St-g-PLLA 1	Starch	0.1	48	99.0	14	11.23
St-g-PLLA 2	SM-St 1	0.1	48	99.2	36	13.24
St-g-PLLA 3	SM-St 2	0.1	48	99.6	45	15.10
St-g-PLLA 4	SM-St 3	0.1	48	98.6	64	25.32
St-g-PLLA 5	SM-St 3	0.1	96	99.5	51	19.20
St-g-PLLA 6	SM-St 3	0.3	48	98.7	54	21.42
St-g-PLLA 7	SM-St 3	0.5	48	98.1	49	17.86

Bulk reaction process; starch/L-LA = 50/50 wt%; the polymerization temperature was at 130 °C.

<sup>a</sup> The mean diameter of the coated starch particles, determined by the microscope, the grafted copolymer were dispersed in water at room temperature.

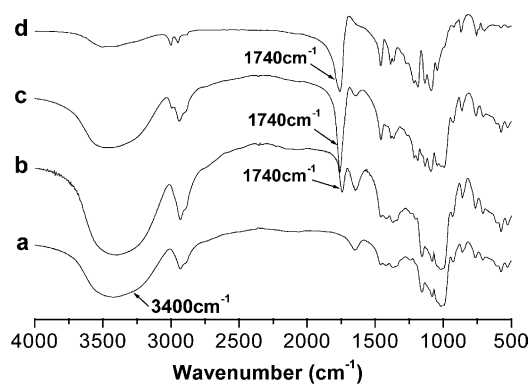


Fig. 1. IR spectra of starch (a); surface modification starch (SM-St) (b); St-g-PLLA/PPLLA (the crude product S-4 from the Table 2), before extraction in toluene (c) and St-g-PLLA, S-4 after toluene extraction (d).

The scanning electron microscopy images of the starch (a), SM-St (b) and St-g-PLLA (c and d) copolymer are presented in Fig. 4. The grafted lactic acid can be seen clearly on the surface of the starch in Fig. 4(b). A large amount of the tight coating covers the starch granules by the grafted PLLA and attests to the very good interfacial adhesion between the starch and the PLLA chains (Fig. 4(c) and (d)). In the magnified image of the St-g-PLLA (Fig. 4(d)), the grafted PLLA encapsulates the starch granules to form a composite with a core-shell structure by the core of hydrophilic starch and the shell of hydrophobic grafted PLLA as Scheme 2. Actually, the meaning diameter of the encapsulated particles measured by the microscope (Table 2) increase obviously with the growth of the PLLA grafting efficiency. Therefore, it shows that the PLLA located on the surfaces of the starch granules will be helpful to improve the mechanical properties and waterproof stability of the modified composites.

### 3.3. Mechanical properties of St-g-PLLA

Although a lot of papers on starch grafted aliphatic polyester (St-g-PCL and St-g-PVL) have been published, their mechanical properties have seldom been reported probably because the mechanical properties of St-grafted-

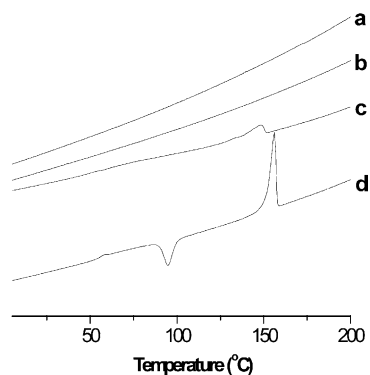


Fig. 2. The second heat DSC curves of starch (a); SM-St 3 (b); St-g-PLLA 4 (c) and PLLA (d) ( $M_n = 17,800$ ).

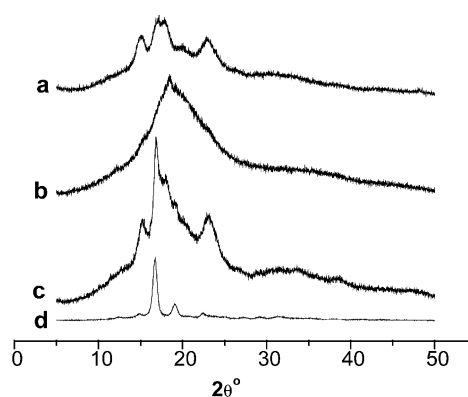


Fig. 3. WAXD of starch (a); SM-St 3 (b); St-g-PLLA 4 (c) (from Table 2 after toluene extraction) and homo-PLLA (d) ( $M_n = 17,800$ , from GPC).

copolymers are not excellent enough to be used as material alone. However, the grafted copolymers can be used as plasticizer when blending the starch with PCL or other polyesters. In this paper, PLLA/starch and PLLA/starch/St-g-PLLA compositions are blended by an internal mixer (Haake) at 160 °C for 15 min. Then they are moulded into 2–3 mm thick sheets by hot-pressing at 130 °C. The addition of starch fillers into PLLA matrix leads to significantly reduce the mechanical properties due to the poor filler/matrix interfacial adhesion (Table 3). If St-g-PLLA as an efficient compatibilizer is added into the blend of the starch and PLLA, it does not only promote a better dispersion in the PLLA/starch matrix and bring about a lower interfacial tension, but also reinforce the adhesion between the filler and the matrix. With the increasing content of the St-g-PLLA in the blended composite, the mechanical properties of the material are improved greatly, but cannot reach the properties of the pure PLLA material. The cheap composite material of starch and PLLA compatibilized by St-g-PLLA in industrial application can be prepared by a simple method.

### 3.4. Medium-resistance

It is well known that the water resistance is a very important factor for the practical application of the starch-based materials, because the starch is sensitive to moisture and poor in storage stability. The medium-resistance of the St-g-PLLA/PLLA to 0.5 mol/L acid solution, 0.5 mol/L alkalis solution and water is performed at room temperature for 24 h. Dispersed in water or an acid solution, the film increases a certain weight while in an alkali solution it loses weight. The weight increase is due to the water absorption by St-g-PLLA/PLLA and the weight-loss is due to the degradation of the starch catalyzed by the alkali solution. As shown in Table 4, the stability of the products in all three media increases with the increasing the graft efficiency of PLLA, especially in the alkaline medium. Compared to starch/PLLA blend (50/50), the grafting products showed the improved resistance to the three media. Owing to the

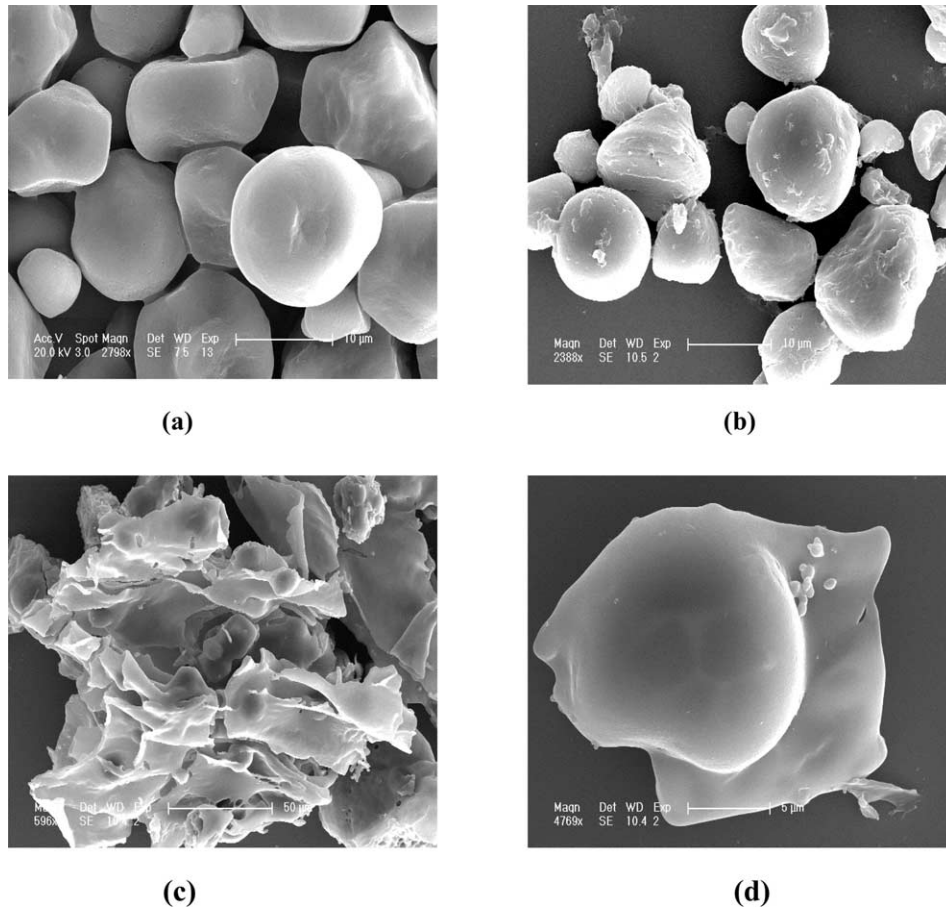


Fig. 4. SEM images of starch (a); SM-St (b); St-g-PLLA 4 (c) (from the Table 1 after toluene extraction), and the magnification image of St-g-PLLA 4 (d).

Table 3

The mechanical properties of St-g-PLLA, PLLA/starch blend and PLLA/St-g-PLLA/starch composites

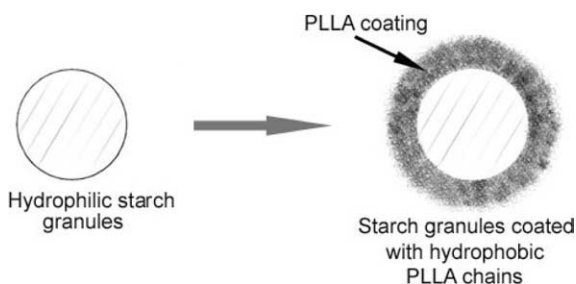
Composition	$\sigma_b$ (MPa)	$\epsilon_b$ (%)	$E$ (GPa)	$\sigma_y$ (MPa)
PLLA/starch (50:50)	9.3	1.5	0.05	6.2
PLLA/Starch/St-g-PLLA <sup>a</sup>	24.9	2.4	0.36	21.3
PLLA/Starch/St-g-PLLA <sup>b</sup>	35.7	3.6	0.95	30.6
PLLA ( $M_n=100,000$ )	55.4	6.0	3.00	50.9

$\sigma_b$ , strength at break;  $\epsilon_b$ , elongation at break;  $E$ , tensile modulus;  $\sigma_y$ , strength at yielding.

<sup>a</sup> PLLA/starch (50:50) blends added with 5 wt% of the St-g-PLLA 4.

<sup>b</sup> PLLA/starch (50:50) blends added with 10 wt% of the St-g-PLLA 4.

improved water resistance, the St-g-PLLA is expected to find the industrial use because it does not become swollen or sticky when contacted with water or moisture.



Scheme 2. The encapsulated starch granules.

#### 4. Conclusion

In conclusion, the surface of the raw starch granules could be readily modified by the lactic acid, and then the hydroxyl groups on the surface of the modified starch were reacted with  $\text{Sn}(\text{Oct})_2$  to form a living center  $\text{Sn}-\text{O}$  to initiate the ring-opening polymerization of L-lactide (L-LA) by a coordination–insertion mechanism. Homopolymerization of L-LA simultaneously occurred during the grafting polymerization, and thus the grafting products were composed of St-g-PLLA and homo-PLLA. The grafting efficiency could reach as high as 64 wt%. The amphiphilic character of St-g-PLLA was a good compatibilizer in the blend of hydrophobic PLLA and hydrophilic granular corn

Table 4  
The medium-resistance of St-g-PLLA/PLLA films compared with PLLA/starch blend film

St-g-PLLA/ PLLA	Grafting efficiency (%)	Weight change (wt%)		
		In 0.5 mol/L HCl	In 0.5 mol/L NaOH	In H <sub>2</sub> O
Blend	PLLA/ starch = 50:50	+19.5	−37.3	+19.5
St-g- PLLA1 <sup>a</sup>	14	+14.3	Broken into pieces	+10.3
St-g- PLLA2 <sup>a</sup>	36	+12.6	−4.9	+6.1
St-g- PLLA3 <sup>a</sup>	45	+4.3	−2.6	+2.4
St-g- PLLA4 <sup>a</sup>	64	+2.1	−1.8	+1.3

<sup>a</sup> See from the Table 2 without extraction in toluene.

starch to produce a good composite thermal plastic. The St-g-PLLA had proven efficiently to improve the interfacial adhesion and the mechanical properties of the compatible composites. The St-g-PLLA/PLLA mixture had good water- and acid-resistance properties. The starch/PLLA composite compatibilized by St-g-PLLA can be one of the good candidates in the potential application as plastic or a drug delivery carrier.

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