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A novel approach to grafting polymerization of ε-caprolactone onto starch granules

Li Chen[a,b], Yushan Ni[a], Xinchao Bian[a], Xueyu Qiu[a], Xiuli Zhuang[a], Xuesi Chen[a,*], Xiabin Jing[a]

[a]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Renmin street 5625, Changchun 130022, People's Republic of China*

[b]*Department of Chemistry, Northeast Normal University, Changchun 130022, People's Republic of China*

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Abstract

A new biodegradable starch graft-copolymer, starch-*g*-poly(ε-caprolatone) (St-*g*-PCL), was synthesized in situ by the ring-opening graft-polymerization of a ε-caprolactone (CL) monomer onto starch granules in the presence of $Sn(Oct)_2$. The polymerization was carried out in three different polymerization methods: in bulk, in toluene suspension or in suspension/bulk polymerization, where a suspension/bulk process resulted in highest PCL grafting efficiency in 40 wt%. The structure of St-*g*-PCL was characterized by IR, DSC, SEM and WAXD. Both of the CL monomer and amylose corn starch were of industrial grade, without further purifications. The medium-resistance of St-*g*-PCL and the mechanical properties of the PCL composite blending with St-*g*-PCL were better than that of the PCL/starch blending composite.

Keywords: Starch; ε-Caprolactone; Ring-opening polymerization; Grafting polymerization

1. Introduction

The research and development on biodegradable polymers have been attracting more attention owing to the concerns related to the environmental pollution by non-degradable plastic wastes. 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, such as the thermoplastic starch, have some drawbacks including the poor long-term stability caused by the water absorption, the poor mechanical properties, and the process capability. In order to solve some of these problems, various physical or chemical modifications of the starch granules have been considered, including the blending (Dubois, Krishnan, & Narayan, 1999; Koenig & Huang, 1995; Kweon, Cha, Park, & Lim, 2000; Kweon & Lim, 2001; Lee, Lee, & Hong, 1997; Stenhouse et al., 1993; Vaidyia & Bhattcharya, 1994) and the chemical modification (Krishnan & Narayan, 1996; Narayan Dubois & Krishnan, 1996, 1997).

The starch graft-copolymer is representative of the modification of the starch molecule by chemical method. The starch graft-copolymers such as starch-*g*-polystyrene (St-*g*-PS) (Cho & Lee, 2002), starch-*g*-methacrylonitrile (Athawale & Lele, 2000), starch-*g*-polyvinyl alcohol (Zhai, Yoshii, Kume, & Hashim, 2002) and starch-*g*-acrylonitrile (Fanta, Felker, & Shogren, 2004), 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 properties are acceptable for applications.

Another effort in chemical modification of starch is grafting starch with biodegradable polymers (Rutot, Degee, Narayan, & Dubois, 2000), such as PCL and PLA.

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* Corresponding author. Tel.: +86 431 5262112; fax: +86 431 5685653.
E-mail address: xschen@ciac.jl.cn (X. Chen).

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The graft-copolymers such as starch-*g*-PCL and starch-*g*-PLA can be completely biodegraded by bacteria or under natural conditions and have improved 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, Kim, and Park (1999) have reported that the preparation of starch-*g*-PCL from highly purified CL monomer under careful protection with high purity N_2. In the experiment, both of the CL monomer and the starch granules in industrial grade were directly used to carry out the grafting polymerization in their suspension system in toluene or simply in bulk system. The chemical structure and physical properties of the St-*g*-PCL obtained were evaluated by modern analytical methods and discussed in details.

2. Experimental

2.1. Materials and measurements

The corn starch was from Changchun Dacheng Starch Limited Company in Jilin province, China. The water content in the starch was about 12% in weight measured by water lost at high temperature. Stannous octoate ($Sn(Oct)_2$) and ε-CL were purchased from Sigma and Aldrich Chemical Company, 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 ($\lambda = 0.154$ nm) source. 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

Following three procedures were employed for grafting polymerization of CL onto the starch granules.

2.2.1. Suspension polymerization

Sixty grams corn starch containing 12 wt% water and 120 ml toluene were added into a three-necked flask equipped with a mechanical stirrer, a drop funnel and a water separator. The reaction temperature was maintained in an oil bath. After removing the water in the starch by the azeotropic with toluene for 2 h, a 30 ml solution containing 0.1–0.3 g $Sn(Oct)_2$ in toluene was dropped into the reaction flask. The reaction mixture was stirred for another 2 h at 130 °C before 50 ml of CL was added totally into the reaction flask. The polymerization was kept for a desired time at 130 °C and the toluene in reaction flask was gradually distilled out at the end of polymerization. The PCL modified starch product was washed twice with ethanol and three times with hot water of 80 °C to remove unreacted CL and residual catalyst. The feed ratio of dry starch to CL in weight is about 53–50.

2.2.2. Bulk polymerization

The polymerization procedure consisted of following four steps: (1) azeotropic dehydration of starch with toluene for 2 h at 120 °C; (2) a toluene solution of $Sn(Oct)_2$ was dropped into a reaction flask and reacted with starch for 2 h; (3) complete removal of toluene from the system by distillation; and (4) batch addition of a weighed amount of CL monomer and bulk polymerization of CL at 130 °C for 20–62 h.

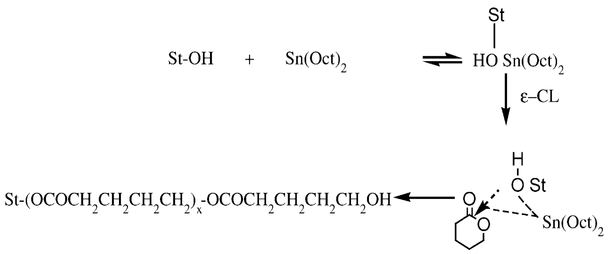
2.2.3. Suspension/bulk polymerization

The grafting polymerization of St-*g*-PCL was performed by following five steps: (1) azeotropic dehydration of the starch with toluene for 2 h at 120 °C; (2) addition of $Sn(Oct)_2$ to form living centers with hydroxyl groups on the starch surfaces; (3) drop-wise addition of all CL into reaction system within 2 h at 130 °C; (4) removal of toluene by distillation; and (5) accomplishment of bulk polymerization of CL at 130 °C for 20 h. The same amounts of starch, CL, catalyst, and toluene were used as in the case of suspension polymerization.

The product directly obtained from the above three methods was regarded as PCL modified starch (St-*g*-PCL/PCL).

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

St-*g*-PCL copolymer and PCL homopolymer might co-exist in the reaction product of PCL modified starch (St-*g*-PCL/PCL). They were separated by toluene extraction. Two grams of the PCL 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 filtrates were collected together, concentrated to proper extent, precipitated into *n*-heptane, and dried in vacuum. IR, WAXD, DSC and SEM considered the solids after toluene extraction as St-*g*-PCL for further characterization.



Scheme 1. The $Sn(Oct)_2$ initiated polymerization mechanism of ε-CL with the starch.

2.4. Monomer conversion and grafting efficiency

The monomer conversion (%) is calculated as follows

$$\text{Monomer conversion} = \frac{m_2 - m_1}{m} \tag{1}$$

Where m_1 is weight of dried starch, m_2 is weight of the PCL modified starch, and m is the weight of CL monomer in the feed.

The grafting efficiency is defined as

$$\text{Grafting efficiency} = \frac{\text{grafted PCL wt\%}}{\text{grafted PCL wt\%} + \text{homo-PCL wt\%}} \tag{2}$$

2.5. Medium-resistance measurements

The PCL modified starch (St-*g*-PCL/PCL) was pressed into thin films of 50–100 μm in thickness. The films were immerged 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. Suspension and bulk polymerization

The polymerization procedure is depicted in Scheme 1. After azeotropic dehydration of the starch with toluene, the hydroxyl groups on the surface of the starch granules are reacted with $Sn(Oct)_2$ to form a living center Sn–O, which initiated the ring-opening polymerization of ε-caprolactone (CL) by a coordination–insertion mechanism. The polymerization strategy is based on fixation of Sn–O functions onto the starch surface by in situ reaction of $Sn(Oct)_2$ with the hydroxyl groups of starch. Indeed, residual water of the starch and other impurity in the reaction system should have a strong influence on the ability to generate the active species at the starch surface. In fact, it is well known that $Sn(Oct)_2$ can readily react with water or other impurity molecules to form the active derivatives. This promotes the lactones polymerization directly with formation of non-grafted polyester chains as PCL homopolymer.

Table 1 reports some results of the reaction and polymerization time on the grafting polymerization under three different experimental conditions. The grafting products of starch with ε-CL could be separated into toluene-insoluble and soluble parts (Narayan et al., 1996, 1997). The former is considered mainly as graft-copolymer (St-*g*-PCL) and the latter as homopolymer (homo-PCL). As shown in Table 1, under the reaction conditions, the monomer conversion is usually 98–99% and the homo-PCL takes 30–47 wt% depending on the reaction process. It means that after azeotropic dehydration, there still exists free water or other undesired species in the system, which initiates the homo-polymerization of ε-CL. The polymerization in bulk is more effective than that in toluene dispersion (lower grafting efficiency even after longer polymerization time, S-2 and S-3) and the suspension/bulk process is the best among the three. The highest grafting efficiency can reach as high as 40 wt% as shown in S-7. Accordingly, the grafting efficiency data show the same order.

Table 1
The effect of reaction conditions on the ε-caprolactone grafting polymerization on the surface of starch granules

Sample	Reaction process	Reaction time[a] (h)	Polymerization time[b] (h)	Monomer conversion (%)	Extraction (wt%)		Grafting efficiency (%)
					Insoluble	Soluble	
S-1	Suspension[c]	2	70	99.0	54	46	8
S-2	Suspension[c]	2	133	98.0	53	47	6
S-3	Bulk[c]	2	48	98.0	59	41	18
S-4	Bulk[c]	2	62	99.5	57	43	14
S-5	Suspension/bulk[d]	6	20	98.0	63	37	26
S-6	Suspension/bulk[d]	16	20	99.5	68	32	36
S-7	Suspension/bulk[d]	24	24	99.0	70	30	40

[a] The time used for reaction of starch with $Sn(Oct)_2$.
[b] The time used for polymerization at 130 °C.
[c] Starch/CL = 50/50 (wt/wt); $Sn(Oct)_2$ content: 0.3 wt% of starch and CL.
[d] Starch/CL = 50/50 (wt/wt); $Sn(Oct)_2$ content: 0.1 wt% of starch and CL.

Table 2
The effect of catalyst content on the grafting polymerization

Sample	Catalyst (wt%)	Polymerization time (h)	Monomer conversion (%)	Extraction (wt%)		Grafting efficiency (%)
				Insoluble	Soluble	
S-8	0.3	48	99.0	59	41	18
S-9	0.3	162	99.2	57	43	14
S-10	0.2	48	99.6	62	38	24
S-11	0.2	90	98.6	57	43	14
S-12	0.1	48	99.5	68	32	36

Bulk reaction process; starch/CL = 50/50 wt%; the time used for reaction of starch with $Sn(Oct)_2$ is 2 h and the reaction temperature and the polymerization temperature are both at 130 °C.

As shown in Table 1, for the suspension process and the bulk process (S-2 and S-4), the longer polymerization reaction time always leads to lower grafting efficiency, whereas for the suspension/bulk process, the longer reaction time between starch and $Sn(Oct)_2$ leads to higher St-*g*-PCL content as shown in S-5, S-6 and S-7. This can be attributed to the fact that leaving more time for $Sn(Oct)_2$ to react with the hydroxyl groups available at the starch surface. Therefore, more active sites are formed at the surface allowing the fixation of more PCL chains leading to a higher grafting efficiency. The results from longer polymerization time imply that transesterification or other side reactions occur during the polymerization, especially at the later stage, resulting in the formations of the PCL homopolymer. And the transesterification is critical for a successful grafting to ensure the reaction between the starch and $Sn(Oct)_2$. On the other hand, the highest grafting efficiency also can be obtained due to the drop-wise addition of CL only for the suspension/bulk procedure, while in the other two there was batch addition.

The effect of catalyst content on the grafting polymerization is shown in Table 2. The samples in S-8, S-10 and S-12 are prepared by bulk process each in 48 h but with different catalyst concentrations. Among them, S-12, the lowest catalyst content, has the highest copolymer content and grafting efficiency, being 68 wt% and 36%, respectively. It seems that the excess catalyst is propitious to the homopolymerization of CL. At the same time, Table 2 indicates that the longer reaction time over 48 h leads to lower grafting copolymer yield and the grafting efficiency for the transesterification to form the homopolymer PCL.

3.2. Characterization of St-g-PCL

Fig. 1 shows the spectra of pure starch (a) as well as the polymerization products (b, c and d). Comparing the IR spectra of the crude product (b) and that after the first (c) and the second (d) extraction with toluene in Fig. 1, it can be seen that the main difference between spectra (a) and (b) is at 1730 cm^{-1}, the characteristic of the ester group of PCL. The peak intensity of the hydroxyl groups in starch (3400 cm^{-1}) is reduced in the spectrum (b). The spectra (c) and (d) look similar, confirming that the homo-PCL was essentially removed from the St-*g*-PCL copolymer after two extractions with toluene. The characteristic peaks at 1730 and 3400 cm^{-1} in the spectra (c) and (d) illuminate that the starch has initiated the polymerization of the ε-CL and the surface of the starch has been grafted by CL to form St-*g*-PCL.

The typical DSC traces for starch, St-*g*-PCL, and PCL ($M_n = 70{,}000$) are collected in Fig. 2. The PCL homopolymer has a T_m at 61.0 °C and a T_c at 31.7 °C, while St-*g*-PCL exhibits a T_m at 54.4 °C and a T_c at 35.4 °C. This lower T_m and higher T_c indicate that the St-*g*-PCL is really a graft-copolymer, not a blend of starch and PCL. In the St-*g*-PCL, the PCL graft is still crystalline, but its crystalline parameters have changed much due to the restriction from the starch surfaces and the grafting efficiency of PCL.

The crystallizability of the pure St-*g*-PCL copolymer can be also confirmed on the basis of WAXD patterns shown in Fig. 3. The PCL ($M_n = 70{,}000$, in Fig. 3c) shows two main

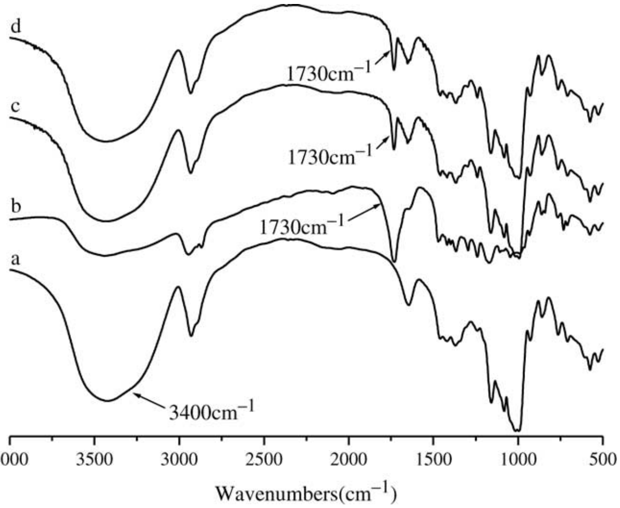


Fig. 1. The IR spectra of the starch and St-*g*-PCL, (a) starch; (b) St-*g*-PCL/PCL (the crude product S-7 from the Table 1), before extraction in toluene; (c) St-*g*-PCL, S-7 after first extraction; (d) St-*g*-PCL, S-7 after second extraction.

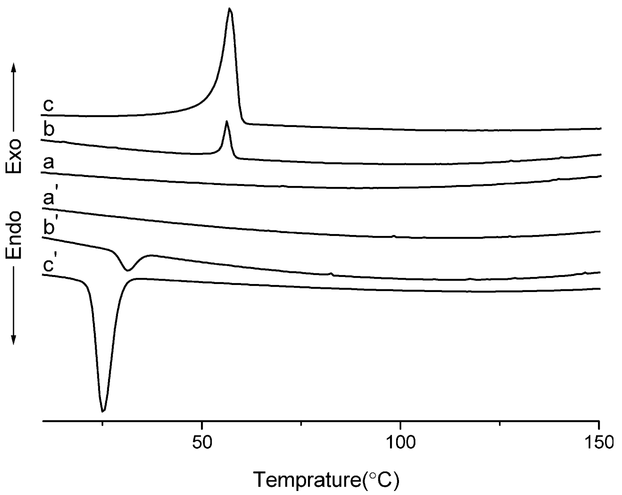


Fig. 2. The DSC curves of starch (a, a′), St-*g*-PCL (S-7 after toluene extraction) (b, b′) and PCL homopolymer (c, c′).

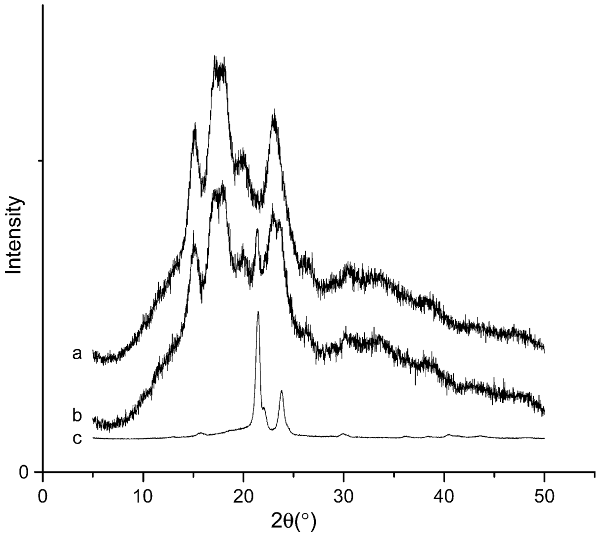


Fig. 3. The WAXD of starch (a), St-*g*-PCL copolymer (b) (S-7 from the Table 1 after toluene extraction) and homo-PCL (c).

diffraction peaks at $2\theta = 21.4$ and 23.8°, respectively, whereas the starch show peaks at $2\theta = 15.2$, 17.1, 23.1° (Fig. 3a). In Fig. 3b, in addition to the peaks associated with the starch, there appear narrow peaks at 21.4 and 23.6° attributed to PCL grafted on the starch surface in comparison with Fig. 3a, due to the crystallization of the grafted PCL. Therefore, the WAXD results show again the exact structure of the graft-copolymer St-*g*-PCL, not the blend of PCL with starch.

The Scanning Electron Microscopy images of the starch (a) and St-*g*-PCL (b) copolymer attest to the very good interfacial adhesion between the starch and the PCL chains (Fig. 4). The surfaces of the starch granules look smooth (Fig. 4a), whereas the surfaces of St-*g*-PCL (Fig. 4b) exhibit roughness and polygonal appearance, and some connections between granules could be also seen clearly. Therefore, it obviously showed that the PCL was located on the surfaces of the starch granules, which will be helpful to the improvement of the mechanical properties of the modified composites.

3.3. Mechanical properties of St-g-PCL

Although a lot of papers on St-*g*-PCL have been published, their mechanical properties have seldom been reported probably because the mechanical properties of St-grafted-PCL are not excellent enough to use as material alone. However, the grafted copolymers can be used as plasticizer when blending the starch with PCL or other polyesters. PCL/starch compositions are blended by an internal mixer (Haake) at 130 °C for 15 min. Then they are moulded into 2–3 mm thick sheets by hot-pressing at 100 °C. As well known, PCL is quite a ductile polymer and is able to undergo large deformations. Unfortunately, it possesses a relatively low elastic modulus making it useless for many applications where a high rigidity is required. The addition of starch fillers into PCL contributes to improve its modulus, but reduce significantly all the other mechanical properties. Such behavior results from the poor filler/matrix interfacial

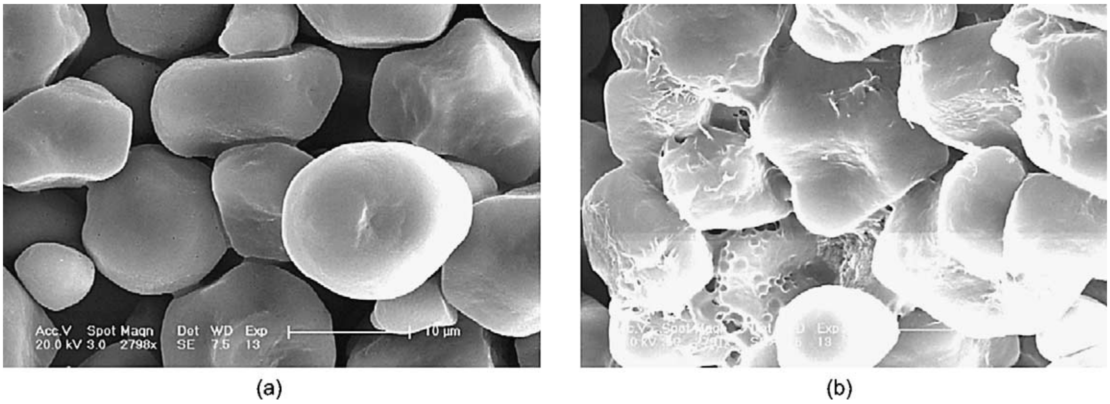


Fig. 4. SEM images of starch (a) and St-*g*-PCL (b) (S-7 from the Table 1 after toluene extraction).

Table 3
The mechanical properties of St-*g*-PCL, PCL/starch blend and St-*g*-PCL/PCL composites

Composition	σ_b (MPa)	ε_b (%)	Young's modulus (MPa)	σ_{v} (MPa)
S-6[a]	8.4	298	390	6.5
PCL/Starch (50:50)	9.3	315	280	8.0
PCL/Starch/S-2[a,b]	21.7	591	310	10.5
PCL (M_n = 50,000)	48.1	1370	210	16.0

[a] St-*g*-PCL in S-6; S-2 are from Table 1.

[b] PCL/Starch (50:50) blends added with 5 wt% of the St-*g*-PCL (S-2 from the Table 1).

adhesion. When the St-*g*-PCL copolymer is first melting blended with the PCL/starch, St-*g*-PCL acts as an efficient compatibilizing agent. This means that St-*g*-PCL does not only promote a better dispersion in the PCL/starch matrix and a lower interfacial tension, but also reinforce the adhesion between the filler and the matrix. From Table 3, it can be seen that all tensile parameters of PCL/starch/St-*g*-PCL are improved obviously in comparison with the blend of PCL/starch so that a stiffer and tougher composite material is prepared by the 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*-PCL/PCL (starch/PCL = 53/50 see the experimental) 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*-PCL/PCL and the weight-loss is due to the hydrolysis of the starch catalyzed by the alkali solution. As shown in Table 4, the stability of the products in all three media decreases with the increasing starch content, especially in the alkaline medium. Compared to starch/PCL blend (50/50), the grafting products showed the improved resistance to the three media. Generally speaking, the grafting products showed better resistance to water and the acid solution than to the alkali solution. Owing to the improved water resistance, the St-*g*-PCL is expected to find the industrial use because it does not become swollen or sticky when contacted with water or moisture.

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

St-*g*-PCL/PCL	Grafting efficiency (%)	Weight change (wt %)		
		In 0.5 mol/L HCl	In 0.5 mol/L NaOH	In H_2O
S-6[a]	36	+2.5	−1.2	+4.0
S-5[a]	26	+3.8	−1.6	+4.5
S-3[a]	18	+11.1	Broken into pieces	+10.6
S-1[a]	8	+12.4	Broken into pieces	+11.3
Blend	PCL/starch = 50:50	+18.3	−44.3	+19.5

[a] See from the Table 1 without extraction in toluene. The experiments of medium-resistance were carried out at room temperature.

4. Conclusion

In conclusion, St-*g*-PCL copolymers could be readily prepared by three different controlled synthesis methods. After the azeotropic dehydration of the starch with toluene, the hydroxyl groups of the starch were reacted with $Sn(Oct)_2$ to form a living center Sn–O, which initiated the ring-opening polymerization of ε-caprolactone (CL) by a coordination–insertion mechanism. Homo-polymerization of CL simultaneously occurred during the grafting polymerization, and thus the grafting products were composed of St-*g*-PCL and homo-PCL. The grafting efficiency and the ratio of St-*g*-PCL to homo-PCL were dependent on reaction process. A high grafting efficiency could be achieved by a suspension/bulk polymerization process. Their hydrophobic character of St-*g*-PCL had prompted us to incorporate them as compatibilizers in PCL/granular corn starch compositions. These copolymers had proven efficiently to improve the interfacial adhesion and the mechanical properties of the compatible composites. The St-*g*-PCL copolymers had good water- and acid-resistance properties. The St-*g*-PCL copolymers and their composites can be the good candidates in the potential application as plastics or drug delivery carriers.

Acknowledgements

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