

Thermoforming Starch-graft-Polycaprolactone Biocomposites Via One-Pot Microwave Assisted Ring Opening Polymerization

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ABSTRACT: A thermoformable starch-graft-polycaprolactone biocomposite was prepared by initiating ring-open polymerization of caprolactone monomer onto starch under microwave irradiation. In this case, the thermoplastic and hydrophobic modification of starch could be realized by one-pot grafting PCL, where the grafted PCL chains acted as the “plasticizing” tails of thermoforming and as the hydrophobic species of water-resistance. The resultant biocomposites were injection-molded as the sheets and their structure and properties were investigated by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, differential scanning calorimetry, dynamic mechanical analysis, contact angle measurement, and tensile testing. In this case, the grafted

PCL chains entangled each other, and hence contributed to the strength and elongation of biocomposites. This work provided a simple strategy of one-pot thermoplastic and hydrophobic modification of starch, and may be applied in a continuous process of modification, compounding, and molding. Meanwhile, the resultant biocomposites containing starch are believed to have a great potential application as an environment-friendly and/or biomedical material. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2973–2979, 2009

Key words: starch; graft; polycaprolactone; biocomposite; thermoforming; water-resistance; biodegradable; graft copolymers

INTRODUCTION

Starch is a versatile renewable biopolymer with immense potential, low cost, and abundant availability, that is independent of fossil sources, for use in nonfood industries.^{1–3} The use of starch in the plastics industry has received considerable attention as a

biodegradable thermoplastic polymer, because it would reduce dependence on synthetic polymers made from imported oil and offer socioeconomic benefits by generating rural jobs and a nonfood agricultural-based economy. However, starch is not truly thermoplastic,^{4,5} but it can be converted into a continuous polymeric entangled phase by mixing with enough water or nonaqueous plasticizer, such as general polyols (glycerol),^{6–12} sorbitol,¹³ xylitol,⁵ maltitol,⁵ poly(ethylene glycol) with various molecular weight,^{5,14} and polypropylene glycol,⁵ and urea,^{12,14} sodium lactate,¹⁴ dimethyl sulfoxide,¹⁵ and low molecular weight sugars.¹⁶ The so-called thermoplastic starch resulting from plasticizing could be extruded or molded as an object;^{17–20} however, the hydrophilic nature of thermoplastic starch makes it susceptible to moisture attack and resultant changes in dimensional stability and mechanical properties. In addition, the crystallization of the mobile starch chains, known as retrogradation, leads to an undesired change in thermomechanical properties. Although blending destructured starch with synthetic^{20–24} or natural polymers^{25–28} is an effective way to remedy the drawback of thermoplastic starch

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for the development of new and inexpensive biodegradable materials, it is restricted due to the immiscibility between starch and most synthetic polymers at the molecular level. Grafting of synthetic polymers on starch is known to improve their miscibility under the compulsion of covalent bonding. In addition, the grafted polymer chains may play a key role in plasticization and hydrophobicity, and hence provide thermoformability and water-resistance.

In this work, a kind of thermoformable composite containing starch was prepared via one-pot microwave assisted ring-open polymerization of grafting polycaprolactone (PCL) onto starch. Different from the previous reports,^{29–33} this work applied a fast and “green” method of microwave assistance. Moreover, the resultant starch-graft-polycaprolactone (St-g-PCL) composites were directly injection molded as the sheets without any plasticizer. The structure and properties of the molded sheets were investigated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), contact angle measurement, and tensile testing.

EXPERIMENTAL

Materials

Pea starch (St) composed of 35% amylose and 65% amylopectin, and with average particle size of about 30 μm , was supplied by Nutri-Pea, Canada (Portage la Prairie, Canada) and used as received. ϵ -Caprolactone (CL) monomer (99%) was purchased from Alfa Aesar and used as received. Tin(II) octoate ($\text{Sn}(\text{Oct})_2$) and other reagents of analytical grade were purchased from the Shanghai Sinopharm (Shanghai, China), and used as received.

One-pot grafting PCL on pea starch

The mixtures of St powder and CL monomer with the given weight ratios of 1 : 40, 1 : 50, and 1 : 60 were placed into an ampoule, respectively. Subsequently, the catalyst of $\text{Sn}(\text{Oct})_2$ was added, whose weight was 0.5% of the CL weight. The mixture was homogenized by using a Lab Dancer (IKA, Germany), and then vacuum-exhausted for 30 min. Thereafter, the ampoule containing reactant was conditioned under a microwave irradiation of 255 W power for 3 min. At last, the crude product was dissolved by CH_2Cl_2 followed by precipitating with methanol. This process of purification was carried out many times until the monomer, homopolymer, and residual catalyst were removed. At this stage, the removal of homopolymer is a key issue. Considering that the St-g-PCL is more easily precipitated

than homopolymer, due to the poor solubility of the St component in CH_2Cl_2 and a greater PCL fraction in the St-g-PCL, the classification method in every precipitation process was used to collect the initial precipitate.³⁴ FTIR was used to trace every precipitate until the relative intensity of $-\text{C}=\text{O}$ peak assigned to PCL was almost invariable. The purified products were vacuum-dried, and coded as St-g-PCL(I) (1 : 60), St-g-PCL(II) (1 : 50), and St-g-PCL(III) (1 : 40), respectively, according to the feeding ratio of St vs. CL listed in bracket.

Injection molding of St-g-PCL

The inject-molding of the resultant St-g-PCL composites was carried out on a micro-injection molding machine (Thermo Electron, USA). The temperature, time and pressure of injection were 65°C, 20 s and 0.55 MPa, respectively, while the mold temperature was 40°C.

Characterization

Elemental analysis of the St-g-PCL and St powders was measured on Vario EL III elemental analyzer (Elementar, Germany).

FTIR spectra of the St and St-g-PCL powders as well as all the sheets were recorded on an FTIR 5700 spectrometer (Nicolet, USA). The powders were measured by using a KBr-pellet method in the range of 4000–400 cm^{-1} , and the sheets were scanned using Smart OMNT reflect accessories in the range of 4000–700 cm^{-1} .

XRD measurements were performed on a D/max-2500 X-ray diffractometer (Rigaku Denki, Japan) with $\text{Cu K}\alpha_1$ radiation ($\lambda = 0.154 \text{ nm}$) in a range of $2\theta = 3\text{--}60^\circ$ using a fixed time mode with a step interval of 0.02°.

SEM observation was carried out on an S-3000N scanning electron microscope (Hitachi, Japan). The sheets were frozen in liquid nitrogen and then snapped immediately. The fractured surfaces of the sheets were sputtered with gold, and then observed and photographed.

DSC was carried out on a DSC-Q200 instrument (TA Instruments, USA) under nitrogen atmosphere at a heating or cooling rate of 20°C min^{-1} . The sheets were scanned in the range of -90 to 200°C after a pretreatment (heating from 20 to 100°C and then cooling down to -90°C) of eliminating thermal history.

DMA was carried out on a DMA 242C dynamic mechanical analyzer (Netzsch, Germany) at a frequency of 1 Hz. The temperature ranged from -150 to 100°C with a heating rate of 3°C min^{-1} . Measurements were performed using a dual cantilever

device and the size of the testing samples was 40 mm × 10 mm.

Contact angle measurements of water on the St-g-PCL surface were performed at room temperature using a DSA100 contact angle analyser (Kruss, Germany).

The tensile strength (σ_b), elongation at break (ϵ_b), and Young's modulus (E) of the St-g-PCL sheets were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine, Shenzhen, China) with a tensile rate of 5 mm min⁻¹ according to ISO527-3:1995(E). The tested samples were kept in the humidity of 35% for 7 days before measurement. An average value of five replicates of each sample was taken.

RESULTS AND DISCUSSION

Compositions of the St-g-PCL copolymers

FTIR spectra of the St-g-PCL(III) and St powders are depicted in Figure 1, where St-g-PCL(III) is used as the representative of three graft copolymers. Compared with the spectrum of St, the prominent change after the grafting process was the appearance of one distinct peak located at 1730 cm⁻¹ assigned to the ester-carbonyl group of grafted PCL chains. In virtue of the confirmation of removing homopolymer by experiment, it suggested that the PCL and St were linked together to produce a new kind of brush-like graft copolymer. Furthermore, the mean contents of C element in St-g-PCLs and St were determined by elemental analysis to be 55.76% ± 0.12% ($C_{\text{St-g-PCL(I)}}$), 55.91% ± 0.07% ($C_{\text{St-g-PCL(II)}}$), 56.59% ± 0.05% ($C_{\text{St-g-PCL(III)}}$), and 39.64% ± 0.23% (C_{St}), respectively; while the content of C element in PCL was fixed as the theoretical value of 63.16% (C_{PCL}). Consequently, the

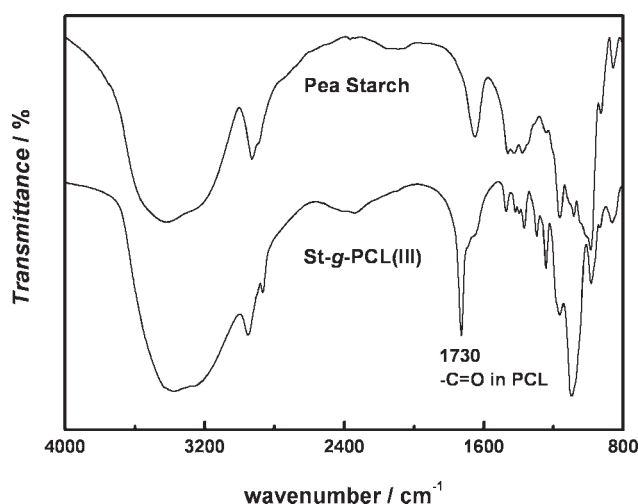


Figure 1 FTIR spectra of the St and St-g-PCL(III) powders, where the St-g-PCL(III) is used as the representative of grafted starch.

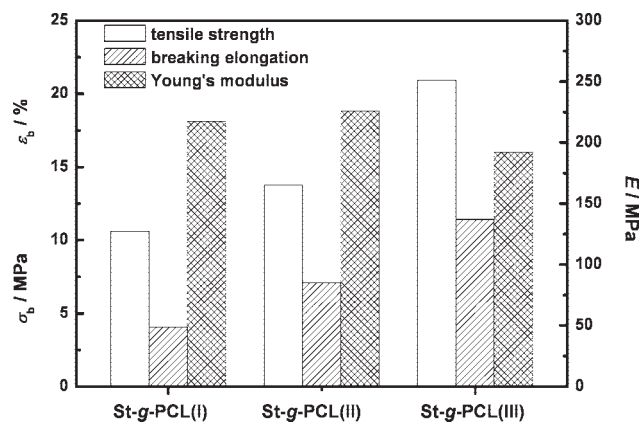


Figure 2 Mechanical properties of the thermoforming St-g-PCL sheets containing various PCL contents.

mean content of grafted PCL chains in St-g-PCL was calculated by the following equation:

$$xC_{\text{PCL}} + (1 - x)C_{\text{St}} = C_{\text{St-g-PCL}}$$

where x is the weight percentage of grafted PCL chains in St-g-PCL. The results showed that the grafted PCL contents in St-g-PCLs were 68.54 wt % of St-g-PCL(I), 69.18 wt % of St-g-PCL(II), 72.07 wt % of St-g-PCL(III).

Mechanical properties of the St-g-PCL sheets

Figure 2 shows the mechanical properties of the thermoforming St-g-PCL sheets, including tensile strength (σ_b), Young's modulus (E) and elongation at break (ϵ_b). In spite of the fact that the PCL contents of three St-g-PCLs were analogous with each other, they showed an obvious influence on the mechanical parameters. With an increase of the PCL content in St-g-PCL, the tensile strength and elongation simultaneously increased. However, the Young's modulus firstly increased followed by a slight decrease with an increase of the PCL content in St-g-PCL. The St-g-PCL(III) with the highest PCL content showed the maximum tensile strength of 20.9 MPa and elongation of 11.4%. Based on the same initiating probability of —OH on starch, it can be hypothesized that the St-g-PCL with higher PCL content might have longer PCL tails attached onto the main chain of starch. Furthermore, longer grafted PCL chains contributed to more entanglements, and hence produced higher strength and elongation during tensile testing. At this time, the relatively rigid starch chains acted as the concentrated point of stress.

Hydrophobicity of the St-g-PCL sheet

As is well-known, starch is a hydrophilic polymer, and enhancing water resistance is a key issue for

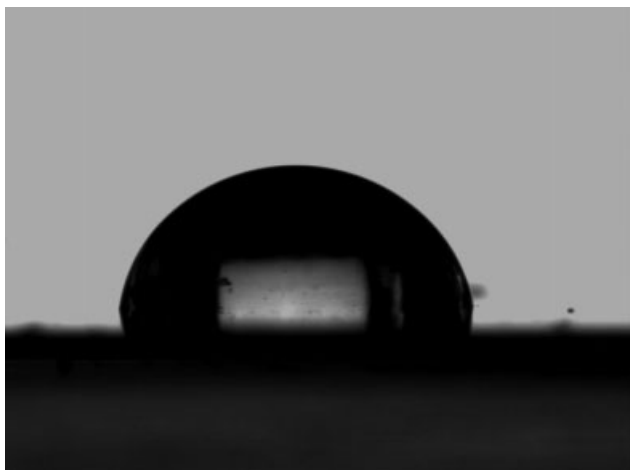


Figure 3 Photograph of a water drop on the surface of the thermoforming St-g-PCL (III) sheet as a typical representative.

developing starch-based plastics. The contact angles of water (θ_{water}) on the surface of three St-g-PCLs were determined as 64.9° (St-g-PCL(I)), 65.3° (St-g-PCL(II)), and 65.8° (St-g-PCL(III)), and Figure 3 shows the photograph of one drop of water on the surface of the St-g-PCL(III) sheet. The improvement in water-resistance for the plastics containing starch, in this case, was attributed to the grafted PCL chains. Furthermore, although the weak difference of the PCL content in three St-g-PCLs resulted in an obvious variance of mechanical properties, it had almost no effect on the θ_{water} values and showed analogous hydrophobicity.

Structure of the St-g-PCL sheets

XRD patterns of the thermoforming St-g-PCL sheets, as well as neat St powder, are depicted in Figure 4. The neat St showed a semi-crystalline character with three diffuse diffractions located at 15.1° , 17.1° , and 22.8° of 2θ . However, these characteristic diffractions of St were submerged into the strong diffraction assigned to the grafted PCL chains of St-g-PCL. All the St-g-PCLs showed analogous diffraction patterns, i.e. the two predominant crystalline peaks located at 21.8° and 24.1° of 2θ . This suggested that the PCL chains in St-g-PCL mainly existed in the crystalline state.

In general, the vibration of groups in FTIR spectrum of a semi-crystalline polymer should be composed of three components arising from its crystalline and amorphous phases as well as hydrogen bonding. As a result, the stretching vibration of —C=O located at ca. 1723 cm^{-1} for the grafted PCL chains was divided into three peaks, which were assigned to the states of crystalline, amorphous and hydrogen bonding by curve-fitting (seen in Fig. 5).

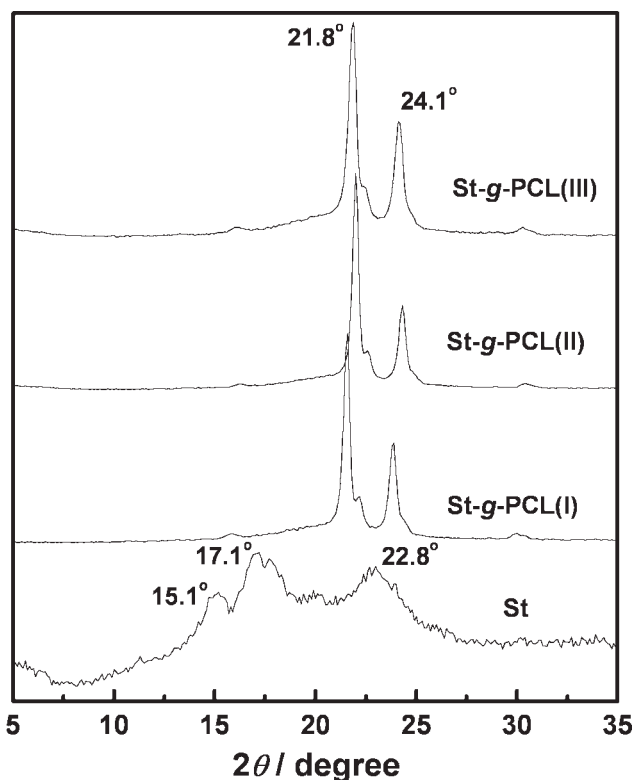


Figure 4 XRD patterns of the thermoforming St-g-PCL sheets containing various PCL contents as well as the neat St powder as reference.

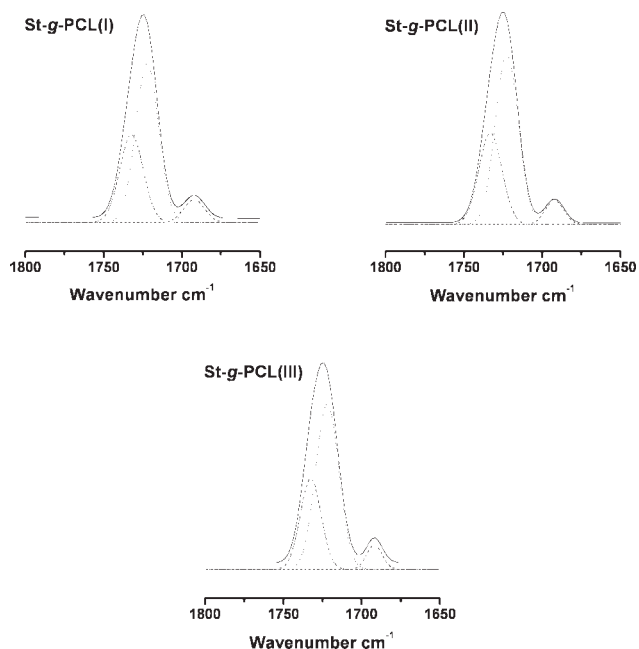


Figure 5 Experimental and curve-fitted FTIR spectra of the thermoforming St-g-PCL sheets containing various PCL content in the range of $1650\text{--}1800\text{ cm}^{-1}$. (— experimental curve; --- —C=O in amorphous region; —C=O in crystalline domain; ---- hydrogen-bonded —C=O).

TABLE I
Location and Fraction of Curve-Fitting Peaks for the —C=O Absorption in the FTIR Spectra of the Thermoforming St-g-PCL sheets Containing Various PCL contents

Sample	FTIR data					
	Peak I		Peak II		Peak III	
	Location/ cm^{-1}	$F_{\text{amorp.}}/\%$	Location/ cm^{-1}	$F_{\text{crys.}}/\%$	Location/ cm^{-1}	$F_{\text{H-bond}}/\%$
St-g-PCL(I)	1732.2	33.25	1722.2	59.04	1692.1	7.71
St-g-PCL(II)	1733.1	32.67	1722.5	60.45	1692.1	6.88
St-g-PCL(III)	1732.5	30.94	1721.9	62.73	1691.9	6.33

Peak I: —C=O in amorphous region; Peak II: —C=O in crystalline domain; Peak III: hydrogen-bonded —C=O .

The fraction and location of three peaks are summarized in Table I, where the fraction of crystalline peak is proportional to crystalline degree (χ_c). With an increase of the PCL content in St-g-PCLs, the fraction of crystalline peaks increased while the fractions of amorphous peaks and hydrogen-bonding peaks decreased. Same as the above hypothesis that higher PCL content corresponded to longer grafted PCL

chains, higher PCL content in St-g-PCL might be relevant to longer PCL tails attached onto the main chain of starch. As a result, longer PCL chains facilitated forming a higher degree of crystalline. Meanwhile, more entanglements and ordered arrangement of PCL chains inhibited the formation of hydrogen bonds when the PCL content was higher, shown as the decreasing fraction of hydrogen bonding.

Furthermore, the St-g-PCL sheets had a coarse fractured surface, and the SEM image of St-g-PCL(I), and St-g-PCL(III) are shown in Figure 6. This kind of characteristic fractured surface indicated that the grafted PCL chains entangled each other. When the PCL content was higher, the fractured stripes were denser. This indicated that more entanglements of grafted PCL chains existed.

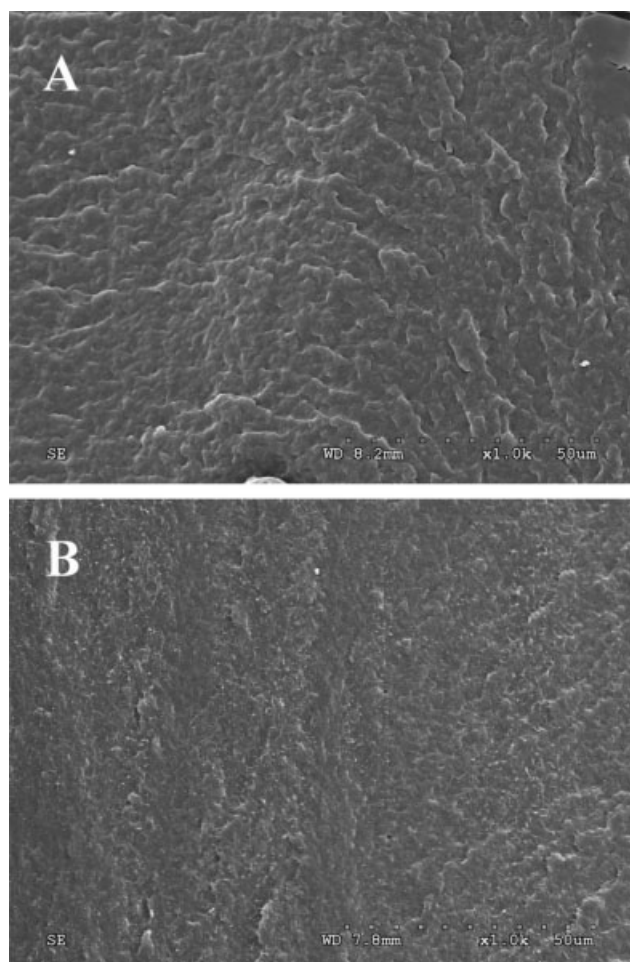


Figure 6 SEM image of fractured surface for the thermoforming St-g-PCL(I) (A) and St-g-PCL(III) (B) sheets.

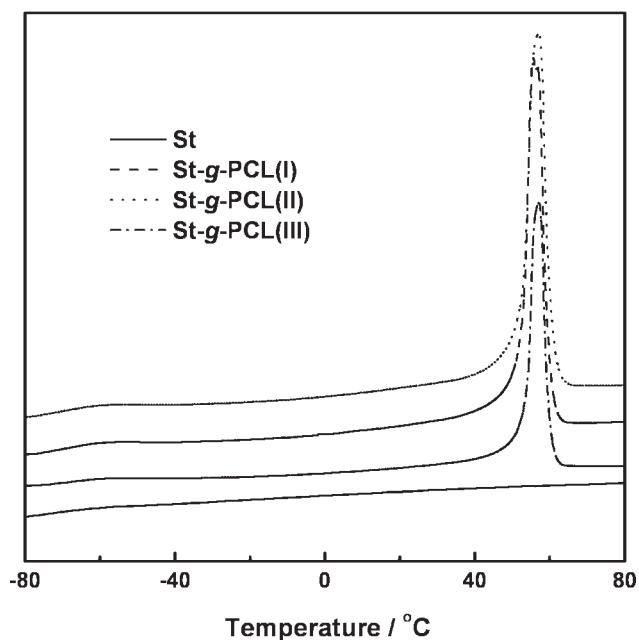


Figure 7 DSC thermograms of the thermoforming St-g-PCL sheets containing various PCL contents and the neat St powder as reference.

Thermal properties of the St-g-PCL sheets

Figure 7 shows the DSC thermograms of the St-g-PCL sheets and neat St powder. The melting temperature (T_m) and heat enthalpy (ΔH_m) assigned to the PCL component are summarized in Table II. The occurrence of T_m and ΔH_m verified the presence of the crystalline fraction of grafted PCL chains. This was consistent with the XRD and FTIR results. DMA is a powerful technique to reflect the mobility of segment through α -relaxation at the molecular-level, for which the specific heat increment of glass transition measured from DSC is generally ill-defined. As a result, the glass transition of PCL component, which was absent in DSC thermograms, was shown as α -relaxation determined by DMA. Table II also summarizes the α -relaxation temperature ($T_{\alpha, \max}$) and the height of loss-peak ($H_{\text{loss-peak}}$) of all the St-g-PCL composites from the $\tan \delta$ - T curves (Fig. 8). FTIR results showed that the crystalline fraction of grafted PCL chains increased with an increase of the PCL content in St-g-PCL. As a result, the increasing crystalline domains inhibited the motion of PCL segments in the amorphous region, resulting in the shift of the $T_{\alpha, \max}$ s up to high temperature with an increase of the PCL content.

CONCLUSIONS

The thermoformable biocomposites of St-g-PCL were synthesized via microwave assisted ring-open polymerization, and then injection molded as the sheets by virtue of long "plasticizing" PCL tails. Except for the contribution to thermoformability, the grafted also PCL chains determined the mechanical properties and water-resistance of biocomposites. With an increase of the PCL content in St-g-PCL, the strength and elongation were simultaneously increased. This was attributed to increasing entanglements of longer PCL chains. Furthermore, the grafted PCL component improved the water-resistance of the biocomposites containing hydrophilic starch. Such new biocomposites, derived from one-pot thermoplastic and hydrophobic modification of starch, are believed

TABLE II
DSC and DMA Data of the Thermoforming St-g-PCL Sheets Containing Various PCL Contents

Sample	DSC data		DMA data	
	T_m (°C)	ΔH_m (J g ⁻¹)	$T_{\alpha, \max}$ (°C)	$H_{\text{loss-peak}}$
St-g-PCL(I)	55.6	69.95	-55.3	0.13
St-g-PCL(II)	57.1	69.61	-51.3	0.15
St-g-PCL(III)	57.2	65.00	-48.5	0.12
St	—	—	n.d.	n.d.

n.d., no being determined.

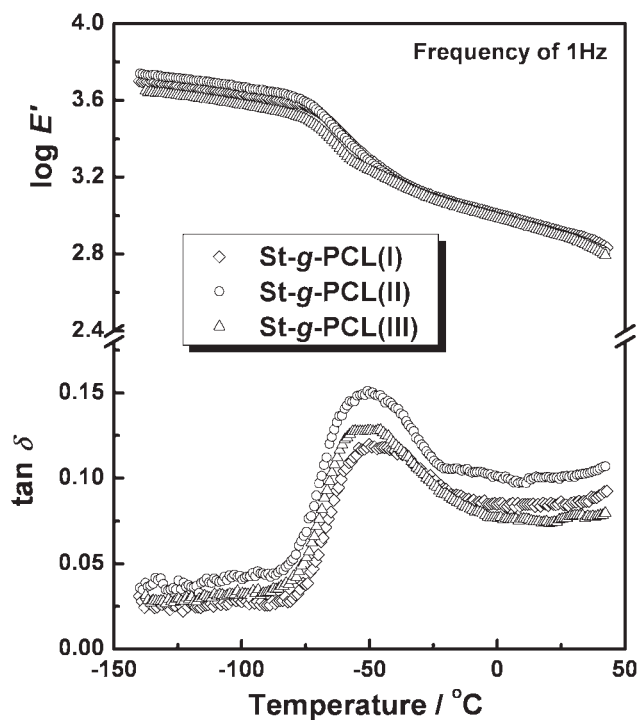


Figure 8 Log E' and $\tan \delta$ as functions of temperature for the thermoforming St-g-PCL sheets containing various PCL contents.

to have great potential applications. Furthermore, this facile one-pot grafting method could be applied in a continuous process of modification, compounding, and molding.

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