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Preparation and characterization of biodegradable PLA polymeric blends

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Abstract

The purpose of this study was to fine-tune the mechanical properties of high molecular-weight poly-L-lactic acid (PLLA), especially to increase its toughness without sacrificing too much of its original strength. Besides of its long degradation time, PLLA is usually hard and brittle, which hinders its usage in medical applications, i.e., orthopedic and dental surgery. Some modifications, such as the addition of plasticizers or surfactants/compatibilizers, are usually required to improve its original properties. PDLLA can degrade quickly due to its amorphous structure, thus shortening the degradation time of PLLA/PDLLA blends. Blends of biodegradable poly-L-lactic acid (PLLA) and poly-DL-lactic acid (PDLLA) or polycaprolactone (PCL), in addition to a third component, the surfactant—a copolymer of ethylene oxide and propylene oxide, were prepared by blending these three polymers at various ratios using dichloromethane as a solvent. The weight percentages of PLLA/PDLLA (or PCL) blends were 100%/0%, 80%/20%, 60%/40%, 50%/50%, 40%/60%, 20%/80% and 0%/100%, respectively. Physical properties such as the crystalline melting point, glass transition point (T_g), phase behavior, degradation behavior, and other mechanical properties were characterized by thermogravimetric analysis, differential scanning calorimetry (DSC), infrared spectroscopy, gel permeation chromatography, and dynamic mechanical analysis (DMA). DSC data indicate that PLLA/PDLLA blends without the surfactant had two T_g's. With the addition of the surfactant, there was a linear shift of the single T_g as a function of composition, with lower percentages of PLLA producing lower glass transition temperatures indicating that better miscibility had been achieved. DMA data show that the 40/60 PLLA/PDLLA blends without the surfactant had high elastic modulus and elongation, and similar results were observed after adding 2% surfactant into the blends. The 50/50 PLLA/PDLLA/2% surfactant blend had the highest elastic modulus, yield strength, and break strength compared with other ratios of PLLA/PDLLA/2% surfactant blends. The elongation at break of 50/50 PLLA/PDLLA was similar to that of PLLA. Again, the elongation at break of 50/50 PLLA/PDLLA/2% surfactant was almost 1.2–1.9 times higher than that of 50/50 PLLA/PDLLA and PLLA. Elongation of PLLA increased with the addition of PCL, but the strength decreased at the same time. In conclusions, adding PDLLA and surfactant to PLLA via solution-blending may be an effective way to make PLLA tougher and more suitable to use in orthopedic or dental applications.
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1. Introduction

Research in biodegradable and bioresorbable polymers has received increased attention in recent years because of their wide applications in environmental and clinical medicine (e.g., dental/orthopedic surgery). The most popular and important biodegradable polymers are aliphatic polyesters, such as polylactic acid (PLA), polycaprolactone (PCL), polyethylene oxide (PEO), poly(3-hydroxybutyrate) (PHB), and polyglycolic acid (PGA). However, each of these has some shortcomings which restrict its applications. Blending techniques are an extremely promising approach which can improve the original properties of the polymers [1].

Aliphatic polyesters are used in tissue fixation (i.e., bone screws, bone plates, and pins), drug delivery systems (i.e., diffusion control), wound dressing (i.e., artificial skin), and wound closure (i.e., sutures and

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surgical staples). Bone screws, bone plates and pin structures made of polylactic acid (PLA) and poly-DL-lactic-co-glycolic acid (PLAGA) are being used and are likely to replace metal implants in the near future [2,3]. These bioabsorbable products have several advantages over metal implants: (1) no stress-shielding effect, (2) no need for removal after surgery, and (3) no metallic corrosion [4–7].

In this study, a copolymer of ethylene oxide (PEO) and propylene oxide (PPO) was used as a surfactant to blend with the matrix polymers PLLA and PDLLA. The main function of a surfactant/compatibilizer in blends is to reduce the surface tension between the two polymers, and to increase their miscibilities [8]. Both PEO and PPO, as well as their mutual copolymer, have been used in clinical medicine [9,10]. PEO is more hydrophilic and tougher than PPO. Co-PEO/PPO is usually applied in implants which will be in contact with blood for long periods of time [9]. Being hydrophobic, implants usually adsorb protein from the blood which can cause some side effects. Adding some surfactant can soothe this phenomenon, since the hydrophobic PPO is compatible with the hydrophobic bulk material, whereas the hydrophilic PEO will mitigate protein adsorption by the bulk material. A similar theory was also utilized in this study. The miscibility of PLLA/PDLLA was improved by adding a surfactant, and the mixture was further fine-tuned by adjusting its proportions. This is possible due to the similar hydrophobic properties of both PLLA and PPO; thus they have a tendency to mix well with each other.

2. Materials and methods

2.1. PLA

Two kinds of PLA (both obtained from Birmingham Polymers, Birmingham, AL, USA) were used in this study: PLLA (Mw: 137 kD) and PDLLA (inherent viscosity: 0.68 dl/g in CHCl$_3$ at 30°C). Amorphous poly-DL-lactic acid (PDLLA) and partially crystalline poly-L-lactic acid (PLLA) were selected based on their different degradation speeds. Some of the reasons for PLLA being widely used in the medical field include its biocompatibility, mechanical properties, and biodegradability. PLLA degrades by hydrolysis, and its degradation products can be metabolized. PLLA degrades to lactic acid via hydrolytic deesterfication, and lactic acid forms pyruvate by lactate dehydrogenase. Pyruvate is an intermediate product in metabolic pathways, and it can generate glucose via gluconeogenesis or be metabolized to form CO$_2$ and water by the citric acid cycle [11]. PLLA is a thermoplastic material derived from lactic acid, with a glass transition temperature of around 57°C, crystalline temperature of 105°C and melting point of around 174°C; like other thermoplastic materials, it can be manufactured to have different complicated shapes via extrusion and injection molding processes [12].

2.2. PCL

Polycaprolactone (Mw: 27 kD, PI: 1.9, inherent viscosity: 0.33 dl/g; Alkermes, Cincinnati, OH, USA) is also an important member of the aliphatic polyester family [13]. The degradation process of PCL can be divided into two stages. The first stage involves non-enzymatic, random hydrolytic ester cleavage, and autocatalysis by carboxylic acid end groups of the polymer chains. The second stage includes the beginning of weight loss of the polymer because of the diffusion of oligomeric species from the bulk. PCL is prone to fragmentation, and lower-molecular-weight fragments of PCL can be consumed by macrophages. The degradation rate of PCL is slower than those of PLLA and PGA, so PCL is suitable for long-term use in implants.

2.3. Copolymer of ethylene oxide and propylene oxide

Polyoxypropylene-polyoxyethylene (Empilan P series, Albright & Wilson, Cincinnati, OH, USA) is a non-ionic surfactant, and is a polyethylene oxide (PEO) and polypropylene oxide (PPO) block copolymer. PEO is comparatively more hydrophilic and flexible than PPO, so PPO is prone to have closer contact with PLLA. It is possible to improve the miscibility of blended polymers by adjusting the copolymer ratio of ethylene oxide and propylene oxide.

2.4. Blends

Solution blending was used in this study. For example, PLLA/PDLLA blends were prepared by mixing different percentages (100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100, respectively) of a 10% w/w solution of PLLA and PDLLA in methylene chloride solutions.

PLLA/PDLLA solutions were poured into Teflon trays for vaporization of solvent, with the help of a vacuum in the final drying stage. In the blending process, we found that a 10% PLLA and PDLLA mixing solution had better membrane-forming properties and was easier to remove from the Teflon trays than were solutions with different concentrations. Blending processes of PLLA/PCL, PLLA/PDLLA/surfactant and PLLA/PCL/surfactant were carried out the same way as described above.

2.5. Infrared measurements

IR spectra were obtained using Fourier-transform infrared spectroscopy (BioRad Laboratories, FTS 165, Cambridge, MA, USA). Each spectrum was recorded with a total of 16 scans.

2.6. Gel permeation chromatography

Molecular weight distributions of the blended polymers were determined in chloroform by gel permeation chromatography (GPC, detector: Perkin Elmer Series 200 refractive index detector; pump: Perkin Elmer Series 200 LC pump, Shelton, CT, USA) using polystyrene as the standard. Specimen concentrations were 0.03 g sample/10 ml chloroform, and the flow rate was 1.5 ml/min at 7.1 MPa.

2.7. Wide-angle X-ray diffraction

X-ray scattering was used to probe the crystallinity of the blend and its components. Thin film samples were analyzed using a wide-angle X-ray diffraction apparatus (MaxRC, Rigaku, Japan). X-ray scans were made over a 2θ range of $10°$ to $60°$ at $10°$ min.

2.8. Thermal analysis

Thermal analysis data were measured by thermogravimetry (TGA, 2050, TAI, New Castle, DE, USA) and differential scanning calorimetry (DSC, Perkin Elmer Pyris 1, Norwalk, CT, USA). All measurements were performed under nitrogen. In this study, the thermal degradation behavior of the samples was recorded with heating from room temperature to $400°C$ at a rate of $20°C/min$. TGA data showing the thermal degradation onset temperatures of the samples were used as references for ensuing DSC measurements. DSC measurements were carried out by: (1) heating from room temperature to $200°C$ at a rate of $10°C/min$; (2) cooling to $30°C$ at $50°C/min$; (3) maintaining for 3 min at $30°C$; and (4) then repeating the above procedures. DSC studies revealed the significant thermal properties of the samples, such as transition temperature (T_g), crystallinity temperature (T_{cc}), and melting temperature (T_m). T_g determination from the DSC data followed these steps: first, two smooth base lines were determined for before and after the transition. Second, a tangent line in the transition region was drawn. A line equally positioned between the two base lines was drawn, and this line crossed the experimental data line. The point at which that they cross is the half-height T_g. These data are important indices for observing the miscibilities of the blends. All DSC data presented here are from the second heatings.

2.9. Mechanical properties

Dynamic mechanical analysis (DMA, Perkin Elmer, DMA7) was used to measure the mechanical properties of PLLA/PDLLA/surfactant and PLLA/PCL/surfactant blends. In the tension mode measurement, a force of 10 mN was initially applied, which was increased to 240 mN/min until the sample broke. Five specimens were tested for each type of sample. Measurements of elastic modulus, yield strength, yield elongation, break strength, and elongation at break were recorded.

3. Results and discussion

3.1. FT-IR

PLLA, PDLLA and PCL are all aliphatic polyesters with similar structures. The C=O, C–O–C, and C–C peaks were clearly visible at 1754, 1175 and 1200 cm^{-1}, respectively, in the IR spectra.

3.2. GPC

The weight-averaged molecular weights of PLLA, PDLLA, and PCL were 115,784, 71,675 and 28,265, respectively. There were two prominent peaks in the molecular weight distributions of PLLA/PCL and PLLA/PCL/surfactant blends (Figs. 1 and 2), representing the PLLA and PCL components, respectively. From these figures it is clear that there was no significant shift of the two peaks, regardless of whether surfactant was added or not. This indicates that no severe degradation occurred during the preparation process. The same
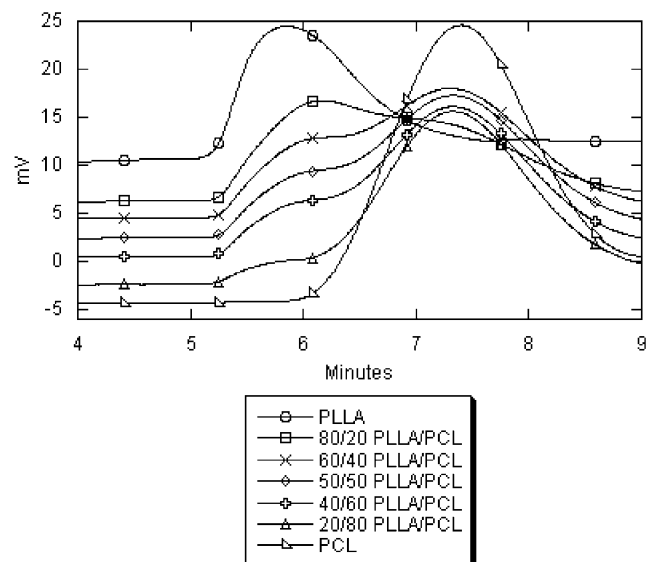

Fig. 1. GPC data of PLLA/PCL blends.

phenomenon was also found in the PLLA/PDLLA and PLLA/PDLLA/ surfactant blends.

3.3. WAXD

X-ray diffraction (XRD) data show the crystalline structures of PLLA and PCL. The XRD diffraction peaks for PLLA were at $2\theta = 17.49$, and for PCL at 21.42 and 23.83; there was no XRD diffraction peak for amorphous PDLLA. These peaks were still evident after

adding the surfactant, which indicates that no new crystal forms were apparent.

3.4. TGA

Thermal onset degradation temperatures were determined for PLLA to be at 329.8°C, PDLLA at 308.8°C, PCL at 358°C and a copolymer of ethylene oxide and propylene oxide at 331.3°C. The thermal onset
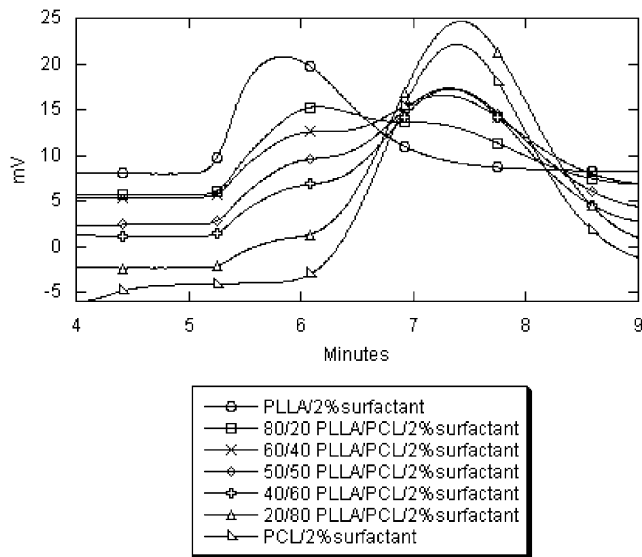

Fig. 2. GPC data of PLLA/PCL/2% surfactant blends.

Table 1
DSC data of PLLA/PDLLA blends (second heating)

PLLA/PDLLA	100/0	80/20	60/40	50/50	40/60	20/80	0/100
T_g (°C)	57.4	58.1	56.6	57.6	53.3	52.2	51.6
T_{cc} (°C)	109.9	116.8	120.7	123.4	130.2	—	—
ΔH_{cc} (J/g)	−39.1	−32.6	−24.1	−20.5	−13.6	—	—
T_m (°C)	175.1	174	171.8	171.7	172.5	173.8	—
ΔH_m (J/g)	39.8	33.3	24.5	23.3	18	1.1	—

Table 2
DSC data of PLLA/PDLLA/2% surfactant blends (second heating)

PLLA/PDLLA with 2% surfactant	100/0	80/20	60/40	50/50	40/60	20/80	0/100
T_g (°C)	55	54.4	51.7	51.1	50	49.4	47.2
T_{cc} (°C)	106.9	119.1	114.3	116	122.3	148.3	—
ΔH_{cc} (J/g)	−35.4	−32.3	−23.2	−17.5	−15.6	−2.3	—
T_m (°C)	173.5	173.8	173.2	174.3	175.3	173.5	—
ΔH_m (J/g)	36.4	34.9	24.7	21.4	18	4.8	—

Table 3
DSC data of PLLA/PCL blends (second heating)

PLLA/PCL	100/0	80/20	60/40	50/50	40/60	20/80	0/100
T_g (°C)	57.3	56.4	—	—	—	—	—
T_{cc} (°C)	109.9	91	91.3	90.2	91.1	91.1	—
ΔH_{cc} (J/g)	−42.5	−22.4	−16.5	−13.0	−14.3	−6.9	—
$T_{m\ (PLLA)}$ (°C)	175.1	170.3	170.1	170.5	171	171.7	—
$\Delta H_{m\ (PLLA)}$ (J/g)	39.7	33.9	28.1	22.4	22.4	12.1	—
$T_{m\ (PCL)}$ (°C)	—	—	52.0	52.3	52.3	52.8	53.1
$\Delta H_{m\ (PCL)}$ (J/g)	—	—	13.9	20.7	8.4	47.7	67.9

Table 4
DSC data of PLLA/PCL/2% surfactant blends (second heating)

PLLA/PCL with 2% surfactant	100/0	80/20	60/40	50/50	40/60	20/80	0/100
T_g (°C)	50.6	—	—	—	—	—	—
T_{cc} (°C)	106.9	86.6	88.1	89.6	88.7	87.4	—
ΔH_{cc} (J/g)	−35.7	−19.3	−15.1	−13.4	−11.3	−3.7	—
$T_{m\ (PLLA)}$ (°C)	170.7	170.8	170.8	171.3	171.1	170.3	—
$\Delta H_{m\ (PLLA)}$ (J/g)	41.5	32.5	25.3	21.3	23.8	8.1	—
$T_{m\ (PCL)}$ (°C)	—	54.5	52.3	52.7	52.5	52.6	53.1
$\Delta H_{m\ (PCL)}$ (J/g)	—	2.0	5.9	14.3	27.5	41.9	69.5

(a)

(b)
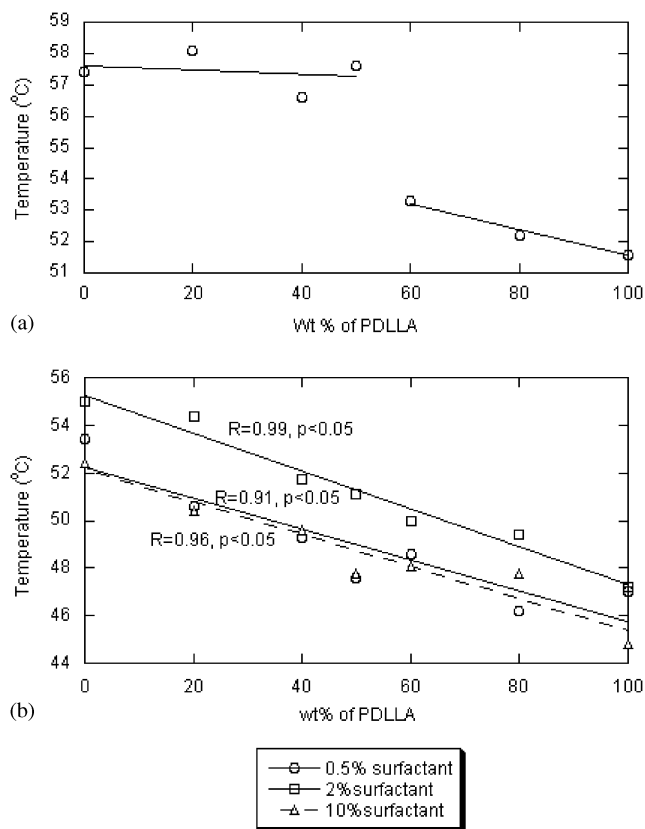
Fig. 3. (a) T_g's of PLLA/PDLLA blends (2nd heating). (b) T_g's of PLLA/PDLLA/surfactant blends (2nd heating).

Fig. 4. T_{cc} of PLLA/PDLLA/surfactant blends (2nd heating).

degradation temperatures of 80/20, 60/40, 50/50, 40/60, and 20/80 PLLA/PDLLA were 315.5°C, 311.4°C, 304.4°C, 311.4°C, 300.7°C, 311.4°C, and 290.3°C, respectively. Moreover, degradation temperatures of 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100 PLLA/PDLLA with 2% surfactant are 337.6°C, 336.6°C, 324.7°C, 328.0°C, 283.6°C, 323.9°C, and 323.2°C, respectively. It is evident that lower degradation temperatures occurred with higher percentages of PDLLA and surfactant.

3.5. DSC

The endothermic peaks at 175°C and 53°C are related to the melting points of PLLA and PCL, and the T_g's of PLLA and PDLLA are 57.4°C and 51.6°C (Tables 1–4). From the DSC data in Fig. 3(a) and (b), the glass transition temperature of PLLA/PDLLA without adding surfactant can be viewed as two regions, while the melting point did not change significantly. On the other hand, the glass transition temperature of PLLA/PDLLA/surfactant changed significantly. This indicates that PLLA/PDLLA has poor miscibility, while there was better mixing with PLLA/PDLLA/surfactant. This behavior can be explained as follows: if PLLA and PDLLA do not mix well, the amorphous portion of each
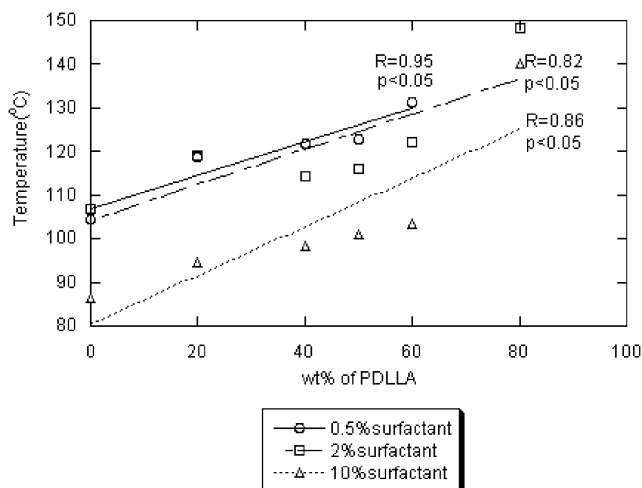
phase, as reflected by the glass transition temperature, would maintain their original properties. Thus, two glass transition temperatures could be observed. In contrast, if PLLA and PDLLA are well blended, their amorphous portions will change, and then a single, and shifting, glass transition temperature could be observed.

Tables 3 and 4 show thermal analysis data for PLLA/PCL and PLLA/PCL/surfactant films, as estimated from DSC results. Among these thermal analysis data, the T_g's of PLLA/PCL and PLLA/PCL/surfactant films cannot be correctly construed as being a reflection of the miscibility of the blends, since the T_g of PLLA is very close to the T_m of PCL. Fig. 4 shows that higher T_{cc} temperatures occur with lower percentages of PLLA. It is clear from the data mentioned above that irregardless of whether PEO-PPO is added, the percentage of PLLA of the blend is linear with respect to its ΔH_m. This arises from the fact that the ΔH_m of the polymer is related to its crystallinity.

3.6. DMA

Table 5 shows the mechanical properties of seven different blend ratios of PLLA/PDLLA films, including the elastic modulus, yield strength, yield elongation, break strength, and elongation at break. As is evident from Table 5, these mechanical properties do not show a definite trend, and PLLA/PDLLA also apparently has poor miscibility. Among the blends, 40/60 PLLA/PDLLA presented harder and tougher mechanical properties than PLLA. The elastic modulus, yield strength and elongation at break of the 40/60 PLLA/PDLLA blend were 22.0 ± 3.4 MPa, 38.5 ± 5.4 MPa and $60.8\% \pm 6.6\%$, respectively. These are better than values of PLLA, respectively of 19.8 ± 3.0, 31.5 ± 4.5 MPa and $56.3\% \pm 1.9\%$.

Concentration of the surfactant is also an important factor which affects the mechanical properties of the

Table 5
Mechanical properties of PLLA/PDLLA blends

PLLA/PDLLA	100/0	80/20	60/40	50/50	40/60	20/80	0/100
Elastic modulus (MPa)	19.8±3.0	11.9±1.7	20.5±3.9	10.1±0.1	22.0±3.4	17.6±2.1	2.8±0.4
Yield strength (MPa)	31.5±4.5	34.5±2.5	39.2±7.7	35.8±1.3	38.5±5.4	32.3±2.0	25.9±3.3
Yield elongation (%)	11.9±0.0	13.8±2.7	8.2±0.9	11.9±1.9	10.9±3.8	6.3±1.4	11.4±1.0
Break strength (MPa)	34.1±2.5	35.2±2.4	41.1±8.1	36.2±1.5	39.2±5.4	32.6±2.1	26.9±3.3
Elongation at break (%)	56.3±1.9	59.8±9.3	38.1±4.6	56.2±3.4	60.8±6.6	62.5±9.0	54.6±3.8

Table 6
Mechanical properties of 50/50 PLLA/PDLLA blends with different concentration of surfactant

Different conc. surfactant	0%	0.5%	1%	2%	3%	5%	10%
Elastic modulus (MPa)	10.1±0.1	10.3±1.4	15.6±3.9	17.4±2.6	6.1±1.0	4.3±0.6	3.4±0.8
Yield strength (MPa)	35.8±1.3	32.4±1.6	32.4±0.8	29.8±1.5	20.9±1.7	14.1±0.6	11.2±0.5
Yield elongation (%)	11.9±1.9	26.7±8.9	21.3±0.7	15.3±1.0	49.7±5.3	21.8±4.7	44.2±1.8
Break strength (MPa)	36.2±1.5	32.6±1.5	30.8±3.9	30.7±1.9	21.3±1.7	14.5±0.7	11.7±0.6
Elongation at break (%)	56.2±3.4	76.8±4.4	43.9±4.9	86.4±12.9	98.9±10.1	92.2±6.7	61.6±6.3

Table 7
Mechanical properties of PLLA/PDLLA/2% surfactant blends

PLLA/PDLLA with 2% surfactant	100/0	80/20	60/40	50/50	40/60	20/80	0/100
Elastic modulus (MPa)	10.5±1.0	8.8±0.3	13.4±1.4	17.4±2.6	10.9±1.0	7.0±1.3	1.0±0.1
Yield strength (MPa)	25.2±3.1	22.1±4.2	26.4±1.3	29.8±1.5	23.4±1.2	24±0.2	16.7±1.9
Yield elongation (%)	7.1±1.8	16.9±4.9	10.2±0.9	15.3±1.0	19.2±2.6	14.6±2.1	44.6±11.3
Break strength (MPa)	25.4±3.0	22.3±4.2	26.9±1.5	30.7±1.9	23.8±1.3	24.5±0.5	16.8±1.9
Elongation at break (%)	84.7±2.2	53.2±5.7	62±13.2	86.4±12.9	85.6±6.3	89.6±22.1	114.6±11.3

Table 8
Mechanical properties of PLLA/PCL blends

PLLA/PCL	100/0	80/20	60/40	50/50
Elastic modulus (MPa)	19.8±3.0	20.7±1.4	10.7±2.2	8.1±2.8
Yield strength (MPa)	31.5±4.5	40.4±1.6	18.9±1.9	16.3±1.3
Yield elongation (%)	11.9±0.0	12.1±4.3	15.0±3.4	18.3±3.7
Break strength (MPa)	34.1±2.5	41.2±1.5	19.3±1.9	16.9±1.3
Elongation at break (%)	56.3±1.9	129.5±32.9	152.1±11.8	139.6±17.4

blends. In order to determine the optimum concentration, seven different concentrations were used with 50/50 PLLA/PDLLA in this study. It can be seen in Table 6 that 50/50 PLLA/PDLLA with 2% surfactant was harder (elastic modulus, 17.4±2.6 MPa), stronger (yield strength, 29.8±1.5 MPa) and tougher (elongation at break, 6.4%±12.9%). From Table 6, it is significant that blends with higher than 5% surfactant showed poor mechanical behaviors. In an immiscible blend system, polymers always agglomerate individually due to their different chemical structures and high molecular weights, and polymers usually form a significant phase boundary. Properties of the phase boundary affect the mechanical properties. At this point, an optimum concentration of surfactant plays a role like a ''bridge'' in the blend system, decreasing the phase boundary between the polymers and improving the miscibility of the blend. The mechanical properties improve while the phases between the polymers permit closer connections. On the other hand, if the surfactant concentration is too high, the surfactant can be seen as a third component of the blend system, and will not serve to improve the miscibility of the blend.

The mechanical properties of PLLA/PDLLA/surfactant blends are presented in Table 7, showing that the elastic modulus, yield strength, and elongation at break of the 50/50 PLLA/PDLLA/2% surfactant blend were 17.4±2.6, 29.8±1.5 MPa, and 86.4%±12.9%, respectively. These values are higher than those of the 80/20 PLLA/PDLLA/2% surfactant blend. Moreover, comparing the elongation at break of the 50/50 PLLA/

Table 9
Mechanical properties of PLLA/PCL/2% surfactant blends

PLLA/PCL with 2% surfactant	100/0	80/20	60/40	50/50
Elastic modulus (MPa)	10.5 ± 1.0	9.5 ± 1.2	4.7 ± 0.7	6.6 ± 0.7
Yield strength (MPa)	25.2 ± 3.1	19.3 ± 2.2	12.7 ± 0.8	9.9 ± 0.5
Yield elongation (%)	7.1 ± 1.8	14.7 ± 1.4	28.9 ± 10.6	4.6 ± 1.7
Break strength (MPa)	25.4 ± 3.0	20.1 ± 1.4	12.9 ± 0.8	10.4 ± 0.5
Elongation at break (%)	84.7 ± 2.2	129 ± 4.8	130 ± 14.2	123.7 ± 13.3

PDLLA/2% surfactant blend, the 50/50 PLLA/PDLLA blend, and PLLA, it is worth noting that values of the elongation of PLLA and the 50/50 PLLA/PDLLA blend were only 56.3% ± 1.9% and 56.2% ± 3.4% which were much lower than the 86.4% ± 12.9% of 50/50 PLLA/PDLLA with 2% surfactant. Tables 8 and 9 present the mechanical properties of the PLLA/PCL and PLLA/PCL/ surfactant blends. From these data it can be deduced that the elongation values of the blends increased after adding PCL and surfactant, but the mechanical properties simultaneously became weaker.

In summary, elongations of the blends increased after adding the surfactant, while some specific ratios of the blends still possessed strong mechanical properties at the same time. The mechanical properties of the blends actually improved by blending with the surfactant in this study. It is worth mentioning that stronger mechanical properties can be achieved with raw materials of higher molecular weight. The proper mechanical properties should always be determined by the intended applications.

4. Conclusions

Several observations in the last few paragraphs have shown that pure PLLA is hard and brittle, and that adding PDLLA or PCL can change its original properties. Solution-blending is an effective and easy way to achieve the purposes mentioned above. PLLA/PDLLA has poor miscibility which can be significantly improved by addition of a copolymer of ethylene oxide and propylene oxide surfactant, and PLLA/PDLLA is hard and tough after adding the surfactant. The DMA data show that 40/60 PLLA/PDLLA has harder and tougher mechanical properties than PLLA, and that adding 2% surfactant to the blends can increase their miscibility, especially for the 50/50 PLLA/PDLLA blend. In comparison with PLLA/PDLLA blends, the PLLA/PCL blends have higher elongation and weaker mechanical properties.

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