

# Preparation and Property Testing of Compatibilized Poly(L-lactide) / Thermoplastic Polyurethane Blends

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**Summary:** Poly(L-lactide) (PLL) has been blended with a polycaprolactone-based thermoplastic polyurethane (TPU) elastomer as a toughening agent and a poly(L-lactide-*co*-caprolactone) (PLLCL) copolymer as a compatibilizer. Both 2-component (PLL/TPU) and 3-component (PLL/TPU/PLLCL) blends were prepared by melt mixing, characterized, hot-pressed into thin sheets and their tensile properties tested. The results showed that, although the TPU could toughen the PLL, the blends were largely immiscible leading to phase separation. However, addition of the PLLCL copolymer improved blend compatibility. The best all-round properties were found for the 3-component blend of composition PLL/TPU/PLLCL = 90/10/10 parts by weight.

**Keywords:** Poly(L-lactide), thermoplastic polyurethane elastomer, poly(L-lactide-*co*-caprolactone), immiscible blend, compatibilization

## Introduction

Poly(L-lactide) (PLL), or poly(lactic acid) (PLA) as it is commonly referred to in industry, is an aliphatic poly- $\alpha$ -ester and is the most important commercial bioplastic currently in the market. Its rise to prominence in recent years has been well documented and there is now a vast library of information available on PLL in both books and journals.<sup>[1-4]</sup> Apart from being recyclable, biodegradable and compostable, the main advantages of PLL are its rigidity, good transparency as film, cups and bottles, and its processability using conventional thermoplastic processing equipment. However, PLL also has some notable disadvantages such as its low softening point of around 60°C, its stiffness and brittleness

in certain applications, and its low water vapor barrier properties. Consequently, in order to diversify PLL's range of applications, there is increasing interest nowadays in how its properties can be modified by, for example, (1) the use of additives such as nucleating agents and impact modifiers, (2) blending with other polymers, and (3) nanocomposites with inorganic materials such as clay, zinc oxide, titanium dioxide and carbon nanotubes. Of these three approaches, blending with other polymers has received the most attention and it is this approach which has been employed in the work described in this paper.

PLL has been blended with a wide range of different polymers, mainly aliphatic polyesters or polymers containing substituent ester groups in the expectation that the polar interactions between the ester groups would increase the blend's molecular compatibility. Examples include blends with polycaprolactone (PCL), polyhydroxybutyrate (PHB), poly(butylene succinate) (PBS), poly(vinyl acetate) (PVAc), and cellulose acetate butyrate (CAB). Invariably however, these blends are largely immiscible over a wide range of composition. Despite the ester group interactions, there is only very limited compatibility in the amorphous part of the matrix. Consequently, these blends have so far found very limited application.

This paper now describes the blending of PLL with a PCL-based thermoplastic polyurethane (TPU) elastomer. This too would be expected to produce a largely immiscible blend and so the novel aspect of this work has been to incorporate a purpose-designed third component which can act as a compatibilizer to decrease the level of immiscibility and phase separation. This third component is an amorphous poly(L-lactide-*co*-caprolactone) 50:50, PLLCL, random copolymer which has structural LL and CL repeat units in common with both the main PLL and PCL-based TPU components respectively. The target application for this 3-component blend is biodegradable film packaging.

## **Experimental Part**

### **Materials**

The PLL used in this work was a commercial product (Ingeo™ 4042D Film Grade, NatureWorks) in pellet form. As received, the PLL had number-average and weight-average molecular weights,  $\bar{M}_n$  and  $\bar{M}_w$ , of  $1.52 \times 10^5$  and  $2.55 \times 10^5$  respectively.

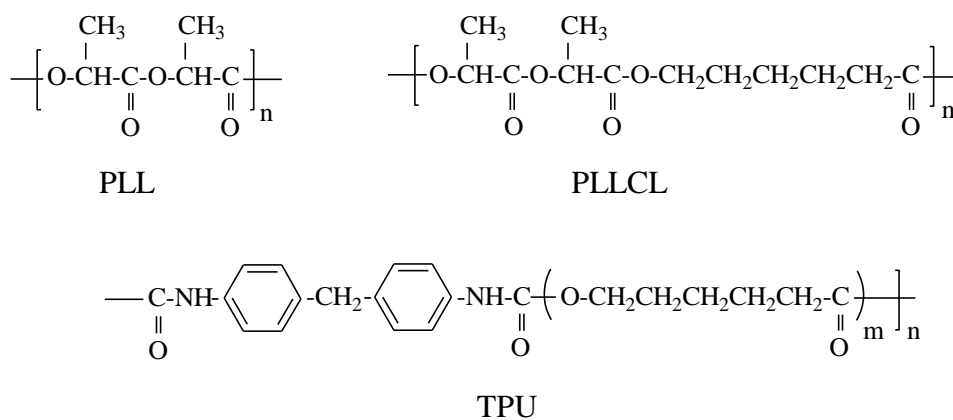
The polycaprolactone-based thermoplastic polyurethane (TPU) elastomer used was also a commercial product (Pellethane™ 2102-75A, Lubrizol Corporation) in pellet form.

Its block-type structure consisted of alternating hard and soft segments based on 4,4'-methylenediphenyl-1,1'-diisocyanate (MDI) and polycaprolactone respectively, plus a chain extender. The TPU elastomer had  $\bar{M}_n$  and  $\bar{M}_w$  values of  $1.28 \times 10^5$  and  $2.62 \times 10^5$ .

The poly(L-lactide-*co*- $\epsilon$ -caprolactone), PLLCL 50:50 (mol %), random copolymer was synthesized via the ring-opening copolymerization in bulk of equimolar amounts of L-lactide (LL) and  $\epsilon$ -caprolactone (CL) at 120°C for 72 h using 0.1 mol % stannous octoate (SnOct<sub>2</sub>) as the initiator. The copolymer was purified by cutting into small pieces and heating under vacuum at 40°C for 24 h to constant weight in order to remove any residual monomer. The PLLCL, which was purposely synthesized to only a medium molecular weight, had  $\bar{M}_n$  and  $\bar{M}_w$  values of  $2.43 \times 10^4$  and  $4.40 \times 10^4$ .

### Chemical Structures

The chemical structures of the PLL, PLLCL and PCL-based TPU are compared below. The PLLCL was purpose-designed so that it would have structural similarities with both the PLL and TPU.



### Blend Preparation

Polymer blending was carried out by means of melt mixing using an internal mixer (Haake PolyLab) at temperatures of 195 °C for the PLL/TPU 2-component blends and 190 °C for the PLL/TPU/PLLCL 3-component blends for 20 mins. The blend components were first pre-dried in a hot air oven and then pre-mixed in their dry state prior to melt mixing. In the case of the PLL/TPU/PLLCL 90/10/10 blend, which will be focused on in more detail later, the 90/10/10 composition represents a parts-by-weight (pbw) ratio. Thus, in a typical 90/10/10 batch for melt mixing, PLL 270 g were mixed with TPU 30 g and PLLCL 30 g.

## Results and Discussion

With PLL as the main component at 90 pbw, various blend compositions were prepared incorporating 0-20 pbw TPU and 0-50 pbw PLLCL. The upper limit of 20 pbw TPU was determined by the marked effect of the TPU in increasing the melt viscosity of the blend leading to difficulties in melt mixing due to the increased torque. These difficulties could be offset to a certain extent by the addition of the PLLCL copolymer as a plasticizer but as the PLLCL content increased towards 50 pbw the blend's mechanical properties became progressively weakened. Thus, both the TPU and the PLLCL had their advantages and disadvantages and so the objective was to find blend compositions which could provide a suitable balance between melt processability and mechanical properties.

From the results obtained for the range of 2- and 3-component blends studied, the best balance of properties was found for the 3-component PLL/TPU/PLLCL 90/10/10 blend. Therefore, the following results describe this formulation in detail and compare it with PLL, PLL/TPU 90/10 and PLL/PLLCL 90/10 in order to analyze and discuss the effects of the TPU and PLLCL components both individually and in combination.

### Thermal Analysis

The differential scanning calorimetry (DSC) thermograms for the PLL, PLLCL and TPU components and the 2- and 3-component blends are shown in Figure 1. Whereas the PLL was a semi-crystalline material with a distinct glass transition temperature,  $T_g$  (mid-point), of 59 °C and melting temperature,  $T_m$  (peak), of 153 °C, the TPU showed a very broad, shallow melting transition over the range of 90-180 °C. This broad transition, which is barely discernable on the scale of Figure 1, corresponds to the gradual dissociation of the crystalline hard segment microdomains which act like physical crosslinks in the TPU matrix. As this dissociation occurs, chain mobility increases until above 180 °C the onset of viscous melt flow is observed. In contrast, the PLLCL was completely amorphous, as expected from its 50:50 mol % composition and randomized monomer sequencing. It did however exhibit a sub-zero  $T_g$  (mid-point) of -13 °C (not shown in Figure 1).

In Figure 1, the most notable effects of adding the TPU and PLLCL to the PLL are:

- (1) For the PLL/TPU 90/10 blend, the addition of the TPU increased the  $T_g$  of the PLL by about 5 °C. It also increased the melt viscosity, as indicated by its lower melt flow

index (MFI) in Table 1. The high melt viscosity of TPUs, similar to polyamides, is generally attributed to the ability of hydrogen bonds to reform in the melt state.

- (2) For the PLL/PLLCL 90/10 blend, the addition of PLLCL slightly decreased the  $T_g$  but significantly decreased the crystallization temperature,  $T_c$ . The PLLCL also decreased the melt viscosity. These effects are symptomatic of increased chain mobility due to plasticization by the lower molecular weight PLLCL.
- (3) For the PLL/TPU/PLLCL 90/10/10 blend, its DSC curve at the top of Figure 1 is seen to be more similar to that of the PLL/PLLCL blend than the PLL/TPU blend. Interestingly, its melt viscosity was also less than that of the PLL, suggesting that the plasticizing effect of the PLLCL was more influential than the stiffening effect of the TPU in terms of chain mobility.

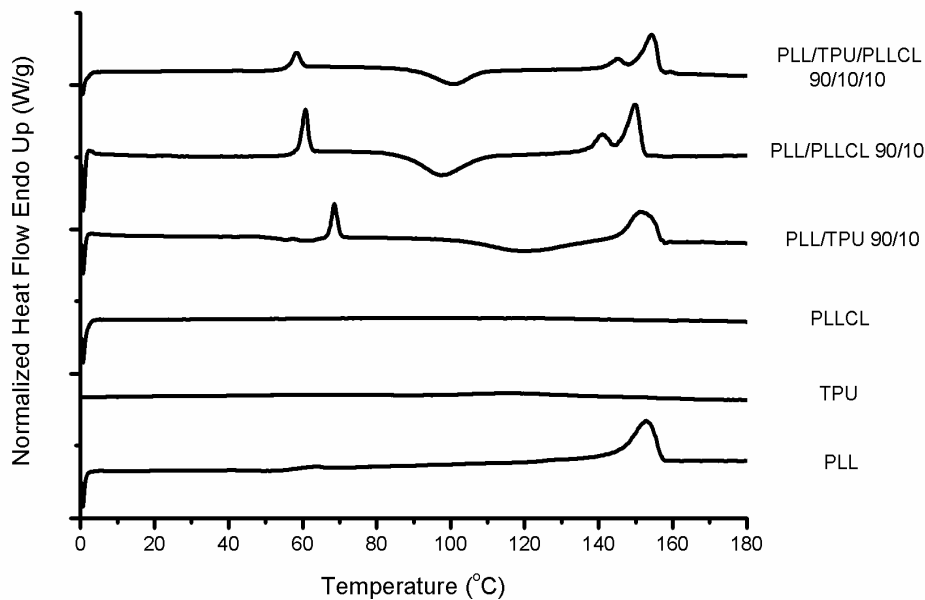


Figure 1. DSC thermograms of the PLL, TPU, PLLCL and the 2- and 3-component blends. (Heating rate = 10 °C/min; scans after melt processing)

### Tensile Properties

Tensile testing was carried out on thin sheet specimens (thickness range 200-300  $\mu\text{m}$ ) prepared by hot-pressing at 180 °C. Tests were carried out according to ASTM Standard Test Method D882-02.<sup>[5]</sup> With reference to their stress-strain curves (a)-(e) in Figure 2, the following inferences can be made:

- (a) PLL by itself is seen to be a strong but brittle material with no obvious yield point and a strain at break of less than 5%.
- (b) In contrast, TPU by itself is a much lower modulus, elastomeric material with a strain at break of  $> 800\%$ .
- (c) The curve of the PLL/TPU 90/10 blend appears to be a combination of (a) and (b) suggesting that the blend is acting like a simple 2-component mixture in which the PLL and TPU are phase-separated and respond independently. The strain at break, not shown in Figure 2, was approximately 110%.
- (d) Addition of the PLLCL copolymer in the PLL/PLLCL 90/10 blend decreases both the stress and strain at break relative to PLL due to a plasticizing effect, as also indicated by a marked decrease in melt viscosity.
- (e) When both the TPU and PLLCL are added in the PLL/TPU/PLLCL 90/10/10 blend, the result is a material which shows a stress-strain curve intermediate in profile between those of PLL and PLL/TPU. The curve (e) is seen to be a much smoother version of curve (c) which suggests that the PLLCL is able to compatibilize the PLL and TPU to a certain extent. This view is supported by an observed increase in light transmission from opaque (for PLL/TPU) to partially translucent (Table 1).

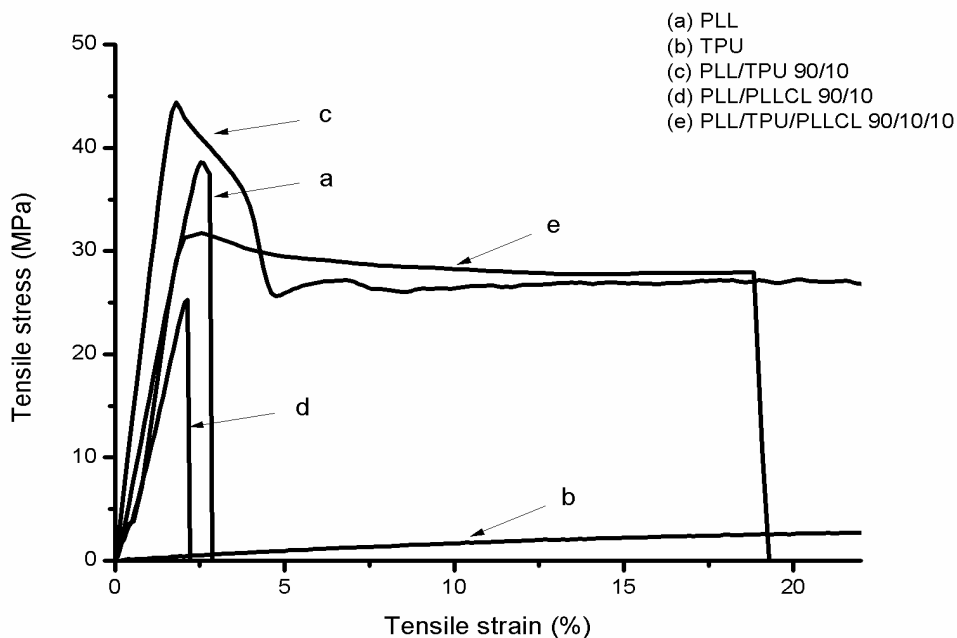


Figure 2. Tensile stress-strain curves of the PLL, TPU and the 2- and 3-component blends. (Each curve is a typical example from tests carried out on a minimum of 5 test specimens.)

## Optical Clarity

The optical clarities of the thin sheet specimens were also compared in terms of their light transmittance. Measurements were carried out using a UV-visible spectrophotometer at a wavelength of 450 nm. Whereas the PLL and PLL/PLLCL 90/10 sheets were essentially transparent with light transmittance values of around 90%, the PLL/TPU 90/10 blend was opaque with only 3% transmittance (Table 1). The fact that only 10% by weight of TPU can transform the otherwise transparent PLL into an opaque material is a clear indication that PLL and TPU are thermodynamically immiscible leading to a phase-separated morphology. This indication is in agreement with the previous work of Li and Shimizu whose scanning electron microscopy (SEM) studies of tensile fracture surfaces showed that the TPU domains were dispersed in the PLL matrix in a 2-phase morphology.<sup>[6]</sup>

However, when the PLLCL copolymer was added in the PLL/TPU/PLLCL 90/10/10 blend, the level of opaqueness noticeably decreased with a light transmittance of 18%. This suggests that the PLLCL was able to decrease the level of phase separation and/or decrease the size of the TPU domains by a compatibilizing effect since it consists of LL and CL structural units in common with both the PLL and (PCL-based) TPU. The light transmittance values are given in Table 1 below.

Table 1. Summary and comparison of the thermal, melt flow, mechanical and optical properties of PLL and the PLL/TPU, PLL/PLLCL and PLL/TPU/PLLCL blends.

Property	PLL	PLL/TPU 90/10	PLL/PLLCL 90/10	PLL/TPU/PLLCL 90/10/10
Glass transition, $T_g$ (°C)	60	65	59	57
Melting point, $T_m$ (°C)	153	152	142, 150	145, 155
Crystallization, $T_c$ (°C)	-	121	100	102
Crystallinity (%) <sup>a)</sup>	33	5	13	8
Melt flow index (g/10 min) <sup>b)</sup>	1.11	0.70	> 10	2.18
Tensile strength (MPa) <sup>c)</sup>	38	44	25	32
Strain at break (%)	3	110	2	18
Toughness (J/mm <sup>3</sup> ) <sup>d)</sup>	0.07	3.29	0.03	0.51
Light transmittance (%)	90	3	86	18

<sup>a)</sup> Initial % crystallinity ( $\propto \Delta H_m - \Delta H_c$ ) from the DSC data in Figure 1 ( $\Delta H_m^* = 93.7$  J/g<sup>[7]</sup>)

<sup>b)</sup> Measured at 160 °C (load 2.16 kg; die diameter 2.1 mm, length 8.0 mm)

<sup>c)</sup> Taken as the maximum stress from Figure 2

<sup>d)</sup> Calculated from the area under the stress-strain curve

## Conclusions

This paper has focused its attention on the role of a PLLCL copolymer as a compatibilizer for PLL/TPU blends. From the results, the following conclusions can be drawn:

- (1) The PLL/TPU 90/10 binary blend appears to be thermodynamically immiscible to the extent that it forms a phase-separated opaque blend. Despite this, the TPU is still able to exert a toughening effect on the PLL matrix, indicating that there are at least some inter-phase dipolar interactions between the ester groups in the amorphous regions of the PLL and the PCL soft segments of the TPU.
- (2) However, when the PLLCL copolymer is added, the PLL/TPU/PLLCL 90/10/10 ternary blend shows signs of increased molecular compatibility which manifests itself as decreased opacity (partial translucency), a slight lowering of  $T_g$ , and a smoothening out of the stress-strain curve. Previous work has interpreted this compatibilizing effect in terms of the compatibilizer locating at the interfaces formed by phase-separation.<sup>[8]</sup> It was with this idea in mind that the PLLCL 50:50 random copolymer was designed as a potential compatibilizer in this work since, apart from being completely amorphous, it consists of LL and CL structures in common with both the PLL and the TPU.
- (3) It is also significant and no less important for processing purposes to note that the PLLCL can lower the melt viscosity and, in doing so, improve the melt rheology of the PLL/TPU blend by acting as a plasticizer as well as a compatibilizer.

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