

Polyurethane toughened polylactide

Yumin Yuan*, Eli Ruckenstein**

Department of Chemical Engineering, State University of New York at Buffalo,
Buffalo, NY 14260, USA

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Summary

Brittle polylactide (PLA) was toughened by introducing 5 wt % of a poly(ϵ -caprolactone)(PCL) diol- and triol-based polyurethane (PU) network. The extent of cross-linking of the PU was varied by changing the ratio between diol and triol. The effects of the PU content and its crosslink density on the mechanical properties and the toughness of PU/PLA blends were investigated. Maximum toughness of PU/PLA blends, an order of magnitude higher than that of pure PLA, could be achieved by the use of a proper amount of PU and a proper extent of cross-linking.

Introduction

Polylactide (PLA) is biodegradable and can be hydrolyzed to nontoxic, water soluble or metabolic products. It has been used successfully for drug delivery, in medical devices, and as an absorbable material^[1–3]. However, owing to its brittleness, wider applications of PLA to replace the non-degradable polystyrene and poly(vinyl chloride) are restricted.

The toughening of brittle thermoplastics and thermosets has been investigated for several decades^[4–6]. Such materials can be toughened significantly by introducing a discrete rubber phase in the brittle matrix, a typical example being high-impact polystyrene, in which the polystyrene is toughened with grafted poly(butadiene) rubber. A number of factors, such as the entanglement density of the matrix, the rubber content, the rubber particle size and size distribution, the interfacial tension and the phase behavior of the matrix and the rubber, affect the toughening of a brittle Material^[7–8].

Poly(ϵ -caprolactone) (PCL) is a biodegradable rubber that has been used to toughen brittle PLA plastics by copolymerization of PCL diol with lactide monomer. Grijpma et al.^[9] improved the impact strength of PLA by synthesizing PCL-PLA-PCL triblock copolymers. Hiljanen-Vainio et al.^[10] toughened PLA via direct polycondensation of L-lactic acid and ϵ -caprolactone followed by chain extension through urethane linkages of the polyester to poly(ester-urethane).

In the present paper, PLA (96 mol % L-isomer) was toughened using a small amount of a semi-interpenetrating polyurethane (PU)-PLA network (SIPN) whose extent of cross-linking was varied by changing the ratio between PCL diol and triol. A maximum toughness of 18 MJ/m³ was achieved by blending the PLA with 5 wt % PU based on an OH mole ratio between diol and triol of 9 to 1; this represents an order-of-magnitude

Present address:

* McMaster Center for Pulp and Paper Research, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, L8S 4L7, Canada

** Corresponding author

increase over the 1.6 MJ/m³ toughness of pure PLA.

Experimental

Materials

Poly(lactide (PLA, 96 mol L-isomer, $M_n = 112,000$), poly(ϵ -caprolactone) (PCL) diol and triol ($M_n = 1250$ and 900 , respectively), toluene-2,4-diisocyanate, dibutyltin dilaurate and anhydrous toluene were purchased from Aldrich and used as received.

Preparation of PU/PLA blends

Three kinds of PU were used with an OH mole ratio between diol and triol of 10/0, 9/1 and 7/3. The corresponding PUs will be denoted as PU-0, PU-1 and PU-3, respectively. PU/PLA blends were prepared by solution blending in toluene, followed by interchain cross-linking. A typical preparation of a PU-1/PLA blend proceeded as follows: 1.125 g of pre-dried PCL diol was dissolved in 20 ml anhydrous toluene, to which 0.191 g toluene-2,4-diisocyanate along with a drop of dibutyltin dilaurate were added. Reaction was allowed to proceed under a nitrogen atmosphere at 90 °C for 1 h and at 60 °C for an additional 1 h. Then 0.06 g of pre-dried PCL triol was added to the solution containing NCO-terminated prepolymer molecules, to promote partial cross-linking. Finally, solutions containing 0.1 g and 0.2 g of PU-1 were removed from the flask, just before the gelation point was reached, and mixed with toluene solutions containing 1.9 g and 1.8 g PLA, respectively. Further, inter-chain cross-linking of PU-1 was carried out for 1 h at 60 °C to complete the formation of a semi-interpenetrating PU-PLA network (SIPN). The resulting polymer blend solutions were poured into aluminum pans and the solvent was allowed to evaporate slowly overnight. The rough films obtained, with PU-1 contents of 5 and 10 wt %, respectively, were dried thoroughly in a vacuum oven at 60 °C, and thin semi-transparent blend films were prepared by a short hot pressing at 180 °C, followed by rapid air cooling to room temperature.

DSC Characterization

The thermal behavior of the sample was examined with a Du Pont 910 differential scanning calorimeter (DSC), under nitrogen. The samples were first heated to 175 °C, with a heating rate of 10 °C/min and then held at 175 °C for 1 min to remove any previous thermal history. The samples were then rapidly quenched in liquid nitrogen. The second scanning was carried out from 0 to 180 °C, also with a heating rate of 10 °C/min. The data were collected during the second scanning.

Determination of Mechanical Properties

Thin films of 0.10–0.15 mm thickness were cut into the dumbbell-shaped form indicated by ASTM D.638-58T. The tensile testing was performed at room temperature, using an Instron Universal Testing Instrument (Model 1000), with an elongation rate of 10

mm/min. The yield and tensile strengths were calculated based on the initial cross-sectional area of the specimen. The toughness is defined as the energy needed to break a sample of unit area and unit length (J/m^3); it is given by the area under the stress-strain curve. The data regarding the mechanical properties represent averages for at least five specimens.

Results and Discussion

Figure 1 presents the stress-strain curves of PLA and PU/PLA blends containing 5 wt % PU, in which the crosslink density was varied by changing the OH mole ratio between diol and triol. PLA (curve a) is a brittle thermoplastic material, which exhibits a yield point and a low elongation of about 6 %. When the linear PU-0 was introduced into the PLA matrix (curve b), neither the tensile strength, nor the elongation were improved. In contrast, the elongation of the PU-1/PLA blend (curve c) increased upto 60 %, and the yield and the tensile strengths decreased somewhat, indicating that the PLA was significantly toughened by the PU-1-PLA SIPN. However, as the crosslink density was further increased (PU-3/PLA blend, curve d), the elongation decreased to 25 %, and the yield and tensile strengths acquired values between those of PLA and the PU-1/PLA blend, demonstrating that the greater cross-linking in the PU-3 SIPN yielded less toughness. The effects of the PU content and the crosslink density on the mechanical properties of PU/PLA composites are summarized in Table 1.

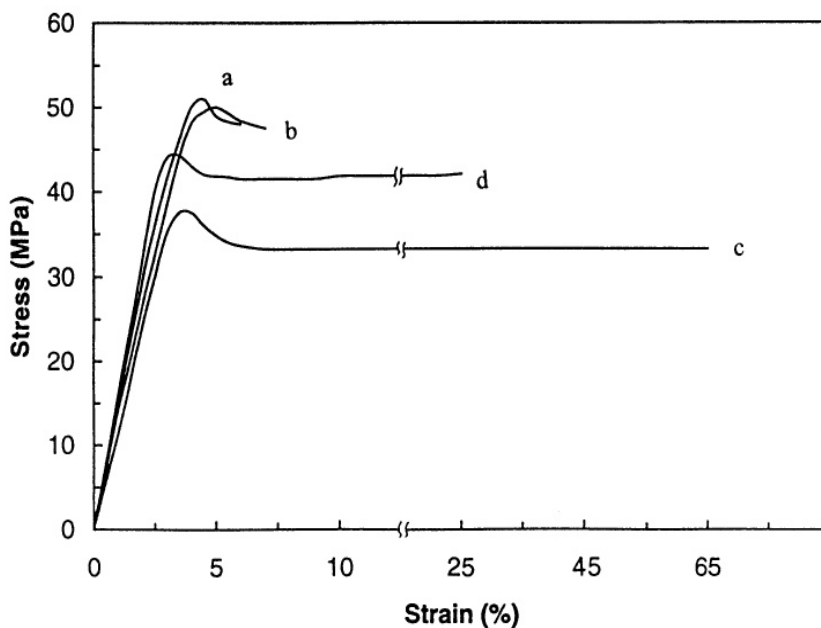


Figure 1 The Stress-Strain Curves of PLA and PU (5 wt %)/PLA Blends
a: pure PLA; b: PU-0/PLA; c: PU-1/PLA; d: PU-3/PLA

Table 1. The PLA and PU/PLA blends: mechanical properties

PU Content wt %	Yield Strength MPa	Tensile Strength MPa	Young's Modulus MPa	Elongation %	Toughness MJ/m ³
0 (PLA)	51	48	1480	6	1.6
Linear PU-0					
5	49	47	1340	7	2
10	/	38	1160	5	1.4
PU-1: diol/triol=9/1					
5	37.8	33.5	1160	60	18
10	35	30.5	1000	35	10.5
PU-3: diol/triol=7/3					
5	44	41	1490	20	13.5
10	31.4	29	1100	15	4

Due to its low elongation (6 %), PLA has low toughness, about 1.6 MJ/m³. When blended with 5–10 wt % linear PU-0 (free of PCL triol), the strengths and moduli decreased, but since the elongation has barely improved, the toughness of the blend remained as low as that of the pure PLA. This occurs because the PU-0 is more polar than PLA, and strong hydrogen-bonding in the former stimulates self-aggregation. Consequently, the adhesion between the polymers is poor. When, however, the PLA was mixed with a properly crosslinked PU-1, the toughness of the material significantly improved. With only 5 wt % of PU-1 in the blend, the elongation increased to about 60% and the toughness increased by one order of magnitude (to 18 MJ/m³). This occurs because some of the PLA interpenetrates the PU-1 networks, generating PU-PLA semi-interpenetrating networks which are more compatible with PLA. With a further increase of the crosslink density (PU-3/PLA blend), the toughness decreases compared to the PU-1/PLA blend. The lower toughness of the PU-3/PLA blend is due to the increased stiffness of the semi-interpenetrating PU-PLA network. This results in less intermingling between the PU-PLA networks and the PLA.

The specimens containing 5 or 10 wt % PU-1 and 5 wt % PU-3 exhibit a well defined yield point followed by the appearance of a stress whitening during the tensile testing. The surfaces of the broken samples have a fibrous structure. This indicates that a large amount of energy is dissipated during the drawing of the fibrils, which enhances the toughness of these materials.

Figure 2 presents the DSC traces of pure PLA and PU/PLA blends. For pure PLA,

the T_g is about 56 °C and the T_m is 150 °C. After being quenched in liquid nitrogen,

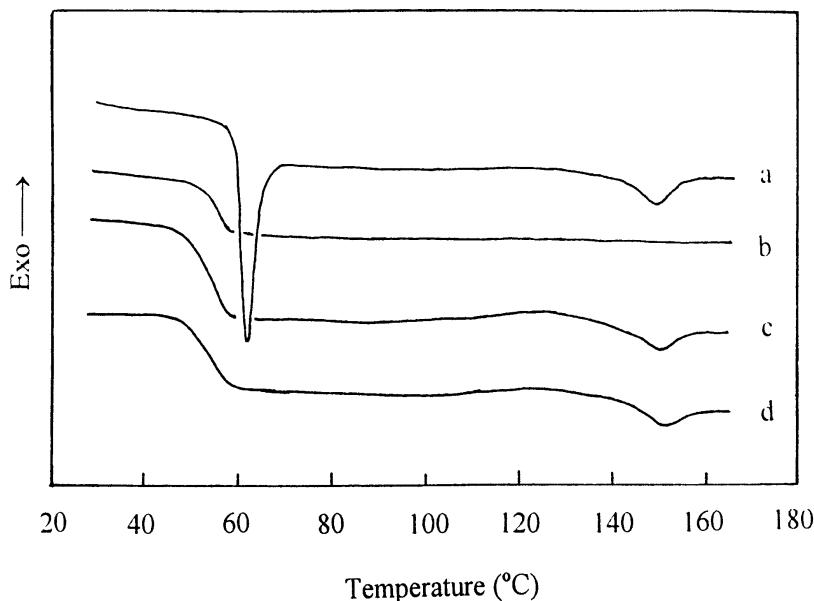


Figure 2 DSC Traces of PLA and PU(5 wt %)/PLA Blends

a: pure PLA, 1st scanning; b: pure PLA, 2nd scanning

c: PU-1/PLA blend, 2nd scanning; d: PU-3/PLA blend, 2nd scanning

the PLA became completely amorphous, since only its T_g (but not its T_m) was detected during the second scanning. The T_g s and T_m s of the PU/PLA blends were not affected by the small amount of PU. However, for the quenched PU/PLA samples, a small, wide exothermic cool crystallization temperature at about 130 °C, and an endothermic melting peak corresponding to the crystalline PLA, appeared during the second scanning. This occurs because of the higher mobility of the PLA chains in the presence of the flexible PU chains.

Conclusion

A maximum toughness of PLA can be achieved by introducing 5 wt % of a properly crosslinked polyurethane network (having an OH mole ratio of diol to triol of 9 to 1). The toughness thus achieved (18 MJ/m³) is an order of magnitude higher than that of pure PLA. Lower toughness occurs when the polyurethane is linear or overly crosslinked. Optimum toughness is a result of a balance between the compatibility of the semi-interpenetrating polyurethane-PLA network with PLA and the stiffness of this network.

Acknowledgment

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