

THERMAL, MECHANICAL AND MORPHOLOGICAL PROPERTIES OF POLYLACTIDE TOUGHENED WITH P[CL-co-LA] COPOLYESTERS AS BIODEGRADABLE IMPACT MODIFIERS

Jérémy Odent¹, Jean-Marie Raquez¹, Philippe Leclère², Philippe Dubois¹

¹Laboratory of Polymeric and Composite Materials (LPCM); ²Laboratory for Chemistry of Novel Materials (CMN), Center of Innovation and Research in Materials & Polymers (CIRMAP), University of Mons (UMONS), 23 Place du Parc, B-7000 Mons, Belgium

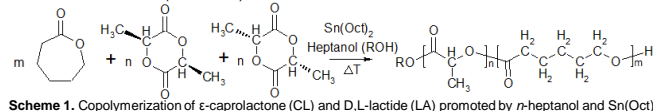
Introduction

Due to its renewability, polylactide (PLA) is the most extensively researched and utilized biopolymer as substitute to conventional petroleum-based polymers in different applications such as in automotive and electronic industries. However, the applications of PLA are currently limited by its brittle nature [1], and impact modifiers are generally required to enhance its impact strength [2]. However, most of commercially available impact modifiers specifically designed for PLA are made of ethylene-based copolymers, and therefore are not biodegradable. In this study, poly(ϵ -caprolactone-co-D,L-lactide) (P[CL-co-LA]) random copolyesters were synthesized and investigated as novel biodegradable impact modifiers for PLA. The effect of the molecular parameters of these as-synthesized copolyesters was investigated on the impact performance of PLA-based materials. The thermal, mechanical and morphological properties of the blends proved highly dependent on the morphology and average size of the rubbery microdomains dispersed throughout the PLA matrix.

Results and Discussion

Synthesis of poly(ϵ -caprolactone-co-D,L-lactide) copolyesters

The random copolymerization was carried out by ring-opening polymerization (ROP) of ϵ -caprolactone (CL) and D,L-lactide (LA) promoted by *n*-heptanol (ROH) and Sn(Oct)₂ (for initial [ROH]/[Sn(Oct)₂] and ([CL]+[LA])/ROH molar ratios of 100 and 200, respectively) at 160°C for 24h in bulk (scheme 1).



Scheme 1. Copolymerization of ϵ -caprolactone (CL) and D,L-lactide (LA) promoted by *n*-heptanol and Sn(Oct)₂.

Table 1. Molecular and thermal characteristics of random P[CL-co-LA] copolyesters with various monomers feed ratios as obtained by ROP of CL with LA using Sn(Oct)₂/*n*-heptanol.

Entry	(CL/LA) ^a (mol/mol%)	M _n ^b (g/mol)	PDI ^b	Yield ^c (%)	T _g ^d (°C)	T _m ^d (°C)	ΔH _m ^d (J/g)
1	91 / 9	34,700	2.2	98	-52	46	41
2	81 / 19	35,200	2.1	98	-47	33	0.9
3	72 / 28	33,900	2.1	99	-37	///	///
4	62 / 38	32,500	2.1	99	-25	///	///
5	51 / 49	31,500	2.1	99	-13	///	///

- a) As determined by ¹H NMR.
 b) As determined by SEC (THF + 2% NET₃) via a relative calibration with PS standards.
 c) As determined by gravimetry.
 d) As determined by DSC (under N₂ flow, heating rate of 10°C/min, second scan).

Table 1 shows that random P[CL-co-LA] copolyesters exhibit a glass transition temperature below room temperature and no melting temperature for experimental molar LA compositions higher than 28 mol%, representing an interesting feature for their use as (rubbery-like) impact modifiers [4].

Melt-blending of PLA with random copolyesters

10 wt% P[CL-co-LA] copolyesters were dispersed by melt-blending within PLA using a DSM twin-screw micro-compounder (Figure 1) at 200°C and 60 rpm for 3 min followed by compression molding at 200°C for 10 min.

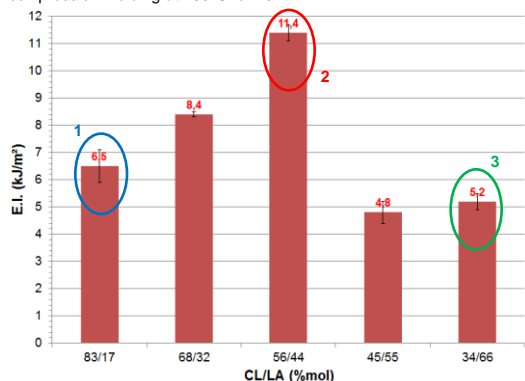


Figure 2. Influence of the comonomer content on the impact strength of PLA-based materials containing 10 wt% of P[CL-co-LA] copolyester.



Figure 1. Photo of DSM microcompounder 15 cc.

While the unfilled PLA matrix displays an impact strength of 2.7 ± 0.1 kJ/m², the introduction of P[CL-co-LA] copolyesters into PLA improves the impact strength of resulting materials, reaching a maximum at 11.4 ± 0.3 kJ/m² for the experimental composition of 28 mol% LA. However, out of this value, the improvement in toughness is less pronounced (Figure 2).

Study of the “composition-structure-properties” relationships

When toughness is considered, a better understanding of the resulting morphology must be achieved because of the great influence of morphological parameters [3, 5]. Accordingly, the mean size and related size-distribution of the microdomains generated from these as-synthesized P[CL-co-LA] copolyesters dispersed throughout the PLA matrix were correlated to the recorded impact strength values.

Table 2. Influence of the comonomer content on the mean size of dispersed rubbery microdomains and impact strength (E.I.) of PLA-based materials containing 10 wt% of P[CL-co-LA] copolyester.

Entry	(CL/LA) ^a mol%/mol%	E.I. ^b (kJ/m ²)	Mean size ^c Width / Length (nm / nm)
1	91 / 9	6.5 ± 0.6	30 / 30
2	72 / 28	11.4 ± 0.3	25 / 250-450
3	51 / 49	5.2 ± 0.3	///

- a) Experimental molar composition of the resulting copolyesters as determined by ¹H NMR.
 b) Determined by Notched Izod impact tests according to ASTM D256.
 c) Determined by AFM.

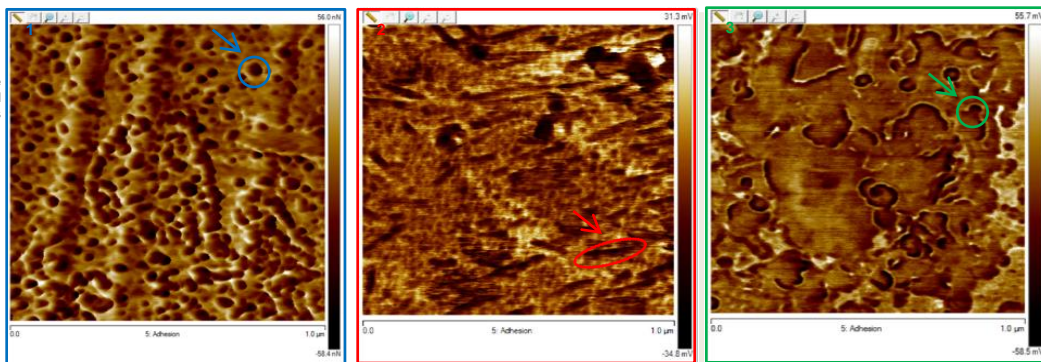


Figure 3. AFM analysis of PLA-based material containing 10% weight of P[CL-co-LA] with various monomers feed ratios (molar composition CL/LA mol%: 91/9 in right, 72/28 in middle and 51/49 in left).

As shown in Table 2, there is an optimum at 11.4 kJ/m² obtained with the P[CL-co-LA] copolyesters containing 28 mol% in LA on the impact strength of resulting PLA-based materials. AFM analyses provided some key-information with respect to the morphologies of resulting PLA materials (Figure 3). Whereas PLA-based materials with the best value in toughness show fibrils regularly dispersed within the matrix, nodular morphologies are observed out of this maximum. For nodular morphologies, a gradual disappearance of the spherical nodules is observed depending on the LA comonomer content, indicating that these copolymers are at least partially miscible with PLA matrix and induce a significant reduction in toughness.

Conclusions

It appears that the use of a P[CL-co-LA] copolyester with a molar composition of 72/28 mol% (CL/LA) gives significant improvement in the impact strength by a factor of ca. 4.2 (E.I. = 11.4 kJ/m²) with respect to neat PLA. In this regard, it came out that the comonomer content of the P[CL-co-LA] copolyesters has an effect on the resulting morphologies of PLA/P[CL-co-LA] blends, together with a significant improvement in toughness. Moreover, improvement in toughness more likely comes from the blend morphology and can be correlated to the shape and average size (and related size-distribution) of the rubbery microdomains.

References

- [1] Rasal, R.M.; Janorkar, A.V.; Hirt, D.E.; *Prog Polym Sci* **35**(3) 338-356 (2010)
- [2] Anderson, K.S.; Schreck, K.M.; Hillmyer, M.A.; *Polym Rev* **48**(1) 85-108 (2008)
- [3] Ishida, S.; Nagasaki, R.; *J Appl Polym Sci*, **113**(1) 558-566 (2009)
- [4] Bucknall, C.B.; *J Polym Sci, Part B: Polym Phys*, **45**(12) 1399-1409 (2007)
- [5] Cho, K.; Yang, J.; Yoon, S.; *J Appl Polym Sci*, **95**(3) 748-755 (2005)

Acknowledgements

This work was supported by the European Commission and Région Wallonne FEDER program (Materia Nova) and OPTI²MAT program of excellence, by the Interuniversity Attraction Pole program of the Belgian Federal Science Policy Office (PAI 6/27) and by FNRS-FRFC. J. Odent thanks F.R.I.A. for its financial support thesis grant. J.-M. Raquez is “chargé de recherche” and Ph. Leclère is “chercheur qualifié” by the F.R.S.-FNRS.

Contact : jeremy.odent@umonts.ac.be