

Supertough poly(lactide)s

C. A. P. Joziasse, M. D. C. Topp, H. Veenstra, D. W. Grijpma, and A. J. Pennings*

Department of Polymer Chemistry, University of Groningen, Nijenborgh 4,
9747 AG Groningen, The Netherlands

Summary

Semi-crystalline and amorphous copolymers of lactide and glycolide were rubber modified with degradable rubbers based on ϵ -caprolactone. The influence of crystallinity of the matrix, type of rubber and chain architecture on the impact resistance of the resulting materials was investigated. With a poly(L-lactide-co- ϵ -caprolactone) rubber semi-crystalline poly(lactide)s could be impact modified to a greater extent than amorphous non-crystallizable lactide matrices. Poly(trimethylene carbonate-co- ϵ -caprolactone) was used in blends and linear and star-shaped block copolymers which yield supertough materials that do not break in Izod notched impact testing. Rubber content appears critical around 20 weight percent, where a sharp transition is observed.

Introduction

Poly(lactic acid) is a well known biodegradable polymer which can be used for biomedical and environmental applications. Unfortunately, semi-crystalline and amorphous poly(lactide)s are brittle under tensile and bending loads and therefore not suitable for engineering applications (1,2). Furthermore, poly(lactide)s exhibit long degradation periods, ranging from 2 years for amorphous stereo-copolymers to more than 8 years for semi-crystalline PLLA (3). To enhance the degradation rate, lactides can be copolymerized with glycolide which renders a more hydrophilic copolymer that is more prone to hydrolytic chain scission (4).

A convenient and very effective way to improve the impact resistance of thermoplastic and thermosetting polymers is rubber modification (5). The success of rubber toughening depends on several factors including entanglement density of the matrix, rubber particle size, type of rubber, interfacial adhesion and phase separation characteristics between matrix and rubber (5-9).

The entanglement density ν_e is widely recognized to be the main factor governing the deformation mechanism of glassy thermoplastic polymers. This entanglement density ν_e is related directly to the molecular weight between entanglements M_e . Highly flexible chains having high ν_e values show pseudo-ductile tensile deformation behaviour, whereas less entangled polymeric materials are brittle (6-9).

For brittle glassy polymers, Wu predicts an optimum entanglement density $\nu_e = 0.1$ mmole/cc at which supertoughening can occur (8). Since poly(lactide)s, depending on composition, have ν_e in the range 0.12-0.14 mmole/cc (10,11), it is expected that rubber

* Corresponding author

toughening may be very effective. It is established that for toughening brittle amorphous polymers there is an optimum rubber particle size d_0 which is related to the entanglement density of the matrix (8). For poly(lactide)s, this optimum rubber particle size can be calculated to be in the range $d_0 \approx 0.1 - 0.3 \mu\text{m}$. To obtain phase separation of the dispersed rubbery phase on this scale, block copolymers which are known to show microphase separation could be suitable.

In this study, two types of fully biodegradable rubbers are used to modify copolymers of lactide and glycolide. ϵ -Caprolactone (ϵ -CL) was copolymerized with L-lactide (L-lac) or trimethylene carbonate (TMC) (1:1 mole ratios) to yield amorphous rubbers with $T_g = -28^\circ\text{C}$ and -45°C respectively.

ABA and star-shaped AB block copolymers (A = lactide, B = rubber) can be synthesized using multifunctional alcohols for the ring-opening polymerization (12,13). To obtain high molecular weight species and to avoid initiation by contaminants like water, the block copolymerizations must be carried out under extremely dry conditions. This includes the use of stannous acetylacetonate as a catalyst which, contrary to the commonly used stannous octoate, can be synthesized free of impurities (14).

The mutual solubility of the matrix and rubber, which can be expressed in terms of a difference in solubility parameter δ , influences phase separation and interfacial adhesion. For poly(lactide) ($\delta = 22.75$), poly(glycolide) (25.9), poly(L-lac/ ϵ -CL) (21.8) and poly(TMC/ ϵ -CL) (19.4) the solubility parameter δ can be calculated using van Krevelen type group contributions (15). Obviously the poly(TMC/ ϵ -CL) rubber is more incompatible with the poly(lactide) matrix than the poly(L-lac/ ϵ -CL) rubber.

Copolymerization of lactide with glycolide will increase this incompatibility even more. In the first part of this study blends of D,L-lactide stereo-copolymers with varying amounts of poly(L-lac/ ϵ -CL) rubber were prepared to establish the effect of crystallinity on the impact properties of the resulting material. The second part of the study deals with linear and star-shaped poly(D,L-lactide-co-glycolide) matrices modified with poly(TMC/ ϵ -CL) rubber. Again the influence of matrix crystallinity, type of rubber and chain architecture on mechanical properties and especially impact resistance was evaluated.

Experimental

Monomers were purified by standard methods. Rubbers and lactide/glycolide copolymers were bulk polymerized at 130°C for 4 days using stannous octoate or stannous acetylacetonate as a catalyst. Block copolymers were prepared by dissolving hydroxyl-terminated linear or star-shaped rubbers in the lactide melt at 130°C and subsequent polymerization. Monomer conversions were checked with 200 MHz $^1\text{H-NMR}$.

Polymer molecular weights were determined by GPC on THF- solutions at 25°C relative to poly(styrene) standards on a Spectra Physics AS1000 (PSS 5μ SDV 10^3\AA and 10^5\AA , Shodex RI71, Viskotek H502).

Blends were prepared by precipitation of a homogeneous chloroform solution of lactide/glycolide matrix and rubber in ethanol. The precipitate was subsequently vacuum dried at 40°C . Blend compositions were verified by 200 MHz $^1\text{H-NMR}$.

Samples for mechanical testing were compression moulded from the dried precipitates at 150°C (amorphous) to 200°C (semi-crystalline). Glycolide containing samples were moulded between Teflon sheets to prevent degradation during moulding.

Compression moulded specimens were tested according to ASTM D1708 at room

temperature on an Instron 4701 tensile tester operated at a crosshead speed of 10 mm/min. Impact tests were performed on Dynstat unnotched (DIN 53453) and Izod notched (ASTM D256-56) samples using a Zwick pendulum apparatus equipped with 0.5 to 4 J hammers. DMTA measurements (dual cantilever mode, 4x60x2 mm samples) were performed on a Rheometrics RSAII apparatus at a heating rate of 5°C/min. at 1 Hz. Thermal properties of the polymers and blends were evaluated on 5-10 mg samples on a Perkin Elmer DSC7 with a scan speed of 10°C/min.

Phase contrast microscopic evaluation of the blends was performed with an Olympus microscope. Samples were spin-coated from chloroform solutions and dried at 40°C *in vacuo*.

Results and discussion

Much research has been aimed at semi-crystalline poly(L-lactide) (PLLA) which is a biodegradable polyester prepared by ring opening polymerization of the cyclic monomer. Although PLLA has interesting (mechanical) properties, crystallinity can be a drawback in biomedical applications where inflammatory reactions can occur (3). The crystallinity of PLLA can be reduced by quenching from the melt, but then recrystallization can occur during degradation. Copolymerization of L-lactide (L-lac) with other monomers, like ϵ -caprolactone (ϵ -CL), trimethylenecarbonate (TMC) or D-lactide (D-lac) also reduces crystallinity. Incorporation of more than 15 mole percent D-lactide yields an amorphous non-crystallizable polymer.

The effect of crystallinity on the impact properties of rubber modified D,L-lactide copolymers was evaluated. Copolymers with three L- to D-lactide ratios (100/0, 95/5 and 50/50) were solution blended with poly(L-lac/ ϵ -CL) rubber ($T_g = -28^\circ\text{C}$).

In Figure 1, Dynstat impact strengths are plotted as a function of the weight percentage poly(L-lac/ ϵ -CL) rubber. For the amorphous 50/50 composition, Dynstat values increase

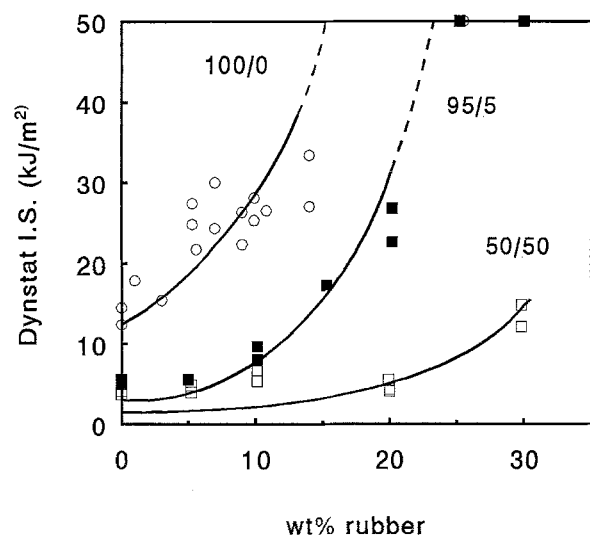


Figure 1. Dynstat impact strengths of poly(lactide) blends with poly(L-lac/ ϵ -CL) rubber.

from 5 kJ/m² for the unmodified matrix to 15 kJ/m² for the blends containing 30 wt% rubber. Unmodified semi-crystalline PLLA (100/0) shows a higher Dynstat I.S. than the amorphous (50/50) composition and responds remarkably well to rubber modification. At rubber contents of more than 15 wt%, the samples do not break upon testing. The composition with intermediate crystallinity (95/5) shows intermediate response to rubber toughening. Blending with more than 20 wt% rubber again yields extremely tough materials. Since the poly(L-lac/ ϵ -CL) rubber contains L-lactide

Table 1. Mechanical properties of compression moulded poly(TMC/ ϵ -CL) rubber modified poly(lactide) and poly(lactide-co-glycolide) compositions.

Matrix composition	Type of modification	Rubber contents (wt%)	σ_m (MPa)	ϵ_b (%)	Izod I.S. (notched) (J/m)
100/0/0 (semi-crystalline)					
	A	0	72	8	83
	A + B blend	20	38	11	420
85/15/0 (amorphous)					
	A	0	57	7	41
	A + B blend	20	36	130	405
	triblock ABA	20	41	120	450
	4-star AB	20	26	600	-
82/15/3 (amorphous)					
	A	0	57	5	55
	A + B blend	20	33	210	no break
	A + B blend	30	27	220	no break

sequences, it can be reasoned that these are miscible with the poly(lactide) matrix. Although this could enhance interfacial adhesion between rubber and matrix, adequate phase separation might be suppressed. Therefore, further research was aimed at the development of a less compatible but still biodegradable rubber. Trimethylene carbonate and ϵ -caprolactone (50/50 mole ratio) were copolymerized to yield a high molecular weight, low T_g (-45°C) rubber. This rubber was solution blended with some lactide/glycolide copolymers. Glycolide was added as a comonomer to increase the degradation rate of the resulting composite. Furthermore, triblock ABA and 4-armed star-shaped AB block copolymers with poly(D,L-lactide) were prepared. At first the rubber B is polymerized as the central (star)block that acts as a macro-initiator for the subsequent polymerization of the matrix A which is amorphous and has an 85L/15D-lactide composition.

In Table 1, mechanical data are listed for compression moulded test specimens. As for the Dynstat unnotched impact strength (Figure 1), the unmodified semi-crystalline PLLA (100/0) has a higher Izod notched impact strength than the unmodified amorphous 85/15 and 82/15/3 lactide copolymers. Both the semi-crystalline PLLA (100/0) and amorphous (85/15) and (82/15/3) matrices respond very favourably to rubber toughening. Blending with 20 wt% rubber results in a five- to ten-fold increase in Izod impact strength to exceptionally high values in the order of 400-420 J/m. This phenomenon is also observed for the linear and star-shaped block copolymers, which show enormously

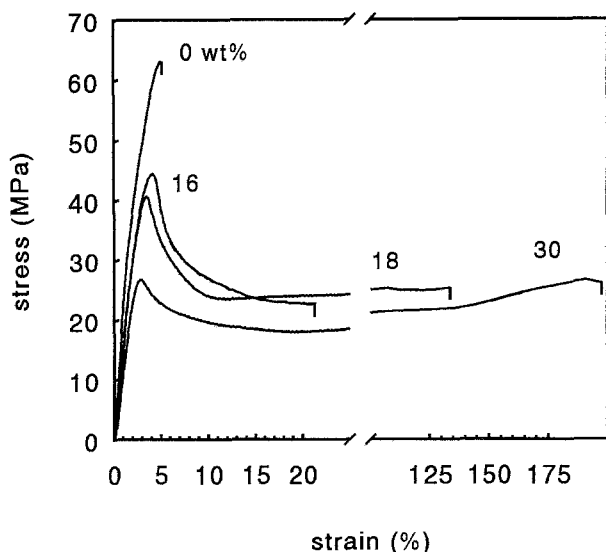


Figure 2. Stress-strain curves for blends of a lactide/glycolide copolymer with different amounts of poly(TMC/ ϵ -CL) rubber.

break (ϵ_b) is strongly increased accompanied by a reduction in yield stress and Young's modulus for higher rubber contents. Upon tensile testing, massive stress-whitening throughout the specimens is observed, followed by necking at higher elongations. The

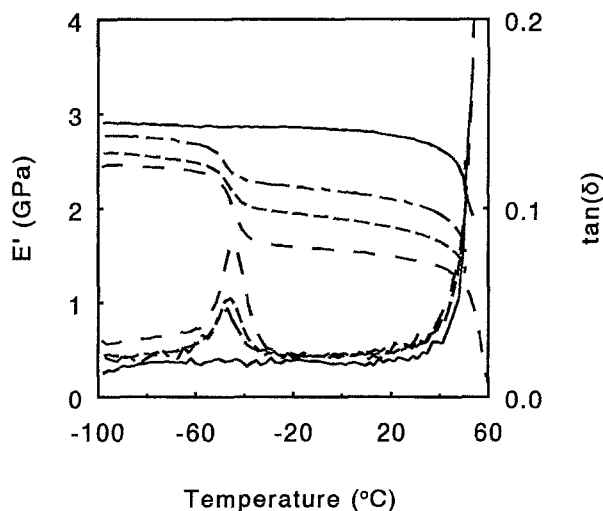


Figure 3. DMTA-curves (E' and $\tan(\delta)$ loss peaks) for blends of a lactide/glycolide copolymer with different amounts of poly(TMC/ ϵ -CL) rubber (see Figure 2).

enhanced impact strengths and elongations to break (ϵ_b). Furthermore, the mechanical data in Table 1 suggest that it be very well possible to make tough composites with glycolide containing matrices if 20 wt% or more rubber is blended. At a rubber load of 30 wt%, Izod notched specimens do not break at the highest impact energy available (1000 J/m) showing supertough behaviour.

In Figure 2, stress-strain curves for blends containing 3 wt% glycolide in the matrix are plotted for several poly(TMC/ ϵ -CL) rubber contents. The trends observed are typical for rubber toughened thermoplastics like HIPS and ABS. Elongation at break (ϵ_b) is strongly increased accompanied by a reduction in yield stress and Young's modulus for higher rubber contents. Upon tensile testing, massive stress-whitening throughout the specimens is observed, followed by necking at higher elongations. The occurrence of a combination of the two basic deformation mechanisms, multiple crazing and multiple shear yielding, could explain the exceptionally high impact energies reported in Table 1 (8).

As noted before, adequate phase separation between matrix and dispersed rubber is required for effective rubber toughening.

Figure 3 shows DMTA-curves corresponding to the same blends as plotted in Figure 2. Both the T_g of the rubber (-45°C) and that of the poly(D,L-lactide-co-glycolide) matrix are clearly discernable by well separated $\tan(\delta)$ loss peaks, indicating good phase separation. This is confirmed

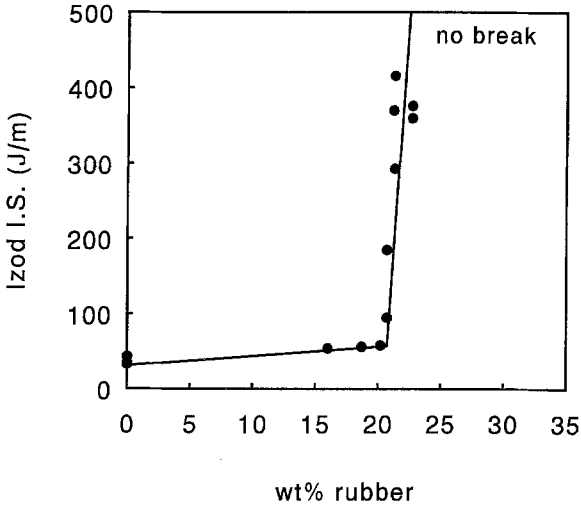


Figure 4. Izod notched impact strengths for blends of lactide copolymers with 0-10 wt% glycolide vs. poly(TMC/ ϵ -CL) rubber contents.

by DSC where two separate glass transitions are found corresponding to the T_g 's of the rubber and matrix. Copolymerization of D,L-lactide with glycolide yields a copolymer with a higher degradation rate (4). The degradation rate is easily tunable by adjusting the amount of glycolide comonomer. Since these terpolymers have promising impact properties (Table 1), a series of copolymers containing 0 - 10 wt% glycolide was synthesized and solution blended with poly(TMC/ ϵ -CL) rubber. In Figure 4, Izod notched impact data are plotted as a function of the amount of dispersed rubber. These brittle

amorphous matrices show moderate improvement of Izod notched impact strengths up to 20 wt% rubber. At 20 wt% rubber, the curve shows a sharp transition point. Addition of more than 20 wt% rubber results in an enormously improved impact resistance. As noted before (data not included in Figure 4), blends containing more than 25 wt% rubber do not break upon impact testing. Furthermore, no significant effect of the amount of glycolide copolymerized in the matrix on the impact properties can be detected.

In recent years, many theories have been developed to explain the mechanism(s) of rubber toughening in thermoplastics and thermosets. These include craze initiation and termination on rubber particles (16,17), matrix/rubber adhesion and rubber cavitation (9,18) and critical interparticle distance (ID_c) or critical ligament thickness (19-21). The impact behaviour of rubber toughened poly(lactide)s shows similarities with that of rubber toughened PS-PPE blends and epoxies where strain at break and tensile toughness also increase dramatically beyond a certain rubber load level (19). Figure 5 shows a phase contrast micrograph of a 20 wt% rubber blend. Rubber particles are clearly observed as

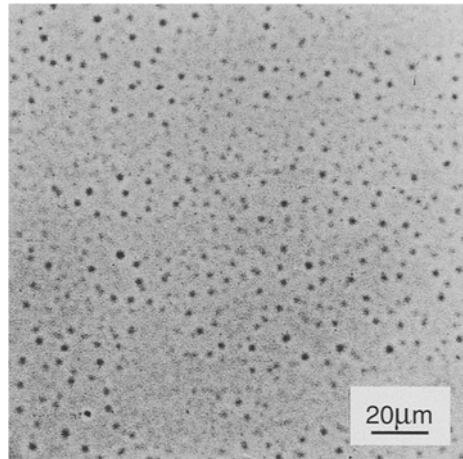


Figure 5. Phase contrast micrograph of a lactide/glycolide matrix blended with 20 wt% poly(TMC/ ϵ -CL) rubber.

dark spheres and have diameters in the range 1-2 μm . This is one order of magnitude larger than the calculated value for optimum impact improvement $d_0 = 0.1\text{-}0.3 \mu\text{m}$ for poly(lactide)s (8). Since these blends were prepared from homogeneous chloroform solutions of matrix and rubber, compression moulding temperature and cooling speed could influence morphology and therefore impact properties. Although the achievement of supertoughening of poly(lactide)s is a very promising development, it should be clear that further research on the factors determining effective impact improvement has to be carried out. Furthermore, research on the degradation rate of blends containing glycolide is in progress and will be published in forthcoming papers.

Conclusions

With this study, we have established that poly(lactide) copolymers can be rubber toughened very effectively with two types of fully biodegradable rubbers. Crystallinity of the poly(lactide) matrix has a pronounced positive effect on the toughness attained at a certain rubber level. All poly(lactide) matrices studied here, including the more rapidly degrading copolymers with glycolide, could be supertoughened at rubber contents $>25 \text{ wt}\%$. The amount of glycolide incorporated has a negligible effect on the mechanical (impact) properties.

The exact mechanism responsible for the observed sharp increase of toughness around 20 $\text{wt}\%$ rubber remains unclear. For the time being, the toughening mechanism involving a critical ligament thickness (ID_c) seems the most appropriate. Further research on blend morphology is in progress.

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