

Miscibility, Morphology and Mechanical Properties of Rubber-Modified Biodegradable Poly(ester-urethanes)

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ABSTRACT: Biodegradable, lactic acid based amorphous poly(ester-urethane)s (PEU) were modified with poly(L-lactic acid-co- ϵ -caprolactone-urethane) elastomer (P(LA/CL)U) by melt blending. The phase separation of P(LA/CL)U elastomer with three different ϵ -caprolactone (CL) compositions (CL content 30, 50, and 70 mol %) and the mechanical properties of the resulting impact-modified linear and branched PEU were investigated. The amounts of P(LA/CL)U elastomer in the PEU blends were 10, 15, 20, and 30 wt %. Dynamic mechanical thermal analysis (DMTA) of the blends with P(LA50/CL50)U and P(LA30/CL70)U elastomers revealed separate glass transition temperatures for rubber and matrix, indicating phase separation. No phase separation was found for P(LA70/CL30)U elastomer. The effect of mixing rate and temperature during processing on composite properties was tested by blending P(LA30/CL70)U rubber with PEU under various processing conditions. Impact modification studies were also made with two P(LA30/CL70)U elastomers having different amounts of functional groups. The influence of end-functionalization and cross-linking on mechanical properties was investigated in blends containing PEU and 15 wt % of these elastomers. Scanning electron microscopy (SEM) showed the morphology to change dramatically with increase in the degree of cross-linking in the rubber. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1074–1084, 2000

Key words: lactic acid; poly(ester-urethane); impact modification; blends; miscibility

INTRODUCTION

The chemical and phase structures are major determinants of the properties of biodegradable polymers.¹ The structures and thereby the physical and mechanical properties of lactic acid based polymers can be influenced through changes in polymerization and processing conditions,^{2–5} variation of the copolymer composition,^{6–9} and by blending.^{10–12} Lactic acid polymers are well-known biodegradable aliphatic polyesters that

are increasingly being used in medical and industrial applications. In addition to ring-opening polymerization of lactide, we have described an efficient route to convert lactic acid to a high-molecular-weight thermoplastic poly(ester-urethane) (PEU).^{13,14} Unfortunately, semicrystalline and amorphous lactic acid polymers tend to be brittle and impact-sensitive, and this could restrict their wider application.^{15,16}

One successful modification routine for improving the impact resistance of polymers is rubber toughening. The resulting composites show significant improvements in impact strength, elongation at break, work to break, and fracture toughness with only slight reductions in modulus

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and tensile strength. There is an optimum rubber particle size for toughening brittle amorphous polymers that is related to the entanglement density of the matrix. Another important factor is the adhesion between matrix and rubber. The two factors are interrelated; changing one will change the other. In any study of these two factors, therefore, they must be carefully controlled. Blends undergo a sharp tough-brittle transition when the interparticle distance is at a critical value. Moreover, this critical interparticle distance has been shown to be the most important parameter determining whether a blend will be tough or brittle. The brittle-ductile (craze-yield) behavior of polymers and blends depends on both extrinsic and intrinsic variables. Extrinsic variables include deformation rate, temperature, stress state, notch, and specimen geometry, whereas the intrinsic variables include phase morphology and chain structure. Under a given set of extrinsic conditions, different polymers or blends may behave differently because they have different phase morphologies and chain structures.¹⁷⁻¹⁹

Adequate phase separation between matrix and dispersed rubber is required for effective rubber toughening. Phase separation between hard and flexible components is important because a rubber that becomes dissolved in the matrix acts as a plasticizer, reducing the glass transition temperature and stiffness of the matrix without increasing its toughness. The strength of the bond at the rubber-matrix interface is another important parameter in rubber toughening, and the ideal rubber is neither completely compatible nor completely incompatible.²⁰ The transesterification in polyesters is a useful reaction for blending noncompatible polyesters²¹ and could also be responsible for some reactions at the rubber-matrix interface.

Usually, toughening of amorphous and brittle polymers by dispersing a discrete rubber phase in the glassy matrix is accomplished by blending the matrix with up to 20 wt % of an incompatible rubber. Grafting of the rubber onto the matrix polymer or the use of a compatibilizer influences the size of the discrete rubber particles and their adhesion to the matrix. Grijpma et al.²² have reported the synthesis of star-shaped rubbers that can be block-copolymerized with glassy and brittle lactide giving phase-separated, chemically bonded rubber particle in an amorphous poly(lactide) glass. Incorporation of more than 15 wt % of

rubber in these star-block copolymers has resulted in materials with excellent properties.

Wu et al.²³ have designed efficient impact modifiers for lowering the ductile-brittle transition temperature of thermoplastic blends by modelling the stress distribution near the notch of an Izod impact test sample and the nature of the stresses in spherical, particle-filled polymers. The model considers the inhomogeneity of a soft phase inside a relatively rigid phase, particle interaction, and the effects of thermal residual stresses imposed as a consequence of processing and differences in matrix and particle thermal coefficients of expansion. The model predicts the importance of the material properties of the rubbery phase in the determination of the impact performance of the blend. It is specific to spherical particles and does not consider the energy dissipation or mechanisms after failure initiation. The elements of shape and shape control are other important factors to consider in selecting thermoplastic elastomers as impact modifiers. The relationship between the size and volume fraction of particles should be derived by statistical means. The effect of the distribution of rubber particles on the impact properties has been assumed to be that a more uniform distribution of particles results in better impact performance. However, recent publications have indicated that for certain polymers, a co-continuous structure rather than uniformly distributed particle morphology may lead to higher impact toughness.²⁴

In a previous study we reported the impact modification of poly(ester-urethane) with copolymers of L-lactide and ϵ -caprolactone synthesized by ring-opening polymerization, and with poly(L-lactic acid-co- ϵ -caprolactone-urethane) prepared by direct polycondensation of L-lactic acid and ϵ -caprolactone followed by urethane bonding.¹⁵ In the present work, linear and branched amorphous PEUs were modified through blending with elastic biodegradable poly(L-lactic acid-co- ϵ -caprolactone-urethane). The comonomer content and degree of cross-linking in the urethane were adjusted so that the rubber possessed a solubility parameter sufficiently different from the matrix polymer to ensure a fine second-phase dispersion, yet close enough to promote adequate adhesion of the rubber particles to the matrix. Our objective was to design and prepare a series of polyurethane blends where the multiphase nature of the system would afford the required versatility in mechanical properties. The miscibility of the

blends, dispersion of the rubbery phase, and mechanical properties of the blends are characterized.

EXPERIMENTAL

Materials

PEU matrices were polymerized in a two-step process for lactic acid polymerization: in the first step the lactic acid was condensation polymerized to low-molecular-weight prepolymer and in the second step the molecular weight was increased with chain extender. The hydroxyl terminated prepolymer was prepared through condensation polymerization of L-lactic acid (initially 88% L-lactic acid in water, purified by distillation; ADM: Archer Daniels Midland Co., Decatur, Illinois, USA) and 2 mol % of 1,4-butanediol (Fluka Chemie AG, Buchs, Switzerland). Sn(II)octoate (Sigma Chemical Co., St. Louis, MO, USA) was used as a polycondensation catalyst. Linking polymerization of the prepolymers was done in a bench scale batch reactor or a twin-screw extruder by using 1,6-hexamethylene diisocyanate (Fluka) as the chain extender. The synthesis and characterization of PEU have been described in detail elsewhere.^{13,14} Poly(L-lactic acid-co- ϵ -caprolactone-urethane) elastomers were synthesized in a similar two-step process, but here the ϵ -caprolactone (Fluka) was used as a comonomer in the synthesis of prepolymer. Preparation, structure, and properties of P(LA/CL)U have been described earlier.²⁵ The numbers in parenthesis below describe the monomer composition in the feed in mol %. All polymers were used without further purification.

Blending and Molding

PEUa and PEUb blends were processed in a Haake Rheomix 600 batch mixer equipped with a Haake Rheocord 9000 controlling unit for 5 min at 140°C and 75 rpm. Test specimens for dynamic mechanical thermal analysis (DMTA) and impact and tensile testing were prepared by compression molding (Darragon, France) at 160°C with 6-min melting, 4-min compression, and 3-min cooling from blends processed in a Haake batch mixer.

The PEUc blends were prepared with a co-rotating twin-screw midiextruder (DSM Research, Netherlands; screw length 150 mm),

equipped with a back-flow channel that allows it to be operated in batch wise. The mixing time was 3 min, after which the blend was injection molded with a mini-injection molding machine into tensile and impact test specimens. The melt temperature in the injection molding was 140°C and the temperature of the mold was 30°C.

Molecular Weight Determination

Molecular weights were determined by room temperature size exclusion chromatography (SEC) (Waters System Interface module, Waters 510 HPLC Pump, Waters 410 Differential Refractometer, Waters 700 Satellite Wisp, and four American Polymer Standards Corp. gel columns: 10⁴ Å, 10⁵ Å, 10³ Å, and 100 Å connected in series). Chloroform was used as solvent and eluent. The samples were filtered through a 0.5 μ m Millex SR filter. The injected volume was 200 μ l and the flow rate 1 mL/min. Monodisperse polystyrene standards were used for primary calibration, which means that the Mark-Houwink constants were not used.

Gel Content

The degree of cross-linking (i.e., gel content) of the blends was measured by extracting the soluble phase into acetone in a Soxhlet apparatus for 20 h (ASTM D 2765). The gel content was determined as the portion, in percent, of the inextractable material divided by the total weight of the original sample.

Thermal Analysis

Glass transition temperatures (T_g) were measured by DMTA (RSA, Rheometrics). The samples (2mm*5mm*53mm) were sawn from the compression molded plates. Dual cantilever geometry was used and the temperature was raised 2°C/min (6.3 Hz). T_g was not determined as the peak of tan because the materials softened near T_g and the values of storage and loss modulus (E' and E'') dropped near to zero when tan reached the peak value. Instead, the peak of E'' was used to determine T_g . In PEUc blends, the DMTA measurements were performed on a Perkin Elmer 7 Series Thermal Analysis System instrument. The measurements were made using the three-point bending method in a temperature range of -70 to 70°C at a rate of 4°C/min. All measurements were performed at 1 Hz. Thermal properties of the matrix

Table I Description of Poly(ester-urethane) Matrices

Polymer	SEC			DSC	
	\bar{M}_n (g/mol)	\bar{M}_w (g/mol)	MWD	T_g (°C)	T_m (°C)
PEUa	46 000	79 000	1.7	43	—
PEUb	64 000	226 000	3.5	45	—
PEUc	41 000	82 000	2.0	42	—

and elastomers were determined with a Mettler Tolero Star DSC821 differential scanning calorimeter (DSC), in a temperature range of -80 to 180°C and a heating and cooling rate of $10^\circ\text{C}/\text{min}$. Glass transition temperatures were recorded during the second heating scan to ensure that thermal histories were the same.

Tensile Testing

The mechanical values for the polymers were measured for parallel air-conditioned specimens that had been left for 72 h at 23°C and 50% relative humidity. Tensile properties were characterized with an Instron 4204 tensile testing machine. Cross-head speed was 5 mm/min and the specimen type was 1BA according to the standard ISO/R 527-1993(E). It should be noted that the rectangular samples of PEUa and PEUb blends were sawn from compression molded plates and their dimensions (3mm*10mm*90mm) were not according to the standard.

Impact Strength

The toughness of the materials was characterized by Charpy impact tests of unnotched samples. The tests were carried out with a pendulum-type impact tester (Zwick, Germany, pendulum of 0.5, 1, or 4 J depending on the sample) at room temperature following the standard ISO 179-1982(E). The samples (4mm*6mm*50mm) were sawn from the compression molded plates. Impact tests of PEUc blend specimens with dimensions of $4 \times 6 \times 50 \text{ mm}^3$ were carried out according to ISO 179/2D f standard.

Morphology

The morphology of cross-section of the cryogenically fractured samples was examined by scanning electron microscopy (SEM) (Zeiss Digital

Scanning Microscope 962). SEM micrographs were taken after coating of the surfaces with a thin layer (10–20nm) of platinum (Agar Sputter Coater).

RESULTS AND DISCUSSION

The first part of this section describes the modification of PEU with rubbery materials containing different amount of comonomer (CL), as well as the effect of incorporating increasing amounts of the rubbers. The phase separation and mechanical properties of the blends were studied under constant blending conditions. Two amorphous biodegradable, PEUa and PEUb, were used as matrix. The PEU were polymerized by condensation polymerization of L-lactic acid followed by an increase in the molecular weight through urethane linking in batch reactor. When the diisocyanate used as chain extender is added in excess, the rate of side reactions increases leading to branching of the polymer.¹⁴ Thus, PEUa was linear and PEUb a branched poly(ester-urethane). The properties are summarized in Table I.

A third matrix, linear PEUc, whose linking polymerization was done in a twin-screw extruder, was used in the second part of the work where the interest was the effects of temperature and shear forces during blending and the effect of the degree of cross-linking of the rubber on the mechanical properties of the blends. Biodegradable aliphatic polyesters are very sensitive to degrade during processing, especially at high temperatures and shear rates. Transesterification reactions also are typical of biodegradable polyesters and may influence the interactions between matrix and rubber.

Table II Properties of Blends of Linear PEU

Blends (wt % Matrix/wt % Rubber)	Gel Content (%)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)	Charpy Impact Strength (kJ/m ²)
PEUa (processed)	0	2500 ± 70	38 ± 2	1.9 ± 0.1	8.3 ± 0.8
PEUa 90/[P(LA70/CL30)U]10	0	1920 ± 70	33 ± 3	2.6 ± 0.4	6.7 ± 0.9
PEUa 85/[P(LA70/CL30)U]15	0	1570 ± 90	31 ± 2	18 ± 5	8.6 ± 0.4
PEUa 80/[P(LA70/CL30)U]20	0.2	1330 ± 100	25 ± 3	>100	13 ± 2
PEUa 70/[P(LA70/CL30)U]30	11.0	740 ± 50	12 ± 1	>100	NB
PEUa 90/[P(LA50/CL50)U]10	0.1	1880 ± 60	31 ± 3	3.8 ± 1.4	7.2 ± 1.7
PEUa 85/[P(LA50/CL50)U]15	0.2	1570 ± 100	29 ± 1	6.8 ± 0.5	15 ± 3
PEUa 80/[P(LA50/CL50)U]20	7.6	1490 ± 40	26 ± 1	9.3 ± 1.0	65 ± 1 ¹ /NB
PEUa 70/[P(LA50/CL50)U]30	13.9	1230 ± 40	22 ± 1	13 ± 3	NB
PEUa 90/[P(LA30/CL70)U]10	2.6	1910 ± 50	31 ± 1	3.1 ± 0.6	7.3 ± 2.1
PEUa 85/[P(LA30/CL70)U]15	7.2	1680 ± 30	28 ± 1	3.6 ± 1.7	18 ± 1
PEUa 80/[P(LA30/CL70)U]20	11.5	1430 ± 20	23 ± 1	10 ± 2	63 ± 3 ¹
PEUa 70/[P(LA30/CL70)U]30	17.4	1170 ± 60	19 ± 1	15 ± 2	NB

NB not broken.

¹ Partially broken.

Effect of ϵ -Caprolactone Content in the Rubber Phase

The phase separation of P(LA/CL)U elastomer with three different CL compositions and the material properties of the resulting impact-modified PEU were studied. Two different PEU matrices were investigated: PEUa a linear and PEUb a branched poly(ester-urethane). Neat PEUa and PEUb were processed in the batch mixer as reference. The amounts of P(LA/CL)U elastomers incorporated in the PEU blends were 10, 15, 20, and 30 wt %. Because the specimens for mechanical testing were cut from plates prepared by compression molding, the level of the mechanical properties reported here should be considered as suitable for comparison between samples but otherwise only indicative.

Urethane elastomers were prepared from copolymers of L-lactic acid (LA) and ϵ -caprolactone with CL contents of 30, 50, and 70 mol %. The composition and structure of the copolymers were determined by ¹³C NMR analysis of the carbonyl signals. Exact compositions of (LA70/CL30), (LA50/CL50), and (LA30/CL70) copolymers were 68.5/31.5, 47.9/52.1, and 27.0/73.0 mol %/mol %; average lengths of the lactyl blocks were 3.3, 2.0, and 1.4; and average block lengths of caprolactone were 1.5, 2.1, and 3.4, respectively. In urethane linking of (LA/CL) prepolymer a slight excess of diisocyanate was used to produce polymer

that was at least partly isocyanate terminated. Thus, in principle, these functionalized elastomers can react with the matrix during processing to give an improved interfacial strength.²⁶ The glass transition temperature T_g of P(LA/CL)U elastomer measured by DSC decreased with increasing ϵ -caprolactone content in the copolymer, from -2°C in P(LA70/CL30)U, to -26°C in P(LA50/CL50)U, and to -45°C in P(LA30/CL70)U. All P(LA/CL)Us exhibited equally high elastomeric tensile properties with maximum stress of 2 MPa and with maximum strain over 1000%.

Tables II and III describe the mechanical properties and gel content of PEU blends. The gel content was 0% in neat PEU polymers, but it increased with CL content in the elastomer and with increasing elastomer content in the composite. The increase in gel content was assumed to be due to the further reactions of isocyanate groups in elastomer phase or at the elastomer-matrix interface.

Rubber toughening is achieved by phase separation in the blend, which yields discrete rubber particles dispersed in a continuous matrix phase. This means that rubber-toughened plastics normally exhibit two glass transition temperatures, a primary transition above room temperature due to the matrix and a secondary transition below room temperature due to the dispersed rubber

Table III Properties of Blends of Branched PEU

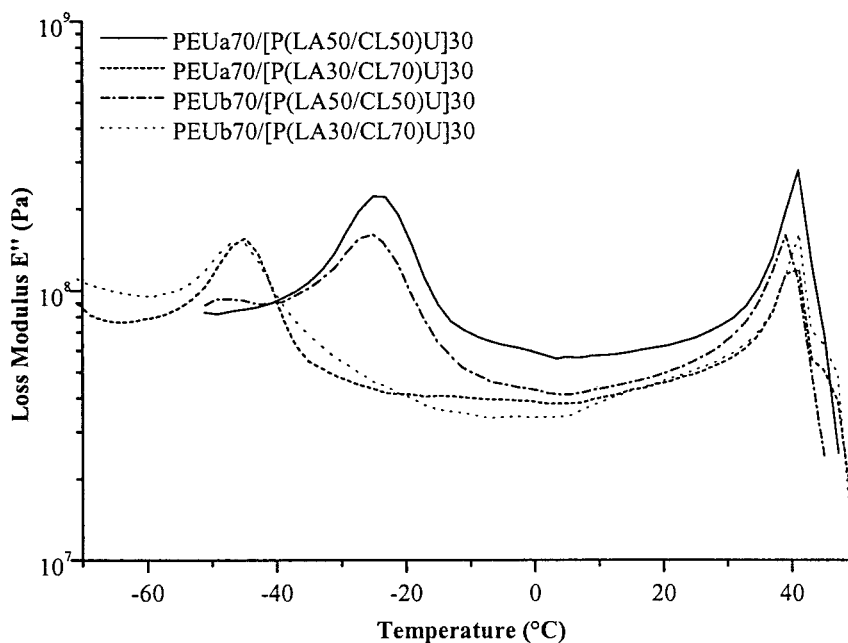
Blends (wt % Matrix/wt % Rubber)	Gel Content (%)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)	Charpy Impact Strength (kJ/m ²)
PEUb (processed)	0	2200 ± 100	39 ± 1	2.5 ± 0.2	7.3 ± 1.1
PEUb 90/[P(LA70/CL30)U]10	0	1940 ± 60	37 ± 4	3.1 ± 0.6	7.8 ± 0.5
PEUb 85/[P(LA70/CL30)U]15	0	1380 ± 90	23 ± 2	>100	8.5 ± 1.4
PEUb 80/[P(LA70/CL30)U]20	3.7	1180 ± 92	19 ± 2	>100	9.6 ± 0.8
PEUb 70/[P(LA70/CL30)U]30	17.2	680 ± 60	11 ± 1	>100	NB
PEUb 90/[P(LA50/CL50)U]10	0.8	1870 ± 100	35 ± 2	6.8 ± 1.4	6.1 ± 1.3
PEUb 85/[P(LA50/CL50)U]15	4.4	1650 ± 40	32 ± 1	21 ± 4	10 ± 1
PEUb 80/[P(LA50/CL50)U]20	6.5	1490 ± 40	30 ± 1	79 ± 21	20 ± 1/36 ± 7 ¹⁾
PEUb 70/[P(LA50/CL50)U]30	11.6	1170 ± 20	23 ± 1	59 ± 14	NB
PEUb 90/[P(LA30/CL70)U]10	2.6	1890 ± 30	34 ± 1	10 ± 1	7.2 ± 0.8
PEUb 85/[P(LA30/CL70)U]15	6.7	1690 ± 50	32 ± 1	23 ± 2	19 ± 3
PEUb 80/[P(LA30/CL70)U]20	12.4	1450 ± 70	28 ± 1	11 ± 3	29 ± 3/52 ± 10 ¹⁾
PEUb 70/[P(LA30/CL70)U]30	18.6	1220 ± 50	19 ± 1	44 ± 18	NB

NB not broken.

¹⁾ Partially broken.

phase.¹⁷ DMTA of the blends of PEUa and PEUb with P(LA50/CL50)U and P(LA30/CL70)U elastomers exhibited separated T_g s for rubber and matrix, indicating phase separation. As can be seen in Figure 1, the loss modulus peak of P(LA50/CL50)U was at approximately -25°C whereas that of P(LA30/CL70)U was at -45°C ,

and the T_g of the matrices was at about 40°C . The T_g of neat PEUa was 43°C and that of PEUb was 45°C . In contrast, P(LA70/CL30)U elastomer was at least partly miscible with PEU. Only a very small peak at about 11°C was seen for blend with rubber contents of 20 and 30 wt %. SEM analysis also revealed this miscibility, without any clearly


Figure 1 DMTA curves of linear PEUa and branched PEUb heterophase rubber blends.

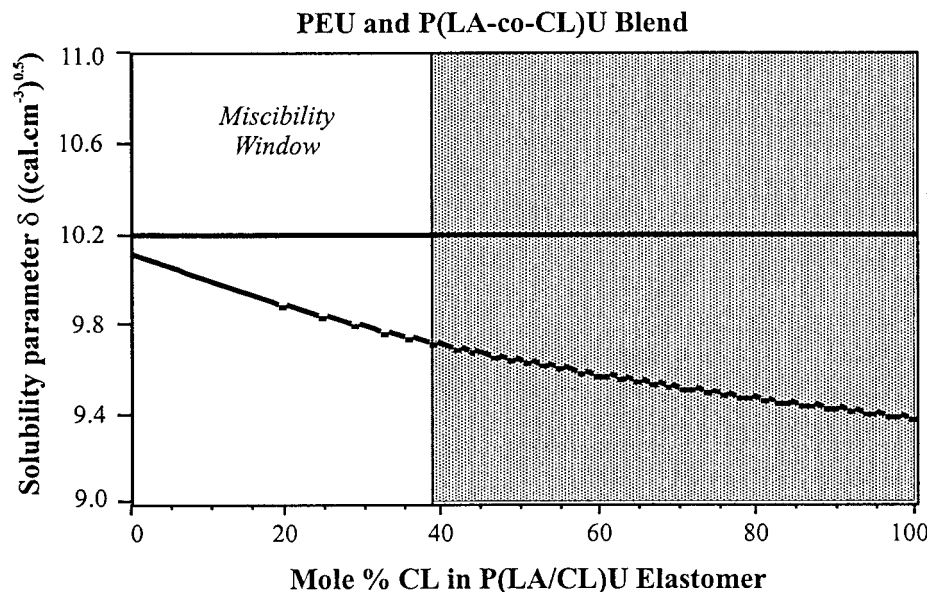


Figure 2 Calculated solubility parameter of P(LA/CL)U as a function of mole percent of ϵ -caprolactone (CL). (The line at $\delta = 10.2$ shows the parameter δ for PEU).

dispersed rubber particles (unpublished data). P(LA70/CL30)U was even more miscible with branched PEU: the rubber T_g was not found even at high rubber loadings.

Mutual solubility of the matrix and rubber, which can be expressed as the difference in their solubility parameters, influences the phase separation and interfacial adhesion.²⁷ In our blends, the partial compatibility was assumed to be due to the similar chemical structures of the blend components. The solubility parameters for PEU and P(LA/CL)U were calculated by Coleman et al.²⁸ and are displayed in Figure 2. Increasing the amount of ϵ -caprolactone in the elastomer decreased the solubility parameter and increased the phase separation. The calculations predict that PEU should be immiscible with P(LA/CL)U elastomer that contains about 40–100 mol % of ϵ -caprolactone.

Although phase separation was found, also interaction was observed at the rubber-matrix interface. Partial mixing of the rubber and matrix phases causes the secondary loss peak to move upwards and the primary loss peak to move downwards in temperature, and as the two polymers approach complete miscibility their loss peaks merge into one. The T_g s of the PEU matrix and P(LA/CL)U rubber moved slightly towards each other. In the PEUa/P(LA30/CL70)U blend, for example, T_g of the rubber increased from -46

to -45°C , whereas the T_g of PEU decreased from 43 to 40°C with increasing rubber content from 10 to 30 wt %. The T_g of the branched PEU deviated even more from the initial value. In the PEU_b70/[P(LA70/CL30)U]30 blend, T_g decreased to as low as 32°C due to miscibility, and in the heterophase structures with P(LA50/CL50)U and P(LA30/CL70)U to 39°C and 4°C , respectively. Small differences between linear and branched PEUs were also noticed in T_g of the rubber phase. The T_g of branched PEU blends was mostly at slightly lower level. In PEU/P(LA50/CL50)U and PEU/P(LA30/CL70)U blends, SEM analysis revealed round dispersed rubber particles with linear PEU, but island-like areas with branched PEU (unpublished data).

As a general pattern, addition of the rubber increased the impact strength markedly, in particular at higher rubber loadings. Tensile modulus and strength, in turn, showed a downward trend as a function of rubber concentration. The toughening effect of P(LA50/CL50)U and P(LA30/CL70)U rubbers was about the same, which suggests that formation of a heterophase structure is the factor setting them apart from P(LA70/CL30)U rubber. P(LA70/CL30)U softened the PEU, causing a greater decrease in the tensile modulus and strength, and the strain at break reached values over 100%. The tensile properties of the blends obtained from linear and branched

PEU were closely similar. For example, at rubber content of 20%, P(LA50/CL50)U and P(LA30/CL70)U rubbers softened branched PEU more than linear PEU indicating less improvement in impact strength but greater increase in strain.

Effect of Processing Conditions

Processing conditions during compounding and molding may be important factors affecting the performance of polymer blends. Phase morphology can be significantly influenced by rheologic characteristics and shear conditions during both mixing and molding. To investigate how the toughness and elasticity of the blends are related to processing parameters and rubber particle morphology, and how these parameters can be used to control the properties of the blends, 15 wt % of P(LA30/CL70)U rubber was blended with PEU, matrix PEUc, at 120°C and 75 rpm, at 135°C and 50, 75, and 100 rpm, and at 150°C and 75 rpm. The lowest temperature at which PEU still has low enough viscosity to be processed is 120°C. Interfacial reactions and degradation of the components may also occur under excessively severe processing conditions. PEU, like other lactic acid-based polymers, is highly thermo-labile, so very high temperatures are not reasonable, and 150°C was chosen as the highest processing temperature. In this part of the work, injection molding was applied due to the change in processing equipment.

Processing conditions had little effect on tensile modulus or strength of the PEUc85/[P(LA30/CL70)U]15 blends, but as can be seen in Figure 3, strain varied markedly. The highest strain at break, 86%, was achieved for the blend processed at 120°C. This blend also had the highest molecular weight ($\bar{M}_w = 99\,000$ g/mol). Molecular weight of the samples decreased with increasing temperature and mixing speed, achieving the lowest value of 77 000 g/mol for 150°C. The same decreasing trend was seen in the values of strain when temperature and screw speed were increased. The different processing conditions also led to differences in the morphology of the blends, and to differences in the size and shape of the rubber particles, and these changes might explain the changes in strain and also of impact strength. DMTA measurements showed that T_g s of the rubber and matrix moved closest to each other for the blend processed at 120°C. Changes in the rubber particle dispersion could be seen in SEM micro-

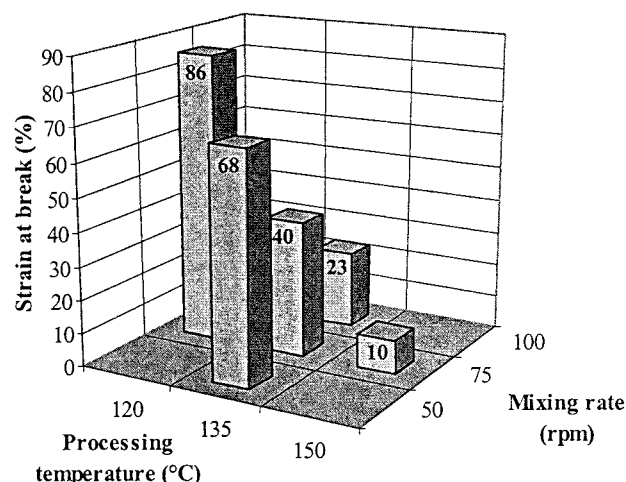


Figure 3 Effect of processing temperature and mixing rate on strain of rubber modified poly(ester-urethane).

graphs (not shown here). As the melt temperature decreased, the melt viscosity of PEU increased significantly and the difference between matrix and rubber viscosities was reduced. At 120°C, rubber particles were dispersed in very small particles ($<0.5\ \mu\text{m}$) resembling co-continuous phase structure, while in the blend prepared at 135°C the structure of the fractured surface was much coarser, the rubber particles were bigger, and the size distribution was somewhat broader. Measurements of impact strength revealed, however, that all these blends were super tough. The blends were not broken with the method of unnotched test samples. Only for the blend processed at 150°C where impact strength was lowest, was the high value of 43 kJ/m² obtained. Impact results in any event correlate well with changes in strain values.

Effect of Degree of Functionalization and Cross-Linking

A series of studies was made to investigate the influence of the diisocyanate end-functionalization of the P(LA30/CL70)U rubber on mechanical properties of the blends. Fifteen weight percent of P(LA30/CL70)U rubber was blended with PEU, PEUc, at 135°C and 50 rpm. To obtain two elastomers with different amounts of functional groups, P(LA/CL)U1 (later referred to as U1) was polymerized with 1:1 ratio of hydroxyl end groups of prepolymer and isocyanate groups (OH/NCO), whereas P(LA/CL)U2 (later referred to as U2)

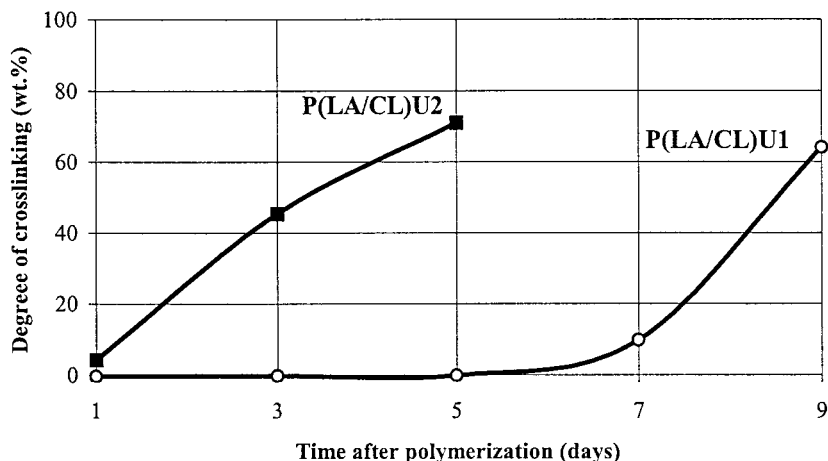


Figure 4 Degree of crosslinking of rubber during progress of the reaction.

was polymerized with ratio of 1:1.2. The melt polymerization of the elastomers was interrupted when they still had reactive end-groups capable of interfacial reactions with the matrix. Left at the room temperature, the reactions in the elastomer continue and the degree of cross-linking increases, as seen in Figure 4. Controlled cross-linking of the rubber phase is a desired feature of rubber-toughened plastics. Under the action of shearing forces during melt processing, uncross-linked particles tend to break down into small fragments or else to form large sheets rather than discrete particles. They also become highly extended during molding. Both tendencies lead to a reduction in mechanical strength.¹⁷ To examine the effect of different degrees of functionalization

and cross-linking, we blended the U1 elastomer with the PEUc matrix 1, 3, 5, 7, and 9 days after the preparation and the U2 elastomer after 1, 3, and 5 days. Further experiments, i.e., at 11 and 7 days, were prevented by the advancing cross-linking in the rubber.

Table IV shows the thermal and mechanical values of the end-functionalized P(LA/CL)U rubbers blended with PEUc. The amount of reactive groups in the rubbers decreased with reaction time, which is assumed to decrease interactions at the rubber-matrix interface. Also, T_g of the matrix moved less toward the T_g of the rubber as the reaction time of the rubber was increased, which shows that the partial miscibility at the interface was weakened. P(LA/CL)U2-1 had the

Table IV Thermal and Mechanical Properties of PEUc Blended with Functionalized Elastomers

Blends	Reaction Time of Rubber (Days)	T_g ¹⁾ (Rubber) (°C)	T_g ¹⁾ (Matrix) (°C)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)	Charpy Impact Strength (kJ/m ²)
PEUc	—	—	45.9	1520 ± 10	48 ± 1	13 ± 4	16 ± 1
PEUc/P(LA/CL)U1-1	1	-40.0	43.3	1110 ± 70	38 ± 3	57 ± 23	20 ± 2
PEUc/P(LA/CL)U1-3	3	-41.0	43.8	1080 ± 30	34 ± 1	54 ± 11	32 ± 6
PEUc/P(LA/CL)U1-5	5	-41.2	44.8	1110 ± 20	35 ± 1	55 ± 12	54 ± 3
PEUc/P(LA/CL)U1-7	7	-42.4	45.3	1160 ± 20	36 ± 1	27 ± 21	38 ± 3
PEUc/P(LA/CL)U1-9	9	-42.5	46.1	1120 ± 40	32 ± 2	16 ± 7	16 ± 2
PEUc/P(LA/CL)U2-1	1	-42.5	44.5	1080 ± 30	34 ± 2	62 ± 26	71 ± 8 ²⁾
PEUc/P(LA/CL)U2-3	3	-42.4	44.5	1120 ± 40	34 ± 1	53 ± 21	23 ± 5
PEUc/P(LA/CL)U2-5	5	-42.5	45.7	1130 ± 40	33 ± 2	11 ± 3	9 ± 1

¹⁾ Determined by DMTA from the peak of loss modulus.

²⁾ Partially broken.

largest number of reactive groups and the blend also exhibited very high impact strength. In the U1 series, however, the best impact values were achieved with the elastomer, that was allowed to react for 5 days. Evidently, the degree of cross-linking of the rubber is more important for impact strength than are interfacial reactions. In blends like these, the interfacial adhesion in any event appears adequate.

Figure 5 shows SEM micrographs of PEUc with P(LA/CL)U1 elastomer. The morphology changed dramatically with increase in the degree of cross-linking in the rubber. In PEUc/P(LA/CL)U1-1 blend, the uncross-linked particles broke down into small streak-like fragments, whereas the highly cross-linked rubber in the U1-9 blend exhibited a structure with large, irregular globules of rubber (Figure 5c). The blends with rubber U2, i.e., the elastomer with larger amount of diisocyanate, showed tough morphology even after a 1-day reaction (see Table IV) due to higher rate of cross-linking reaction. The morphology of PEUc/P(LA/CL)U2-1 blend was intermediate between that of PEUc/P(LA/CL)U1-5 and PEUc/P(LA/CL)U1-9.

Clearly, it is important to find the degree of cross-linking and rubber viscosity that produces optimum particle dispersion for high impact modification. The best degree of cross-linking for the elastomers and compositions used in this study was about 5 wt %. Higher degree of cross-linking was associated with poor values of both strain and impact strength.

CONCLUSIONS

The relationship between phase separation and mechanical properties of PEU blends has been described. In general, addition of rubber increased the impact strength markedly, particularly at higher rubber loadings. Tensile modulus and strength showed a downward trend as a function of rubber concentration but remained at an acceptable level. The toughening effect of P(LA50/CL50)U and P(LA30/CL70)U rubbers was about the same, suggesting that the formation of heterophase structure is the factor differentiating them from the P(LA70/CL30)U rubber. P(LA70/CL30)U softened the PEU, causing greater lowering of tensile modulus and strength, and the strain at break reached values over 100%. Solubility parameter calculations predicted that PEU

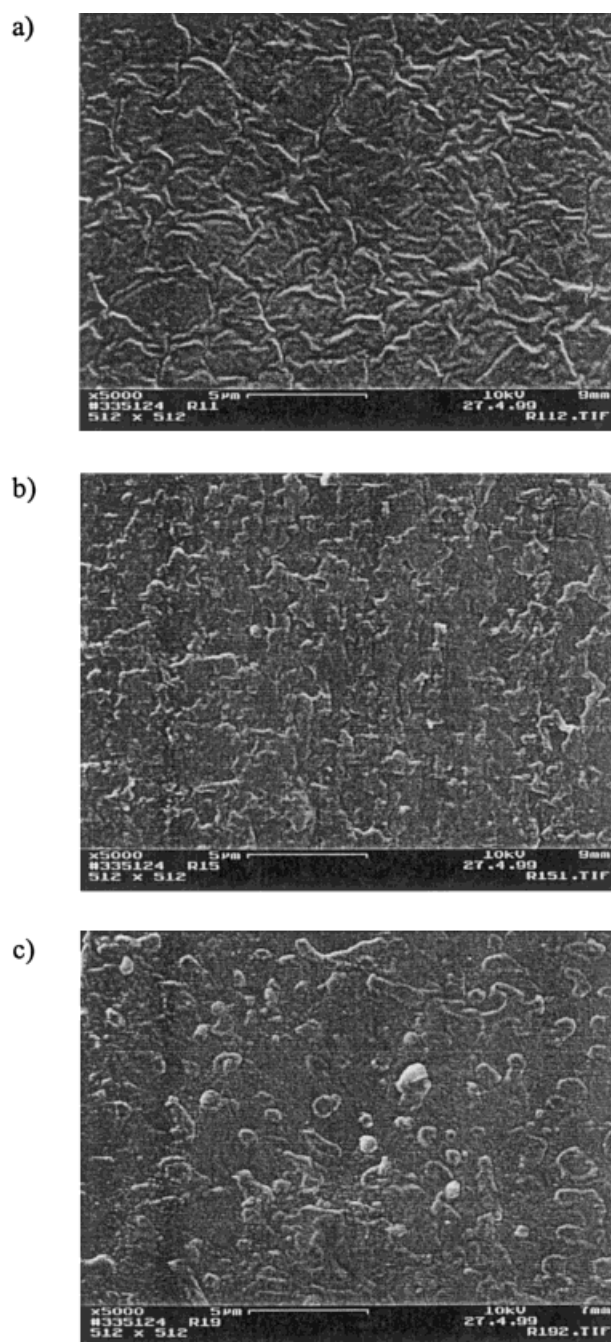


Figure 5 Scanning electron micrographs of fracture surfaces of a) PEUc/P(LA/CL)U1-1, b) PEUc/P(LA/CL)U1-5, and c) PEUc/P(LA/CL)U1-9. For definitions of blends see Table 4.

should be immiscible with P(LA/CL)U elastomer containing about 40 to 100 mol % of ϵ -caprolactone. Tensile modulus and strength of the PEU blends were not influenced by the processing conditions, but the strain varied markedly. The high-

est strain at break was achieved for the blend processed at 120°C, where the rubber was dispersed as very small particles. In the blend processed at 135°C the structure of the fractured surface was much coarser. Measurements of impact strength showed that all these blends were very tough.

It can be concluded that the degree of cross-linking in the rubber is an important factor in the impact modification. For the type and composition of elastomer used in this study, the best degree of cross-linking for impact modification was about 5 wt %. SEM showed the degree of cross-linking in the rubber also to have a marked effect on the blend morphology. The interfacial adhesion between the rubber and matrix was good in all of the blends. The results confirm our belief that the best way to improve the properties of PEU and P(LA/CL)U based blends is to optimize the composition and cross-linking architecture.

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