

Impact Modification of Lactic Acid Based Poly(ester-urethanes) by Blending

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ABSTRACT: Branched biodegradable poly(ester-urethane) (PEU) was blended with two elastic biodegradable copolymers in proportions 5, 10, 15, and 20 wt % to investigate their effect on this hard and brittle polymer. Copolymer of L-lactide and ϵ -caprolactone, P(L-LA50/CL50), was synthesized by ring-opening polymerization and the other elastic poly(L-lactic acid-co- ϵ -caprolactone)urethane, P(LA50/CL50)U, was prepared by direct polycondensation of L-lactic acid and ϵ -caprolactone, followed with urethane bonding. In addition, four elastic biodegradable copolymers, three of them P(L-LA/CL) and one P(LA/CL)U, were blended with linear PEU to investigate their modifying effect on PEU. These compositions studied were 10, 15, and 20 wt % of P(L-LA40/CL60), P(L-LA60/CL40), P(L-LA80/CL20), and P(LA40/CL60)U in PEU. Blending was done in a batch mixer.

PEU became more ductile when blended with P(L-LA/CL) and P(LA/CL)U, and its impact resistance improved markedly. In general, an addition of 15 wt % of copolymer appeared to give the most desirable mechanical properties. Moreover, the more L-lactide in the P(L-LA/CL) copolymer, the better was the miscibility of the blends, as shown by dynamic mechanical thermal analysis (DMTA) and scanning electron microscopy (SEM).

One P(L-LA/CL) was also blended with poly(DL-lactide) (PDLLA) to see if the dispersion of rubbery copolymer particles was the same in PDLLA and PEU. A well-known commercial nonbiodegradable rubber [styrene/ethylene/butylene copolymer (SEBS)] was blended with linear PEU to compare its effect on impact strength. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1335–1343, 1997

Key words: lactic acid; ϵ -Caprolactone; copolyesters; poly(ester-urethane); blends

INTRODUCTION

Blending might often prove a more cost-effective way to modify properties than chemical modification. Macroscopic properties of materials, including processability, impact strength, rigidity, tensile strength, barrier properties, and biodegradation, can be usually modified through appropriate choice of the second polymer. A convenient and very effective method to improve the impact resistance of polymers is rubber modification. Rubber

particles act as stress dispersers, which reduce the overall yield stress of a material, allowing plastic deformation and ductile fracture to take place before the material reaches its brittle strength. The success of rubber toughening depends on several factors, including entanglement density of the matrix, rubber content, rubber particle size and distribution, type of rubber, interfacial adhesion, and characteristics of the phase separation between the matrix and the rubber. Adequate phase separation between matrix and dispersed rubber is required for effective rubber toughening.^{1,2} There is an optimum rubber particle size for toughening brittle amorphous poly-

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mers that is related to the entanglement density of the matrix. Small particles might be inefficient in initiating crazes; thus, cracks can be formed. Or the second possibility is that small particles are ineffective in terminating crazes. The presence of a second particle has little effect upon the crazing stress when the distance between particle centers is greater than $2.90 R$, where R is the radius of the particle. In other words, the stress fields do not overlap significantly unless the particles are less than $0.9 R$ apart. Decreasing the interparticle spacing causes a rise in stress concentration in the region between the particles so that crazes form preferentially in this region.^{2,3}

The solubility of the matrix and rubber in each other, which can be expressed as the difference in the solubility parameters δ of the two components, influences phase separation and interfacial adhesion.¹ Many theories have been developed to explain the mechanism(s) of rubber toughening in thermoplastics and thermosets.^{4–8} Certainly the strength of the bond at the rubber-matrix interface is an important parameter in rubber toughening, and the ideal rubber is neither completely compatible nor completely incompatible.² The strength of this interface can be modified by the use of a compatibilizer, usually a graft or block copolymer. The phase separation can be enhanced by varying the molecular weight of the polymers, adjusting the blending procedures, or annealing the blended materials.⁹

Biodegradable polymers have been used in medicine for a number of years, in applications such as absorbable sutures and controlled release of drugs. They have also been used in commodity applications, such as packaging and film wrap. While polylactides are among the most important of the biodegradable polymers, they suffer from a tendency to brittleness. A number of studies have dealt with the modification of the physical and chemical properties of lactic-acid-based polymers through reaction or blending with other biodegradable and non-biodegradable polymers or low molecular weight additives.^{10–17} We have been studying the polymerization of lactic acid with diisocyanate in our laboratory for several years now.¹⁸

In this work, we studied the rubber modification of lactic acid based poly(ester-urethane) (PEU), a new polymer whose characteristics were recently reported.^{19–21} Hard and brittle PEU has now been modified by blending it with laboratory made elastic biodegradable copolymers. The aim was to achieve an impact resistant PEU and to plasticize the material and to understand the re-

lationship between the morphology and properties of the blends. Both the toughening and softening characteristics of the material were investigated. Of primary interest were the miscibility of the blends, the dispersion of the rubbery copolymer phase, and the mechanical properties of the blends.

EXPERIMENTAL

Materials

Lactic acid based PEUs were synthesized in a bench scale 6.2 l reactor in a two-step process for lactic acid polymerization: in the first step, the lactic acid was condensation polymerized to low molecular weight prepolymer; in a second, the molecular weight was raised by using diisocyanate as chain extender. The hydroxyl-terminated prepolymer was made through condensation polymerization of L-lactic acid and 2 mol % of 1,4-butanediol. The synthesis and characterization of PEU have recently been described in detail.^{21,22} Elastic PEUs based on copoly(L-lactic acid-co- ϵ -caprolactone) prepolymers were synthesized in a two-step process like that used for PEU, except that ϵ -caprolactone was used as comonomer in the synthesis of prepolymer. Preparation, structure, and properties of poly(L-lactic acid-co- ϵ -caprolactone)urethane, P(LA/CL)U, have been described elsewhere.²³ To control the linearity of the elastic material, P(LA/CL)U was polymerized in the second step in the process to isocyanate terminated polymer. L-lactide/ ϵ -caprolactone copolymers P(L-LA/CL) were synthesized by ring-opening polymerization from L-lactide and ϵ -caprolactone monomers. The copolymerization was carried out in bulk at 140°C for 28 h with Sn(II) octoate as catalyst and glycerol as initiator.²⁴ PDLLA was used as received. The basic description of the materials are set out in Table I. All compositions referred to below are expressed as wt % in the feed. The commercial non-biodegradable rubber SEBS (Kraton G-1652 supplied by Shell) employed as reference was used as received. SEBS is a block copolymer with hard polystyrene segments in combination with soft elastomeric segments. According to the manufacturer, the T_g of the rubber block in SEBS is 42°C.

Blending

Blends were processed at 180°C for 5 min at 75 r/min in a Haake Rheomix 600 batch mixer

Table I Description of the Materials

Sample (wt %/wt %)	Description	T_g (DSC; °C)	T_g (DMTA; °C)	\overline{M}_n (g/mol)	\overline{M}_w (g/mol)	D
PEUa	branched poly(ester-urethane)	50	44	45,000	200,000	4.4
PEUb	linear poly(ester-urethane)	49	44	54,000	91,000	1.7
P(L-LA50/CL50)	(L-lactide/ ϵ -caprolactone) copolymer	-25	-19	114,000	219,000	1.9
P(L-LA40/CL60)	(L-lactide/ ϵ -caprolactone) copolymer	-30	-29	172,000	306,000	1.8
P(L-LA60/CL40)	(L-lactide/ ϵ -caprolactone) copolymer	-15	-18	150,000	281,000	1.9
P(L-LA80/CL20)	(L-lactide/ ϵ -caprolactone) copolymer	25	22	243,000	417,000	1.7
P(LA50/CL50)U	(L-lactic acid/ ϵ -caprolactone)urethane	-23	— ^a	63,000	205,000	3.3
P(LA40/CL60)U	(L-lactic acid/ ϵ -caprolactone)urethane	-31	— ^a	42,000	80,000	1.9
PDLLA	poly(DL-lactide)	52	49	80,000	195,000	2.4

^a Not measured due to difficulties in specimen preparation.

equipped with a Haake Rheocord 9000 control unit.

Molecular Weight Determination

Molecular weights were determined by room temperature SEC (Waters System Interface module, Waters 510 HPLC Pump, Waters 410 Differential Refractometer, Waters 700 Satellite Wisp, and four PL gel columns: 10^4 , 10^5 , 10^3 , and 100 \AA connected in series). Chloroform was used as solvent and eluent. The samples were filtered through a $0.5 \mu\text{m}$ Millex SR filter. The injected volume was $200 \mu\text{L}$, 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.

Molding

Test specimens for DMTA, impact, and tensile testing were prepared by compression molding (Darragon), at 160°C for PEU blends and at 180°C for PDLLA blends, in both cases with 6 min melting, 4 min compression, and 3 min cooling.

Thermal Analysis

Glass transition temperatures were measured by dynamic mechanical thermal analysis (RSA, Rheometrics). The samples ($2 \times 5 \times 53 \text{ mm}$) were sawn from the compression molded plates. Dual cantilever geometry was used, and the temperature was raised 2°C/min . T_g was not determined as the peak of $\tan \delta$ because the materials softened near T_g , and the values of storage and loss modulus (E' and E'') dropped to near zero when $\tan \delta$ reached the peak value. The peak of E'' was

used to determine T_g . Some thermal measurements were also made by DSC (Polymer Laboratories). Samples (5–10 mg) were heated twice, at a rate of 10°C/min , to ensure that their thermal histories were similar.

Tensile Testing

The tensile tests were done on an Instron 8031 tensile testing machine equipped with an Instron 8500 control panel, adapting the standard ISO/R527-1966. The non-standard samples ($3 \times 10 \times 90 \text{ mm}$) were sawn from the compression molded plates. The mechanical properties of the blends were measured using a tensile tester at a crosshead speed of 5 mm/min . Since the samples for the tensile tests were made by compression molding rather than injection molding, the results may not be as good as they could be.

Impact Strength

Charpy impact strength tests were carried out with an impact tester (Zwick) and a pendulum of 0.5, 1, or 4 J, depending on the sample, adapting the standard ISO 179-1982(E), at $+23^\circ\text{C}$. The samples ($4 \times 6 \times 50 \text{ mm}$) were sawn from the compression molded plates.

Morphology

The morphology of a fractured (in liquid nitrogen) cross section of the samples was examined by scanning electron microscopy (SEM) (Cambridge Instruments, Stereoscan 120). SEM micrographs were taken after coating of the surfaces with a thin layer of gold.

RESULTS AND DISCUSSION

Elastic amorphous biodegradable copolymers were blended with brittle and amorphous PEU with the aim of increasing the impact strength of hard and brittle PEU and of plasticizing the material. Two different PEU polymers were used. PEUa was a long chain branched poly(ester-urethane), while PEUb was linear. Copolymer of L-lactide and ϵ -caprolactone, P(L-LA50/CL50), was synthesized by ring-opening polymerization; and the other elastic poly(L-lactic acid-co- ϵ -caprolactone)urethane, P(LA50/CL50)U, was prepared by direct polycondensation of L-lactic acid and ϵ -caprolactone followed with urethane bonding. Some blends based on PDLA were studied as reference, and a well-known commercial non-biodegradable rubber (SEBS) was blended with PEUb to compare its effect on impact strength. PEUs alone were processed in the batch mixer as an additional reference. The word rubbery as applied here describes a material property.

Blends of PEUa with P(L-LA50/CL50) or P(LA50/CL50)U

P(L-LA50/CL50) and P(LA50/CL50)U were blended with PEUa in proportions 5, 10, 15, and 20 wt % to investigate their modifying effect on PEUa. The effects of the two copolymers were noticeably different: P(L-LA50/CL50) mainly toughened the material, whereas P(LA50/CL50)U softened it. Processing improved the properties of PEUa, evidently because the isocyanate groups reacted further under the processing conditions. Previous analytical data support this finding.²¹ The PEUa cross-linked somewhat during the processing, and the samples were very elastic in the melt. Molecular weights of the PEUa blends could not be measured because of their insolubility. The thermal and mechanical properties of the blends are seen in Table II.

Dynamic mechanical thermal measurements revealed two separate glass transitions for PEUa/P(L-LA50/CL50) blends with compositions of 15 and 20 wt % of P(L-LA50/CL50). These corresponded to the T_g s of the rubbery copolymer and matrix. However, the P(L-LA50/CL50) induced only a small peak in E'' at about -10°C . SEM micrographs showed a good miscibility in these blends; only a few small particles (particle size $\sim 1\ \mu\text{m}$) were observed for blends containing 15 and 20 wt % of the copolymer. Impact strength increased, while modulus and tensile strength

gradually decreased with increasing amount of P(L-LA50/CL50).

P(LA50/CL50)U was miscible with PEUa and softened the material. Only one glass transition temperature was observed in the dynamic mechanical thermal measurements, and no discrete, separate rubbery copolymer particles were evident in SEM micrographs. This might indicate that P(LA50/CL50)U had reacted with PEU. A detailed investigation of such reactions is under way. Increasing amounts of P(LA50/CL50)U decreased the values of modulus and tensile strength. In contrast, there was no improvement in impact strength until addition of 20 wt % of the rubbery copolymer, at which point a sharp transition occurred and the impact resistance improved dramatically.

In all further processing of PEU materials, it is essential that the PEUs remain thermoplastic. Encouraged by the findings reported above, we decided to continue our investigations with both P(L-LA/CL) and P(LA/CL)U copolymers, whose diverse effects made them of interest for different applications. Since addition of 5 wt % of the copolymer had not had a marked effect on the properties of PEU, we decided to add only larger amounts in subsequent experiments. The PEU material for these experiments was linear PEUb.

Blends of PEUb with P(L-LA/CL)

Molecular weight determinations showed that PEUb degraded slightly during processing, whereas blending with higher molecular weight copolymers increased the molecular weight somewhat. SEC curves showed narrow and distinct peaks without bimodal behavior, indicating a reasonably good miscibility. However, reference blends containing SEBS were not totally soluble in chloroform, which needs to be taken into account in interpreting the SEC results. Molecular weights after blending and the thermal and mechanical properties for PEUb blends are shown in Table III.

Blends were prepared of PEUb and 10, 15, and 20 wt % of P(L-LA40/CL60), P(L-LA60/CL40), and P(L-LA80/CL20); and, for comparison, PEUb was processed alone. Higher molecular weight P(L-LA80/CL20) was harder than the two other copolymers. In thermal measurements of PEUb/P(L-LA40/CL60) blends, two separate glass transitions were found corresponding to the T_g s of the rubbery copolymer and matrix [Fig.

Table II Thermal and Mechanical Properties of PEUa Blends

Sample (wt %/wt %)	T_g (DSC; °C)	T_g (DMTA; °C)	Charpy Impact Strength (kJ/m ²)	Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)
PEUa ^a	50	44	6.7 ± 0.5	2570 ± 80	37 ± 3	2.4
PEUa ^b	52	48	9.2 ± 0.6	2700 ± 50	48 ± 1	4.2
PEUa95/P(L-LA50/CL50)5	49	49	9.7 ± 1.0	2330 ± 150	41 ± 2	3.3
PEUa90/P(L-LA50/CL50)10	52	47	15.0 ± 3.4	2090 ± 150	34 ± 2	3.6
PEUa85/P(L-LA50/CL50)15	48	(-12) ^c 45	26.0 ± 5.1	1800 ± 80	28 ± 1	23.4
PEUa80/P(L-LA50/CL50)20	49	(-8) ^c 41	38.0 ± 1.4/some ^d	1530 ± 80	25 ± 2	29.6
PEUa95/[P(LA50/CL50)U]5	47	44	6.5 ± 1.6	2000 ± 290	36 ± 5	3.3
PEUa90/[P(LA50/CL50)U]10	43	41	9.2 ± 1.5	1890 ± 150	34 ± 4	4.2
PEUa85/[P(LA50/CL50)U]15	39	33	8.9 ± 1.9	1730 ± 30	30 ± 2	8.5
PEUa80/[P(LA50/CL50)U]20	34	28	— ^d	610 ± 200	12 ± 3	> 100

^a Initial.
^b Processed in batch mixer for comparison.
^c The T_g value in parenthesis indicates the small peak in loss modulus induced by the dispersed phase.
^d Not broken.

Table III Molecular Weights and Thermal and Mechanical Properties of PEUb and PDLA Blends

Sample (wt %/wt %)	\overline{M}_n (g/mol)	\overline{M}_w (g/mol)	D	T_g (DMTA; °C)	Charpy Impact Strength (kJ/m ²)	Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)
PEUb ^a	54,000	91,000	1.7	44	4.1 ± 0.5	2560 ± 90	33 ± 4	1.7
PEUb ^b	46,000	77,000	1.7	44	7.2 ± 0.2	2290 ± 150	24 ± 3	1.4
PEUb90/P(L-LA40/CL60)10	52,000	106,000	2.0	(-36) ^c 45	23.0 ± 4.6	1970 ± 30	28 ± 1	2.6
PEUb85/P(L-LA40/CL60)15	50,000	115,000	2.3	(-34) ^c 45	26.2 ± 8.2	1830 ± 130	31 ± 2	3.4
PEUb80/P(L-LA40/CL60)20	63,000	132,000	2.1	(-33) ^c 44	28.2 ± 2.0	1600 ± 50	25 ± 1	3.5
PEUb90/P(L-LA60/CL40)10	47,000	98,000	2.1	43	11.7 ± 2.0	1830 ± 150	29 ± 3	2.9
PEUb85/P(L-LA60/CL40)15	48,000	105,000	2.2	42	20.9 ± 7.8	1870 ± 60	30 ± 2	3.0
PEUb80/P(L-LA60/CL40)20	57,000	124,000	2.2	41	34.0 ± 4.3	1670 ± 160	29 ± 3	3.1
PEUb90/P(L-LA80/CL20)10	44,000	95,000	2.2	42	7.7 ± 1.3	2020 ± 80	30 ± 6	2.2
PEUb85/P(L-LA80/CL20)15	53,000	112,000	2.1	41	10.2 ± 1.9	2050 ± 20	40 ± 4	3.4
PEUb80/P(L-LA80/CL20)20	61,000	138,000	2.3	39	9.3 ± 0.8	1710 ± 140	30 ± 4	2.8
PEUb90/[P(LA40/CL60)U]10	45,000	76,000	1.7	(-31) ^c 42	12.6 ± 5.0	1890 ± 30	28 ± 1	2.0
PEUb85/[P(LA40/CL60)U]15	56,000	126,000	2.2	(-31) ^c 39	33.1 ± 3.5	1730 ± 40	34 ± 1	3.4
PEUb80/[P(LA40/CL60)U]20	59,000	114,000	1.9	(-31) ^c 39	43.4 ± 5.7	1540 ± 30	31 ± 1	3.8
PEUb95/SEBS5	44,000	73,000	1.6	(-56) ^c 45	10.2 ± 4.6	2180 ± 30	30 ± 3	1.9
PEUb90/SEBS10	33,000	68,000	2.1	(-56) ^c 45	6.9 ± 1.6	1730 ± 60	25 ± 2	2.2
PEUb85/SEBS15	44,000	74,000	1.7	(-55) ^c 44	4.8 ± 0.8	1490 ± 90	21 ± 1	2.3
PEUb80/SEBS20	43,000	74,000	1.7	(-55) ^c 45	7.3 ± 1.0	1280 ± 50	18 ± 1	2.3
PDLA ^a	80,000	195,000	2.4	49	— ^d	2180 ± 210	18 ± 1	1.1
PDLA ^b	39,000	72,000	1.8	47	— ^d	1920 ± 40	4 ± 1	0.4
PDLA90/P(L-LA60/CL40)10	43,000	94,000	2.2	(-13) ^c 43	3.4 ± 0.6	1730 ± 80	10 ± 2	0.7
PDLA85/P(L-LA60/CL40)15	46,000	101,000	2.2	(-10) ^c 43	16.8 ± 4.5	1880 ± 50	19 ± 4	1.4
PDLA80/P(L-LA60/CL40)20	40,000	87,000	2.2	(9) ^c 42	15.3 ± 1.1	1660 ± 40	20 ± 2	1.8

^a Initial.
^b Processed in batch mixer for comparison.
^c The T_g value in parenthesis indicates the small peak in loss modulus induced by the dispersed phase.
^d Material was too brittle to prepare the samples by the method used.

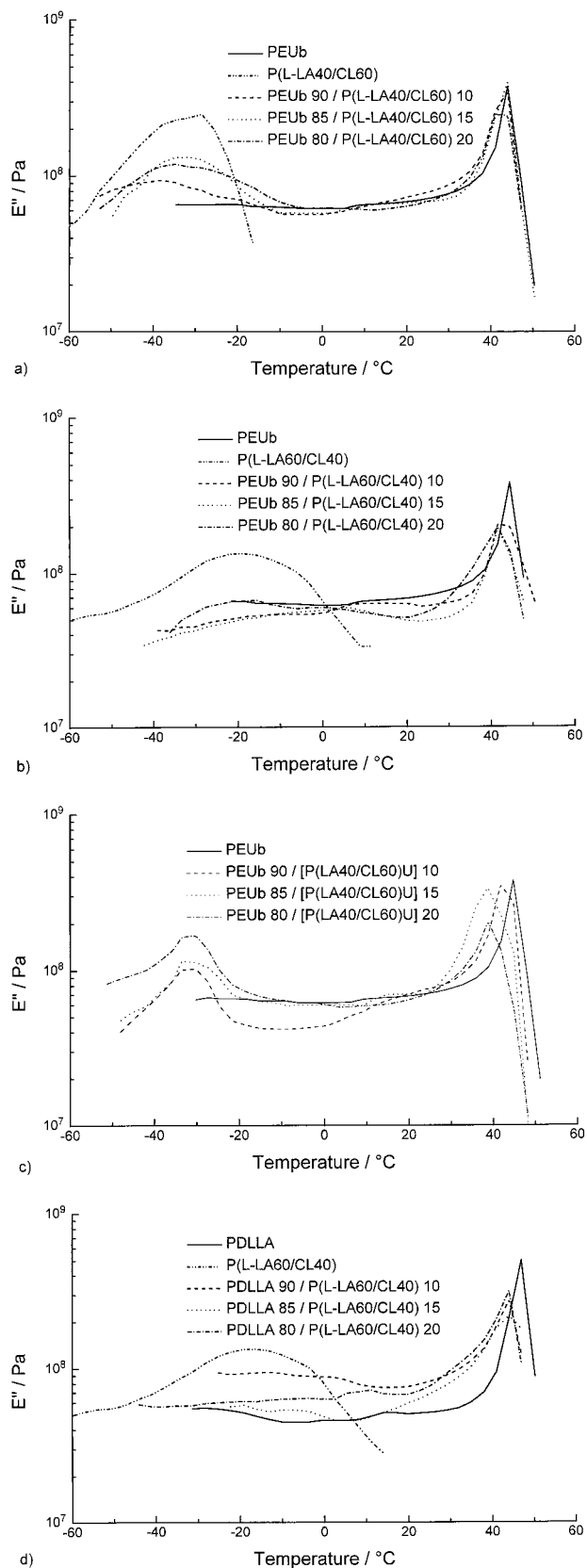


Figure 1 (Continued)

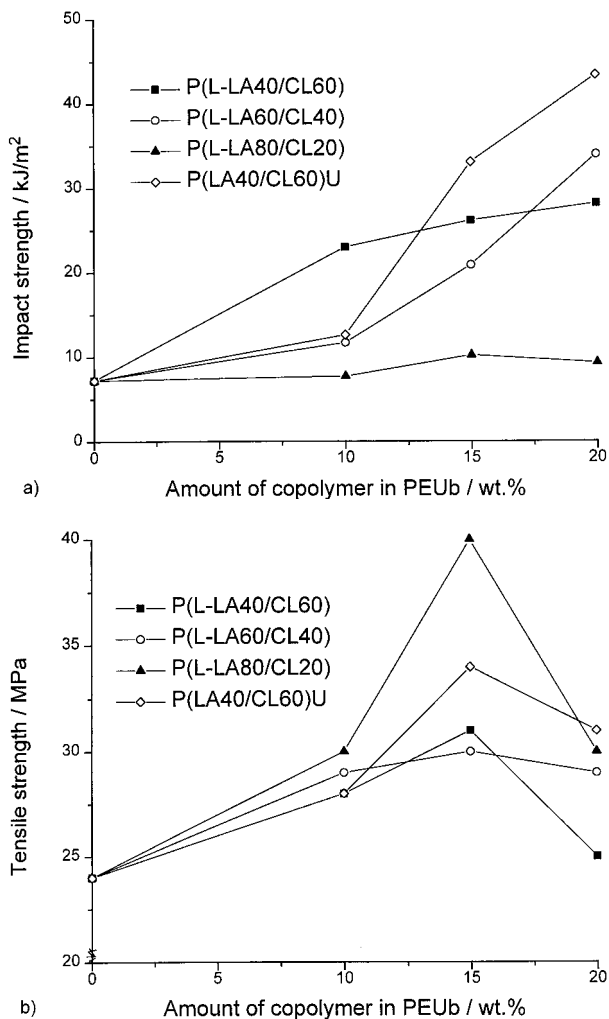


Figure 2 (a) Impact and (b) tensile strengths of PEUb blends as a function of the amount of copolymer in PEUb.

1(a)]. These blends were therefore immiscible. SEM micrographs [Fig. 3(a)] revealed a two-phase morphology with rubbery copolymer particles (size $\sim 1\text{--}3.5\ \mu\text{m}$). PEUb/P(L-LA60/CL40) blends showed only the T_g of the PEUb phase, which had shifted somewhat [Fig. 1(b)]. These blends were partially miscible; in some cases, the copolymer induced a very low peak in loss modulus. Rubbery copolymer particles (particle size $\sim 1\ \mu\text{m}$ and below) were seen in SEM micrographs [Fig. 3(b)], though they were smaller

Figure 1 DMTA curves: loss modulus (E'') as a function of temperature for (a) PEUb/P(L-LA40/CL60), (b) PEUb/P(L-LA60/CL40), (c) PEUb/P(LA40/CL60)U, and (d) PDLLA/P(L-LA60/CL40) blends.

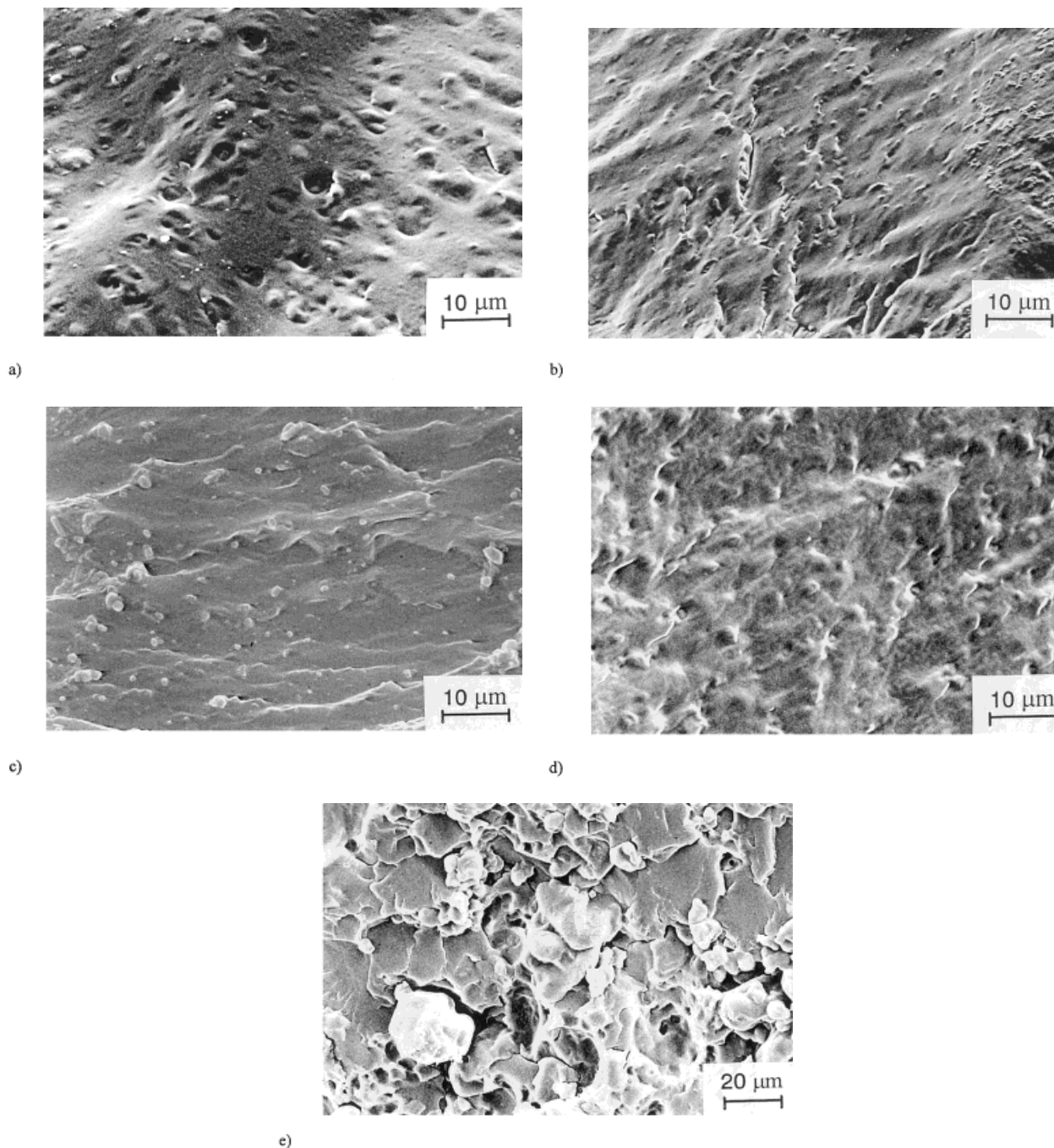


Figure 3 SEM micrographs of blends (a) PEUb85/P(L-LA40/CL60)15, (b) PEUb85/P(L-LA60/CL40)15, (c) PEUb85/[P(LA40/CL60)U]15, (d) PDLLA85/P(L-LA60/CL40)15, and (e) PEUb85/SEBS15.

than in PEUb/P(L-LA40/CL60) blends. According to both DMTA and SEM, the PEUb/P(L-LA80/CL20) blends were miscible.

In the case of tensile values, the difference in the effects of P(L-LA40/CL60) and P(L-LA60/CL40) in PEUb blends was only small. The P(L-

LA80/CL20) had a distinct effect; however, it was less elastic than the other two copolymers. Figure 2 shows the tensile and impact strengths of PEUb/P(L-LA40/CL60), PEUb/P(L-LA60/CL40), and PEUb/P(L-LA80/CL20) blends as a function of the amount of copolymer in the blend. P(L-

LA40/CL60) and P(L-LA60/CL40) increased the impact strength of PEU markedly. An increase in the tensile strength of PEU_b was observed with all P(L-LA/CL) copolymers and was highest with 15 wt % of P(L-LA80/CL20). Materials became more ductile, and the modulus decreased somewhat; but the tensile strength increased. The strain at break increased by only 1–2% units. The impact strength of PEU_b increased when blended with P(L-LA40/CL60) but remained more or less the same with increasing amounts of the copolymer. However, the impact strength increased linearly with increasing amounts of P(L-LA60/CL40) [Fig. 2(a)].

Blends of PEU_b with P(LA40/CL60)U

Additions of 10, 15, and 20 wt % of P(LA40/CL60)U to PEU_b increased the impact strength of PEU_b markedly. PEU_b/P(LA40/CL60)U blends exhibited two separate T_g s [Fig. 1(c)], and rubbery copolymer particles (particle size ~ 0.5 – $3.0 \mu\text{m}$) were seen in SEM micrographs [Fig. 3(c)]. The T_g of the PEU_b phase was shifted a bit towards the T_g of the rubbery copolymer phase, indicating that the blends were partially miscible. The P(LA40/CL60)U particles were not as round as the P(L-LA/CL) particles. P(LA40/CL60)U also increased the tensile strength of PEU_b, but modulus decreased slightly. On the basis of these interesting properties, further studies have commenced on copolymers of this kind with various compositions and molecular weights.

Blends of PDLA with P(L-LA60/CL40)

P(L-LA60/CL40) was also blended with PDLA to see if the dispersion of rubbery copolymer particles was similar in PDLA and PEU_b. The miscibility of P(L-LA60/CL40) with PDLA was virtually the same as it was with PEU_b [Fig. 1(d)], but the particle size (~ 0.5 – $2.5 \mu\text{m}$) of the copolymer phase was somewhat larger in the PDLA blends [Fig. 3(d)]. P(L-LA60/CL40) increased the impact and tensile strengths of PDLA.

Comparison of PEU_b Blended with Nonbiodegradable Rubber

The effect of the well-known rubber SEBS as impact modifier in PEU_b was not as good as expected. The best impact strength for PEU_b/SEBS blends (10.2 kJ/m^2) was achieved with 5 wt % of SEBS. Much better results than this were ob-

tained with both P(L-LA/CL) (34.0 kJ/m^2) and P(LA/CL)U (43.4 kJ/m^2). Two very clear T_g s in DMTA together with SEM [Fig. 3(e)] showed that SEBS was totally immiscible with PEU_b. It was not dispersed well in PEU_b; the particles were loose, cluster-like, and nonround, exhibiting broad size distribution and poor adhesion to the matrix. Particle sizes up to $30 \mu\text{m}$ were observed.

CONCLUSIONS

The modification of PEU was sensible to small differences in matrix polymer and copolymer composition and to differences in the amount of comonomer in the copolymer. Two different PEUs were studied. In the PEU_a blends, the effect of P(L-LA/CL) was mainly to toughen; whereas P(LA/CL)U softened the material. In the blends of PEU_b with P(L-LA/CL), the more L-lactide the copolymer contained, the better was the miscibility. Both P(L-LA/CL) and P(LA/CL)U made PEU_b more ductile; and P(L-LA40/CL60), P(L-LA60/CL40), and P(LA40/CL60)U caused a marked improvement in the impact resistance. Whereas the initial impact strength of PEU_b was 7 kJ/m^2 , the impact strength of PEU_b80/P(L-LA40/CL60)20 blend was 28 kJ/m^2 and that of PEU_b80/P(L-LA60/CL40)20 blend 34 kJ/m^2 . With 20 wt % of P(LA40/CL60)U in the PEU_b blend, the impact strength was 43 kJ/m^2 . SEM micrographs showed that P(L-LA/CL) particles in the PEU_b matrix were round, whereas P(LA/CL)U particles were nonround. In general, the addition of 15 wt % of copolymer gave the best mechanical values.

In no blend was there any noticeable change in the size of the rubbery copolymer particles with the proportion of copolymer in the blend. In the present work, the blending conditions were the same for all blends. In future work, the effects of temperature and shear forces during blending on the viscosity of the different components, and so on the miscibility of the blend, will have to be considered. These become important, for example, in scaling up the mixing. The molecular weight of the copolymer and the structure of PEU are other factors in need of study for blends of this type. Further research on PEU blends is under way.

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