

Ternary-Phase Poly(ester-urethane)/Elastomer/Filler Composites

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ABSTRACT: Impact-modified and reinforced composites, consisting of biodegradable poly(ester-urethane) (PEU), poly(L-lactic acid-co- ϵ -caprolactone-urethane) elastomer, and various organic and inorganic fillers, were prepared by melt blending, and their properties were investigated. The impact strength increased with elastomer addition, and the addition of particulate or fibrous fillers as a third component increased the stiffness. Therefore, the balance between the impact strength and stiffness of the amorphous PEU was significantly improved. Composites with elastomer and 15 wt % particulate fillers, that is, wollastonite, Aktisil, and talc, showed excellent impact strength. However, effective impact modification was lost in highly constrained systems. Dynamic mechanical thermal analysis confirmed the phase separation of elastomer and showed a marked increase in the glass-transition temperature for the PEU matrix in binary blends with wollastonite, talc, and glass fiber. Scanning electron microscopy studies showed good adhesion of the components. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1531–1539, 2001

Key words: blends; rubber modification; fillers; lactic acid; poly(ester urethane)

INTRODUCTION

Aliphatic polyesters such as poly(lactic acids) have acceptable mechanical properties only at high molecular weights. These can be achieved through ring-opening polymerization of the lactides. Direct polycondensation of lactic acid is also possible, but it usually yields low molecular weight polymers. Biodegradable lactic acid polymers based on a two-step process were investigated in our laboratory. The process involves the condensation polymerization of L-lactic acid to low molecular weight hydroxyl-terminated prepolymer, followed by an increase in the molecular weight via the addition of diisocyanate as a chain

extender.^{1–3} The end product is a thermoplastic poly(ester-urethane) (PEU) that has been shown to be biodegradable.⁴ The method not only is highly efficient for converting lactic acid to high molecular weight polymer but also offers considerable scope for structural modification and thus tailoring of the properties.^{5–7}

Polymer modification through blending is a means to obtain materials with a balanced combination of specific properties. One successful route to improving the impact resistance of polymers is rubber toughening. In this process, typically between 3 and 20 wt % rubber is incorporated as a dispersed phase into a rigid plastic matrix. The essential characteristic of rubber toughening is that significant improvements in impact strength, elongation at break, work to break, and fracture toughness are accompanied by only a small reduction in modulus and tensile strength.⁸

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The normal reasons for introducing a filler to a plastic are to enhance general properties, to introduce specific characteristics, and to reduce the cost of the product. Classifications of fillers are generally based on source, performance function, composition, or morphology. Fillers may thus be organic or inorganic, and each group comprises fibrous and nonfibrous types. The natural filler materials, which are composed largely of cellulose, are biodegradable and thus recommended in blends of biodegradable polymers. The mechanical properties of filled polymers are determined by the size, shape, loading, and properties of the filler but more essentially by the interaction of the filler with the surrounding matrix.⁹ The particle shape is reported in terms of aspect ratio, which is defined as the ratio of the longest length of a particle to its thickness. In general, high-aspect-ratio particles in a composite result in better mechanical properties, but they are again more difficult to process and yield higher anisotropy.¹⁰ However, for several types of thermoplastics, high-aspect-ratio fillers are widely reported as giving poor impact properties.¹¹ Particulate fillers may be inert or reinforcing. Inert fillers are not really inert because fillers will always modify the flow characteristics and mechanical properties of a composite. Rigid particulate and fibrous reinforcements often improve such properties as stiffness, hardness, and temperature resistance, although usually at the expense of impact strength, which may fall dramatically, particularly at high levels of filler addition. Reinforcing fillers enhance properties such as tensile strength and modulus through enhanced interaction with the polymer.^{10,12} Glass beads and silica and other rigid particulate fillers have also been added as a second phase to provide toughening. Thus, particulate fillers may be effective in increasing the impact strength of the brittle polymers.¹³

Grijpma et al.¹⁴ described effective toughening of poly(L-lactide) and lactide stereocopolymers: the impact modification of amorphous and brittle copolymers of L- and D-lactide was accomplished through the incorporation of a discrete rubber phase of poly(trimethylene carbonate) or poly(trimethylene carbonate/ ϵ -caprolactone) in the poly(lactide) matrix. Rubber modification resulted in increased impact strengths, lower yield strengths, and higher elongations to break. In a previous study on brittle PEU, we achieved significant improvement in impact strength combined with good tensile properties by incorporating a biodegradable copolymer of L-lactide and ϵ -caprolactone or poly(L-lactic acid-co- ϵ -

caprolactone-urethane) elastomer.¹⁵ Furthermore, the addition of either particulate or fiberlike fillers increased the stiffness of PEU almost linearly with increasing filler content, but the tensile and impact strength and strain at break showed a decreasing trend.¹⁶ Strength and toughness values usually exhibit opposite trends in these two approaches, but a synergy between the two characteristics is desired.

There has been increasing interest in the preparation of multicomponent matrix/rubber/filler polymer composites because of the possibility of increasing, at least to some extent, both the stiffness and toughness of the material. It is believed that the careful incorporation of high modulus and rubbery materials in the same composite could result in an improvement in both the modulus and impact strength.^{17–25} Multicomponent composites consisting of matrix, rubber, and filler are expected to exhibit fairly complex behaviors. Filler–matrix, filler–rubber, and rubber–matrix interfaces and/or interphases may be involved.¹⁸ Kolařík et al.²⁰ showed that composites of polypropylene (PP) matrix/ethylene–propylene elastomer/calcium carbonate filler assume two-phase structures: either the separate dispersion of elastomer and filler or the encapsulation of filler particles by elastomer. Complete separate dispersion or encapsulation was not observed, and the extent of encapsulation depended on the composition and the surface treatment of the filler. Stamhuis²⁴ suggested that differences in the balance of impact strength and stiffness as obtained with various elastomers may be explained by the differing tendencies to coat the filler surface. Furthermore, he significantly improved the balance of impact strength and rigidity of PP composites by applying short glass fibers instead of mineral fillers in elastomer-modified PP. The morphology and mechanical properties of the ternary-phase composites are influenced by the melt rheology of the system, the compounding conditions and, most importantly, the magnitude of the interactions between the components.⁹

In this study, ternary-phase polymer composites containing both rubber modifier and rigid filler were investigated with the aim of achieving an optimum balance of toughness and stiffness. Biodegradable poly(L-lactic acid-co- ϵ -caprolactone-urethane) elastomer was used as an impact modifier, and organic or inorganic fillers with different particle sizes and shapes were studied as reinforcing agents.

EXPERIMENTAL

Materials

Matrix

Lactic acid based PEU was synthesized in a two-step process: the condensation polymerization of L-lactic acid (initially 88% L-lactic acid in water, purified by distillation; ADM) and 2 mol % 1,4-butanediol (Fluka) to low molecular weight hydroxyl-terminated prepolymer followed by an increase in the molecular weight with 1,6-hexamethylene diisocyanate (Fluka) as a chain extender. Sn(II)octoate (Sigma) was used as a polycondensation catalyst. The synthesis and characterization of PEU were described earlier.^{2,3}

Elastomer

Poly(L-lactic acid-co- ϵ -caprolactone-urethane) elastomer [P(LA/CL)U] was synthesized in a two-step process like that used for PEU except that 50 mol % (in feed) ϵ -caprolactone (Fluka) was used as the comonomer in the synthesis of the prepolymer.⁷

Fillers

Wollastonite is naturally occurring calcium silicate (CaSiO₃). Wicroll 10 PA (Partek Nordkalk) had a particle size of less than 10 μm and an aspect ratio (L/D) of 8/1, and it was surface-treated with aminosilane. For comparison, untreated Wicroll 10 (8/1 aspect ratio) and FW 325 (3/1 aspect ratio) were used in some of the experiments. The other silicate filler, Aktisil PF 224 (Hoffmann Mineral), is a natural mixture of coruscular quartz and lamellar kaolinite and was stearyl amine-coated. Talc (31% MgO, 61% SiO₂, 4.8% H₂O; Finntalc M20SL; Finnminerals) had a particle size of less than 20 μm (80% < 10 μm). The organic fiberlike materials investigated were wood fiber (Solka Floc cellulose fiber; particle size = 40–165 μm) and flax. The flax fiber and other fibrous reinforcement glass fiber (diameter = 10 μm ; Ahlstöm Glassfibre) were cut on average to 10 mm long.

Blending and Injection Molding

The blends were prepared with a co-rotating twin-screw midi-extruder (DSM; screw length = 150 mm) equipped with a backflow channel that allowed it to be operated batchwise. Different amounts of elastomer and fillers were blended with PEU at 140 °C (screw speed = 75 rpm). 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 150 °C, and the temperature of the mold 30 °C.

Characterization

Dynamic mechanical thermal analysis (DMTA) was performed on a PerkinElmer 7 Series instrument. The measurements were made with the three-point bending method from -50 to 70 °C at a rate of 4 °C/min. All measurements were performed at 1 Hz. The glass-transition temperature (T_g) was determined as the peak of $\tan \delta$.

The morphology of a cross section of the cryogenically fractured samples was examined by scanning electron microscopy (SEM; Zeiss 962 digital scanning microscope). SEM micrographs were taken after the coating of the surfaces with a thin layer (10–20 nm) of platinum (Agar sputter coater).

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. The crosshead speed was 5 mm/min, and the specimen type was 1BA according to the ISO/R 527-1993(E) standard. Charpy impact tests of unnotched specimens with dimensions of 4 × 6 × 50 mm³ were performed on a Zwick 5102 pendulum-type testing machine according to the ISO 179/2D f standard.

RESULTS AND DISCUSSION

Mechanical Properties

Multicomponent PEU/rubber/filler composites were prepared by the blending of biodegradable lactic acid-based PEU with 0–20 wt % poly(L-lactic acid-co- ϵ -caprolactone-urethane) elastomer and 0–30 wt % organic or inorganic filler. For comparison, neat PEU was processed in the extruder, and the PEU/elastomer and PEU/filler binary systems were prepared. The compositions of the samples and the mechanical and thermal properties of the composites are given in Tables I and II.

The PEU/elastomer binary blends exhibited significantly higher impact resistance than the

Table I Thermal and Mechanical Properties of Multicomponent PEU Blends with Mineral Fillers

Sample (w/w)	T_g (Peak; °C) ^a	T_g (Onset; °C) ^a	Tensile Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)	Impact Strength (kJ/m ²)
PEU	—	41	1550 ± 30	46 ± 4	3.9 ± 1.0	11 ± 2
PEU/elastomer 10	-35	38	1370 ± 20	40 ± 1	4.4 ± 0.6	25 ± 9
PEU/elastomer 15	-34	36	1220 ± 10	36 ± 1	5.0 ± 1.0	39 ± 8
PEU/elastomer 20	-34	37	1070 ± 30	32 ± 1	9.6 ± 3.8	46 ± 10
PEU/elastomer 0/wollastonite 15	—	51	2700 ± 40	52 ± 1	5.1 ± 1.1	23 ± 3
PEU/elastomer 10/wollastonite 15	-30	41	1920 ± 20	45 ± 1	13 ± 7	23 ± 3
PEU/elastomer 15/wollastonite 15	-27	41	1780 ± 30	40 ± 1	45 ± 14	26 ± 2
PEU/elastomer 20/wollastonite 15	-25	40	1510 ± 90	35 ± 2	68 ± 30	38 ± 5
PEU/elastomer 0/wollastonite 30	—	52	3570 ± 220	57 ± 2	3.3 ± 0.3	16 ± 2
PEU/elastomer 10/wollastonite 30	-28	41	2870 ± 130	48 ± 1	8.0 ± 3.3	20 ± 2
PEU/elastomer 20/wollastonite 30	-25	40	2390 ± 50	39 ± 1	18 ± 4	24 ± 3
PEU/elastomer 0/Aktisil 15	—	46	2020 ± 40	45 ± 1	3.0 ± 0.1	14 ± 2
PEU/elastomer 10/Aktisil 15	-34	40	1640 ± 20	41 ± 4	3.2 ± 0.4	26 ± 7
PEU/elastomer 15/Aktisil 15	-29	39	1440 ± 20	37 ± 2	3.6 ± 0.5	27 ± 8
PEU/elastomer 20/Aktisil 15	-31	42	1110 ± 40	30 ± 1	31 ± 8	41 ± 13
PEU/elastomer 0/Aktisil 30	—	40	2700 ± 40	47 ± 5	2.2 ± 0.3	10 ± 1
PEU/elastomer 10/Aktisil 30	-29	39	2050 ± 50	41 ± 2	3.1 ± 0.7	14 ± 4
PEU/elastomer 20/Aktisil 30	-30	37	1360 ± 110	28 ± 1	16 ± 7	26 ± 4
PEU/elastomer 0/talc 15	—	51	2350 ± 50	46 ± 1	4.7 ± 1.0	15 ± 1
PEU/elastomer 10/talc 15	-27	42	1940 ± 70	42 ± 1	6.2 ± 2.9	19 ± 2
PEU/elastomer 15/talc 15	-29	43	1730 ± 50	37 ± 2	30 ± 27	26 ± 2
PEU/elastomer 20/talc 15	-26	42	1450 ± 60	31 ± 1	67 ± 25	35 ± 5
PEU/elastomer 0/talc 30	—	52	3280 ± 220	48 ± 2	2.6 ± 0.1	9 ± 1
PEU/elastomer 10/talc 30	-29	42	2610 ± 360	42 ± 5	12 ± 6	12 ± 3
PEU/elastomer 20/talc 30	-28	43	2270 ± 80	36 ± 2	23 ± 7	15 ± 3

^a Determined by DMTA from the peak of tan δ .

parent polymer. The addition of the rubber phase increased the unnotched Charpy impact strength from 11 to 46 kJ/m². High toughness values are consistent with stress-whitened zones, so that with 20 wt % elastomer, about two-thirds of the fracture surface was whitened; no stress-whitened zone was observed for neat PEU. Tensile properties showed a downward trend; strength and modulus values decreased with the increasing rubber content of the blend.

For the PEU/filler binary blends, the addition of particulate or fibrous filler increased the stiffness almost linearly with filler content. The addition of 30% glass fiber or wollastonite increased the tensile modulus by as much as 130%. In general, tensile and impact strength and strain at break show a downward trend as a function of the filler concentration. However, in our work improvements in tensile strength were achieved with all fillers. As expected, glass fiber gave the highest strength value, 75 MPa, and wollastonite, with a high aspect ratio (8/1), gave up to 57 MPa.

These extensive increases in tensile modulus and strength suggest the suitability of glass fiber and wollastonite as the third component to improve properties in PEU/elastomer blends. Aktisil and talc showed somewhat lower values than neat PEU, but again strength increased with the filler content. A slight decrease in the tensile strength at a higher filler loading was observed only with flax fiber, but the volume fraction was much higher for flax than for the other fillers. Interestingly, some improvements and generally only small reductions in impact strengths were seen in PEU/filler blends. A significant improvement in impact strength was achieved with wollastonite: 15 wt % wollastonite increased the impact strength to 23 kJ/m², which is a level of practical importance. The effect of the aspect ratio of wollastonite is depicted in Figure 1. With a ratio of 8/1, the tensile modulus and strength and impact strength all increased, as mentioned previously. Although the values of wollastonite without sur-

Table II Thermal and Mechanical Properties of Multicomponent PEU Blends with Organic and Fibrous Fillers

Sample (w/w)	T_g (Peak; °C) ^a	T_g (Onset; °C) ^a	Tensile Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)	Impact Strength (kJ/m ²)
PEU/elastomer 0/wood fiber 15	—	46	2060 ± 100	47 ± 2	3.8 ± 0.9	10 ± 1
PEU/elastomer 10/wood fiber 15	-30	40	1860 ± 70	41 ± 1	3.7 ± 0.5	12 ± 1
PEU/elastomer 15/wood fiber 15	-28	36	1700 ± 60	37 ± 3	4.0 ± 1.0	12 ± 2
PEU/elastomer 20/wood fiber 15	-30	39	1530 ± 50	34 ± 2	7.1 ± 1.4	15 ± 2
PEU/elastomer 0/wood fiber 30	—	45	2700 ± 100	56 ± 2	3.3 ± 0.2	9 ± 1
PEU/elastomer 10/wood fiber 30	-27	38	2300 ± 200	43 ± 3	3.8 ± 0.7	11 ± 1
PEU/elastomer 20/wood fiber 30	-26	35	2190 ± 60	37 ± 3	5.5 ± 0.4	12 ± 1
PEU/elastomer 0/flax fiber 15	—	42	2280 ± 60	51 ± 1	4.4 ± 0.4	9 ± 1
PEU/elastomer 10/flax fiber 15	-28	34	1850 ± 170	42 ± 7	4.0 ± 1.4	11 ± 1
PEU/elastomer 15/flax fiber 15	-31	33	1540 ± 90	38 ± 1	5.4 ± 0.9	14 ± 1
PEU/elastomer 20/flax fiber 15	-26	28	1450 ± 70	32 ± 1	7.5 ± 0.5	16 ± 1
PEU/elastomer 0/flax fiber 30	—	42	3150 ± 140	49 ± 6	2.1 ± 0.5	8 ± 2
PEU/elastomer 10/flax fiber 30	— ^b	37	2520 ± 130	45 ± 4	4.0 ± 0.6	9 ± 2
PEU/elastomer 20/flax fiber 30	-25	27	2020 ± 200	35 ± 4	6.4 ± 0.7	12 ± 2
PEU/elastomer 0/glass fiber 15	—	51	2730 ± 70	65 ± 4	3.3 ± 0.2	5 ± 1
PEU/elastomer 10/glass fiber 15	-28	39	2590 ± 70	58 ± 2	3.5 ± 0.1	12 ± 2
PEU/elastomer 15/glass fiber 15	-29	39	2330 ± 40	53 ± 2	4.2 ± 0.2	14 ± 2
PEU/elastomer 20/glass fiber 15	-30	41	2160 ± 60	48 ± 2	5.1 ± 0.6	17 ± 1
PEU/elastomer 0/glass fiber 30	—	52	3590 ± 190	75 ± 2	3.0 ± 0.1	9 ± 2
PEU/elastomer 10/glass fiber 30	-29	39	3190 ± 350	63 ± 4	3.6 ± 0.5	13 ± 1
PEU/elastomer 20/glass fiber 30	-27	39	3280 ± 110	56 ± 4	4.4 ± 0.4	14 ± 1

^a Determined by DMTA from the peak of tan δ .^b Not detected.

face treatment (Wicroll 10) were somewhat lower, they showed the same trend. In contrast, wollastonite with an aspect ratio of 3/1 showed only a slight increase in modulus and decreases in both tensile and impact strength.

The effects of elastomer and filler together on the mechanical properties of the resulting composites can be readily assessed from the data in Tables I and II. Several features are worth noting. In general, all rubber-modified formulations displayed a reduction in tensile modulus and strength. However, the modulus values with a 15 wt % filler addition were all higher than those for neat PEU, even at high rubber loadings. At a 30 wt % filler addition, the increase in stiffness was even as much as twofold. The tensile strength decreased as a function of the rubber content in the same way as for the PEU/elastomer binary blends, although it was still relatively high. Tensile strengths were very high for glass fiber, as well as for wollastonite compositions.

The impact strengths of PEU/elastomer/filler composites with 15 wt % filler are displayed in

Figure 2, with the binary blends presented for comparison. In all blends, the impact strength increased with rubber addition. Roughly two levels of toughness can be discerned. Composites with particulate fillers (i.e., wollastonite, Aktisil, and talc) showed excellent impact strength, but the strength was still slightly lower than that of rubber-modified PEU. In wollastonite blends, where the original impact value was high, small amounts of elastomer increased the impact strength only slightly, and this increase was counteracted by the reinforcing effect of the wollastonite. At a large elastomer content, however, a considerable increase was achieved in the impact strength. All fibrous fillers displayed only a marginal increase in toughness, and the higher filler levels in PEU resulted in only moderate improvement in impact strength. Nevertheless, a comparison of the mechanical properties of neat PEU and compositions containing both filler and elastomer indicated that the addition of elastomer eliminated the decrease in toughness caused by filler and thus improved the balance of properties.

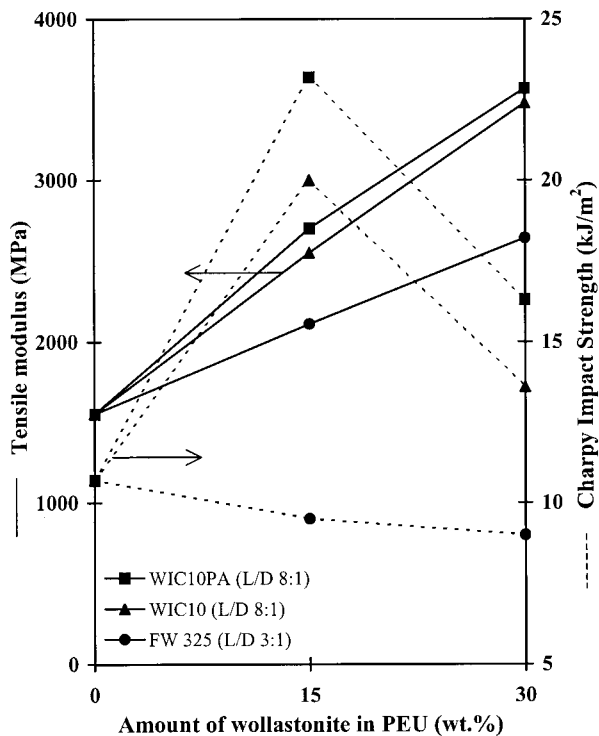


Figure 1 Effect of the aspect ratio and the surface treatment on the mechanical properties of the PEU/wollastonite blend.

Thermal Properties

Adequate phase separation between the matrix and dispersed rubber is required for effective rubber toughening. In phase-separated polymer blends, the transitional behavior of the components remains unchanged, whereas in a miscible blend, a single transition appears. Dynamic mechanical analysis of the blends of PEU with P(LA/CL)U elastomer showed separate T_g 's for the rubber and matrix, indicating clear phase separation. Although the structure was thus two-phase, some interaction was observed at the rubber-matrix interface: the T_g 's of the PEU matrix and P(LA/CL)U rubber were shifted slightly toward each other (Table I). This partial compatibility was assumed to be due to the similar chemical structures of the blend components.

The T_g of the matrix polymer increased in the presence of filler. A marked 10 °C increase in the T_g of amorphous PEU occurred with 15 wt % wollastonite, talc, and glass fiber, and values 1–5 °C higher were measured for binary blends with Aktisil, wood, and flax fiber. The stiffening effect induced by fillers reduced the matrix mobility and caused an increase in T_g . The marked increase in

T_g when wollastonite, talc, or glass fiber was added to the PEU matrix polymer was related to a very strong interaction between the polymer and filler.

Dynamic mechanical thermal properties of PEU and multicomponent formulations of PEU/elastomer/wollastonite blends are given in Figure 3 in terms of the storage modulus, E' , and the loss factor, $\tan \delta$, from -45 to 60 °C. Compared with neat PEU, all ternary compositions showed a marked increase in E' . E' showed a moderate decrease as temperature increased, and this decrease was more evident with a higher elastomer content. In the ternary composites, the increase in the matrix T_g that was achieved with wollastonite, talc, and glass fiber was shifted back to the initial temperature by the addition of an elastomer phase. As seen in Figure 3, the storage modulus of the PEU/wollastonite 15 wt % blend fell abruptly at 52 °C, whereas for neat PEU and for blends containing elastomer, the decrease occurred at approximately 40 °C. In multicomponent blends, the $\tan \delta$ peaks, which were attributed to the T_g of the elastomer, were about -30 °C. These T_g values were somewhat higher than those in PEU/elastomer binary blends, which suggests that at least part of the elastomer was around the filler. Fillers caused this shift of $\tan \delta$

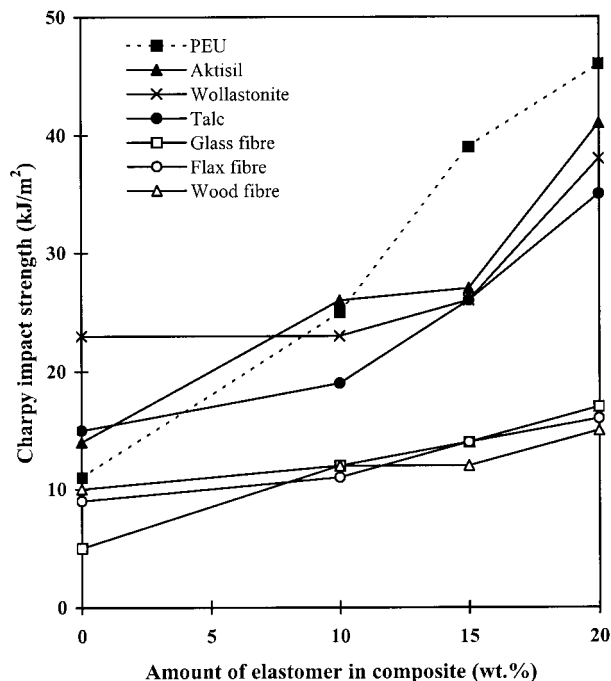


Figure 2 Impact strength of the ternary PEU/elastomer/filler composites with 15 wt % filler.

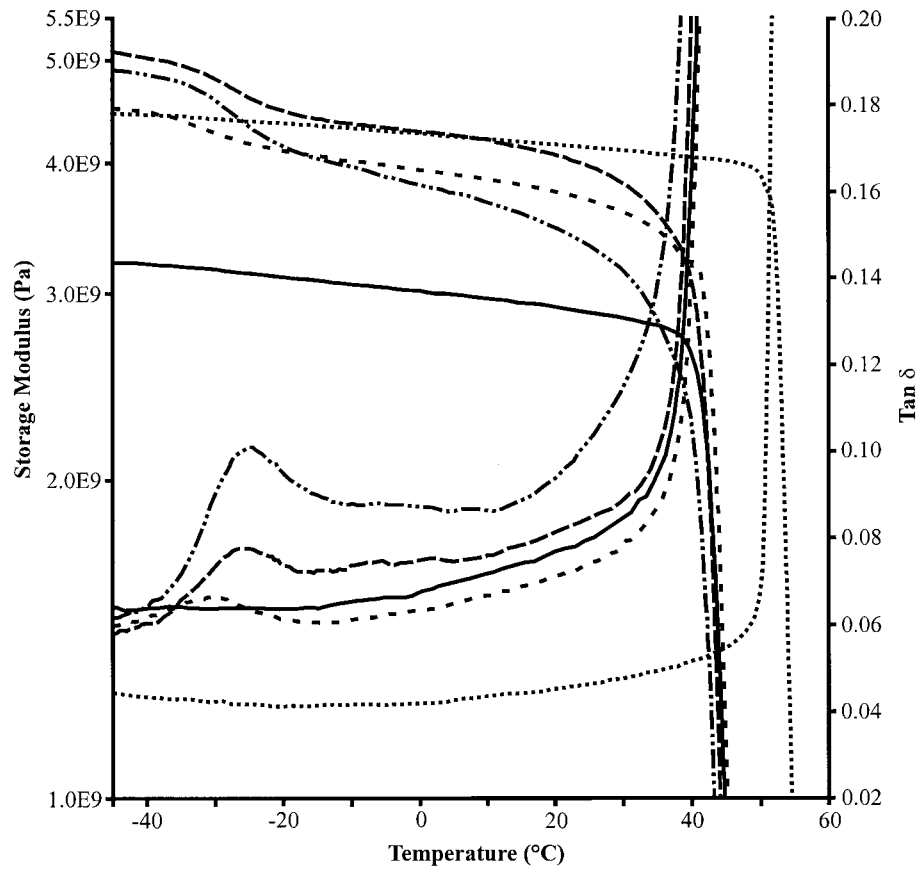


Figure 3 Dynamic mechanical properties of neat PEU (—) and PEU/elastomer/filler multicomponent blends with 15 wt % wollastonite and elastomer weight percentages of 0 (···), 10 (---), 15 (— —), and 20 (— · —).

peaks to higher temperatures by restraining molecular motions.

Morphology

The morphology of the ternary composites was expected to be complex because the fillers were of different particle sizes and shapes and matrix–rubber, matrix–filler, and rubber–filler interphases were possible. Wollastonite particles were fibrous with a diameter of about 2 μm , talc particles were flakes, and Aktisil was in the form of spherical or slightly irregular agglomerated particles. Wood particles were irregular fibers with diameters of about 20 μm . Flax fibers were sheaves with diameters of about 100 μm , and the glass fibers had a circular cross section with diameters of 15–20 μm . SEM observations of fractured samples revealed good adhesion between the matrix and all fillers. Figure 4(a,c,e) shows the SEM micrographs of PEU blended with wollastonite, talc, and flax fiber, respectively.

Mechanical data suggest that the morphology of the rubber-modified blends with organic and glass fibers was basically different from that of the same blends with particulate fillers. Also, as stated previously, a higher filler content (30 wt %) has a marked effect on the properties of the composites. Figure 4(b,d,f) presents scanning electron micrographs for ternary composites with wollastonite, talc, and flax fiber. The elastomer occurred in the matrix phase predominantly in the form of finely dispersed particles, approximately 0.1–1 μm in diameter. We were unable to confirm any encapsulation of the fillers by the elastomer in the SEM analysis. At least partially, the differences in properties may be explained by the densities of the fillers. Although the actual volume content of the high-density inorganic fillers was much less than their weight fraction, that of the wood and flax fibers was somewhat higher. These observations suggest that rubber toughening is less effective in constrained systems.

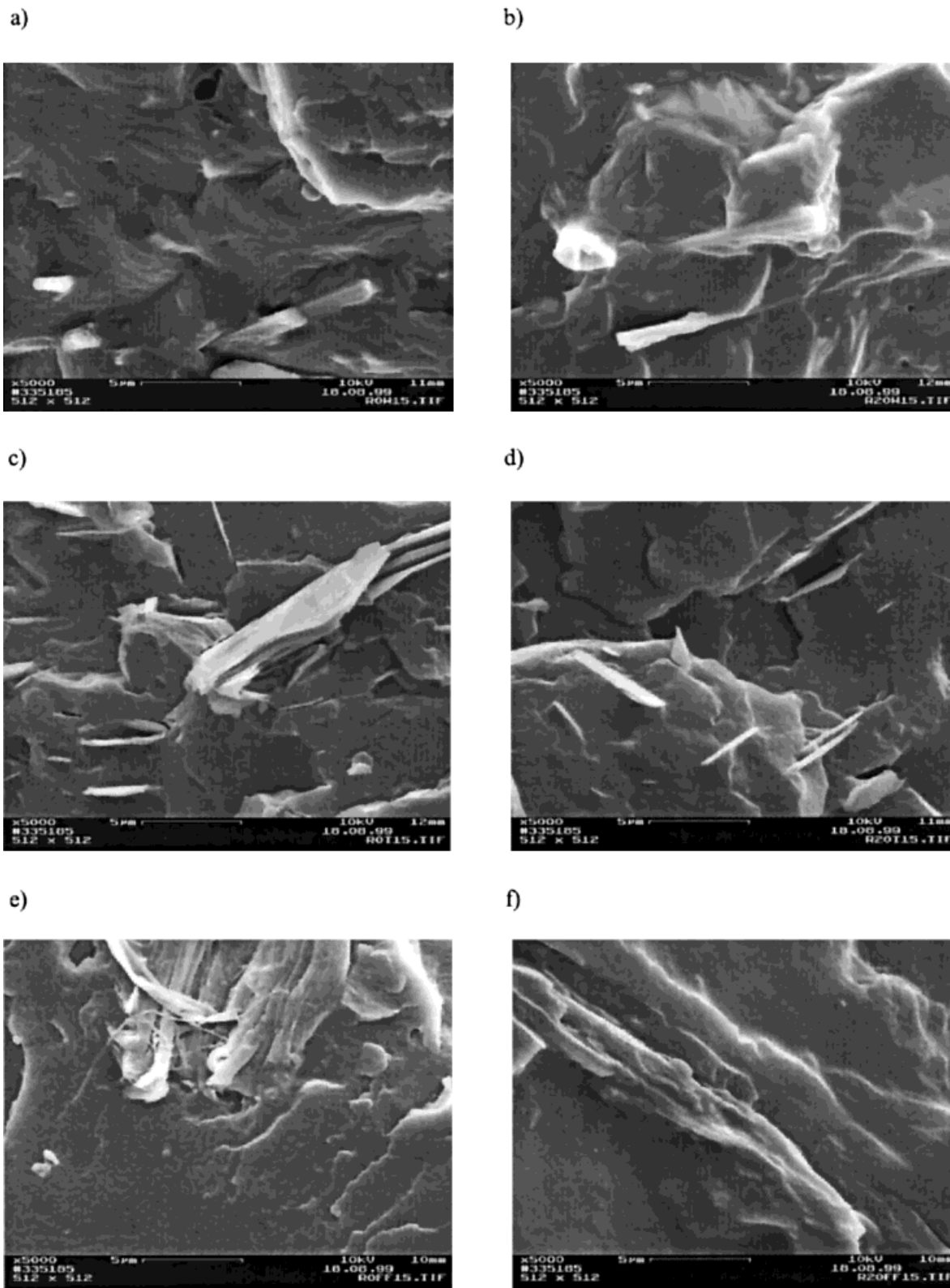


Figure 4 SEM micrographs of (a) PEU/wollastonite 15, (b) PEU/elastomer 20/wollastonite 15, (c) PEU/talc 15, (d) PEU/elastomer 20/talc 15, (e) PEU/flax fiber 15, and (f) PEU/elastomer 20/flax fiber 15 blends.

CONCLUSIONS

New and improved toughened PEU composites containing a combination of rubbery and rigid dispersion phases were prepared. Our results show that useful composites with an excellent balance of properties can be successfully developed through the exploitation of rubber modification and the reinforcing effect of a filler. Even purely rubber-toughened PEU exhibited markedly increased impact strength and thus a better balance of properties than the parent polymer. However, the addition of P(LA/CL)U elastomer slightly softened PEU, causing an inevitable reduction in modulus and tensile strength. The addition of a filler not only lowered the cost of this biodegradable material but increased the stiffness. A unique feature was that 15 wt % wollastonite in a binary PEU/wollastonite blend increased the impact strength to a level of great practical importance. Moreover, a 10 °C increase was observed in the T_g of PEU.

In general, the best improvement in the ternary composites was obtained with wollastonite, Aktisil, talc, and glass fiber. High impact strength together with an increase in stiffness was obtained with particulate fillers. In addition, the glass-fiber composites showed very high tensile strengths. The rubber toughening was less effective in constrained composites, that is, in composites with fibrous fillers, with high filler loadings, or alternatively with organic fillers where the volume fraction was increased. However, completely biodegradable composites can be manufactured from PEU and wood or flax fibers. In summary, a synergy between stiffness and toughness can be achieved with ternary composites containing both a rubber modifier and a rigid filler.

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