Reactive Extrusion of Polycaprolactone Compounds Containing Wood Flour and Lignin

HANSJÖRG NITZ, HINNERK SEMKE, RÜDIGER LANDERS, ROLF MÜLHAUPT

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

ABSTRACT: Biodegradable polycaprolactone (PCL) was melt-compounded in a Werner & Pfleiderer twin-screw extruder (ZSK25) together with wood flour (WF) and lignin with maleic anhydride-grafted polycaprolactone (PCL-*g*-MA) used as a compatibilizer. The grafting of maleic anhydride onto PCL was achieved with reactive extrusion in the presence of 2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexane as an initiator. The graft copolymers were analyzed with size exclusion chromatography and titration. As a function of the initiator and maleic anhydride addition, the grafted maleic anhydride content varied from 1.4 to 3.1 wt %. Compounds compatibilized with PCL-*g*-MA exhibited improved mechanical properties: a compatibilized PCL compound containing 40 wt % WF gave a Young's modulus of 2300 MPa with respect to 400 MPa for neat PCL and a 100% increase in yield stress. The content of WF, lignin, and PCL-*g*-MA was varied systematically to examine stress–strain and impact behavior. Low contents of grafted maleic anhydride and PCL-*g*-MA were required to improve both mechanical properties and interfacial adhesion. Biodegradation was investigated. Lignin addition was found to retard biodegradation. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1972–1984, 2001

Key words: polycaprolactone; wood flour; lignin; fiber reinforcement; grafting; compatibilizers; natural fibers

INTRODUCTION

Natural polymers such as wood flour (WF), lignin, natural fibers, starch, and proteins have attracted attention as components of reinforced plastics. Natural-fiber-reinforced polypropylenes (PPs) and polyethylenes have been developed.[1–8] Many approaches have been described in the literature to improve the adhesion between organic fillers and the polymer matrix. The most prominent method is the addition of maleic anhydride polymers as compatibilizers [e.g., maleic anhydride-grafted polypropylene (PP-*g*-MA) and poly(styrene)-*block*-poly(ethene-*co*-1-butene)-*block*-poly(styrene) triblock copolymer]. During compounding, the maleic anhydride-functional polymers react with the hydroxyl groups of WF to form graft copolymers. This covalent coupling between cellulose and PP-*g*-MA was demonstrated by Gauthier et al.[1] and Felix and Gatenholm[2] via Fourier transform infrared and ESCA measurements on Soxhlet-extracted cellulose samples that were coated with low-molecular-weight PP-*g*-MA. PP-*g*-MA is the most common coupling agent for PP/WF composites. Dalväg et al.[3] dispersed 45 wt % WF in PP and observed a 100% increase in modulus. With 6 wt % PP-*g*-MA on 30 wt % WF, they reached a 20% increase in tensile strength. Meyers et al.[4] examined a similar system with 45 wt % WF and 5 wt % PP-*g*-MA and observed a

Correspondence to: R. Mülhaupt (mulhaupt@fmf.uni-freiburg.de).

20% increase in strength and stiffness. However, the PP-*g*-MA addition was associated with severe losses in the notched impact strength, which decreased drastically when WF content was increased. Oksman and Clemons[7] used poly(styrene)-*block*-poly(ethene-*co*-1-butene)-*block*-poly-(styrene) triblock copolymer (SEBS-*g*-MA), PP-*g*-MA, and EPDM-MA as compatibilizers in compounds containing 40 wt % WF. The addition of SEBS-*g*-MA as a compatibilizer gave better mechanical properties and also much better interfacial adhesion between the filler and the PP matrix.

An important objective is to develop fully biodegradable polymer composites composed of natural fibers or WF reinforcements combined with a biodegradable matrix. A high content of the reinforcing component is desirable to improve mechanical performance and reduce costs related to the use of biodegradable polyesters such as polycaprolactone (PCL) and polyhydroxybutyrate, which are much more expensive than commodity polyolefins. Moreover, the development of biocompatible biostabilizers is necessary to control biodegradation and enhance product lifetime.

Although most biodegradable polyesters exhibit high polarity, research by Mani et al.[9] revealed that the addition of compatibilizers was required to achieve higher interfacial adhesion and a higher strength. For example, Mani et al. used a starch-graft PCL as a compatibilizer in their PCL/starch composites to promote finer dispersion and interfacial adhesion. They obtained a fourfold increase in tensile strength for a PCL/starch blend containing 70 wt % starch and 3 wt % PCL-grafted starch with respect to the tensile strength of noncompatibilized compounds. Koenig and Huang[10] described a PCL/starch composite containing 25 wt % starch that showed an increase in Young's modulus of 50% and a simultaneous decrease in the tensile strength of approximately 15%. Warth et al.[11] developed a reactive-extrusion technology to compatibilize cellulosediacetate with a variety of natural polymers such as lignin and cellulose fibers via *in situ* grafting of caprolactone during reactive extrusion.

The compounding of WF and biodegradable polymers such as PCL afford biodegradable materials a combination of high stiffness and strength with complete biodegradation. Wood contains about 25 wt % lignin, which together with cellulose forms the structural component of trees and various plants. Today, this lignin byproduct in paper manufacturing is used almost exclusively as fuel to generate the energy required to operate paper mills. As a cheap phenolic biopolymer, lignin offers attractive potential as a filler and an additive, especially with respect to the modification of biodegradable polymers. Because of the presence of phenolic groups in lignin, it is expected that lignin fillers can influence both the oxidative stability and biostability of such compounds. Numerous examples of lignin-filled thermoplastics, including PCL, PCL copolymers, and other biodegradable polymers, have been reported in the literature. Glasser and colleagues investigated a great variety of lignin-based materials,[12] including compounds of hydroxypropyl cellulose with lignin.[13] Such lignin compounds exhibited an increased Young's modulus and a tensile strength of around 150% with respect to the polymer matrix. Glasser and colleagues reported that homogeneous lignin/poly(vinyl alcohol) blends can be formed that contain 25 wt % lignin.[14] The preparation of starlike polymers with lignin as the core and caprolactone as the shell[15] and their use as plasticizers in polyvinychloride[16] were also investigated by Glasser and coworkers. In all these studies, lignin showed good compatibility with polar polymers. According to Glasser's investigations, PCL is of great interest because of its attractive miscibility characteristics with other polymers and its biodegradability. Because of the high polarity and moldability of special lignin types, Rösch and Mühaupt[17] succeeded in preparing lignin-based compounds with poly(ethene-*co*-vinylacetate) without adding compatibilizers.

However, most compounding processes require the addition of compatibilizers, which circumvent incompatibility problems relating to poor interfacial adhesion between filler and polymer. The addition of maleic anhydride-modified polymers (e.g., maleic anhydride-grafted polymers) represents a prominent method for compatibilizing fillers and polymers. During compounding, the maleic anhydride-functionalized polymer reacts with the hydroxyl groups of the filler to form graft copolymers. John et al.[18] described the melt grafting of PCL with maleic anhydride in a conical twin-screw extruder with a length/diameter (*L/D*) ratio of 20/1 at a temperature between 90 and 170°C. To achieve a long residence time of approximately 9 min, they set the screw speed at only 14 rpm. They reached a maximum grafting content of 1.62 wt % with 4.5 wt % maleic anhydride and 0.3 wt % dicumyl peroxide as an initiator at 160°C. John et al.[19] also reported the successful

use of maleic anhydride-grafted polycaprolactone (PCL-*g*-MA) in blends with PCL containing up to 75 wt % wheat gluten. For a PCL/PCL-*g*-MA/ wheat gluten blend containing 60 wt % gluten and 2.5 wt % PCL-*g*-MA, they found an increase in the tensile strength from 5 to 18 MPa from the blend without PCL-*g*-MA.

The objective of this study was to prepare several families of thermoplastic PCL compounds containing WF and lignin via reactive-extrusion technology. The key intermediate and compatibilizer was PCL-*g*-MA. Reactive-extrusion processes were developed to vary the content of grafted maleic anhydride over a wide range to examine the influence of PCL-*g*-MA on the mechanical properties of compounds containing different amount of filler. Morphology development and interfacial interactions were studied with transmission electron microscopy (TEM) and environmental scanning electron microscopy (ESEM). An important objective was to examine biodegradation, especially in the presence of lignin additives.

EXPERIMENTAL

Materials

The commercial PCL used in our experiments was obtained from Solvay [CAPA 680; d = 1.15 g/cm^3, melt flow index (MFI) = 7.3 g/10 min at 190°C and 2.16 kg, number-average molecular weight (M_n) = 69,000 g/mol, weight-average molecular weight (M_w)/M_n = 1.74]. The initiator 2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexane (LUPEROX L101; d = 0.87 g/cm^3, 91 wt % technical grade) was obtained from Elf Atochem. The WF obtained from coniferous trees (LIGNOCEL C120) was supplied by Rettenmeier & Söhne (Ellwangen, Germany). The main sieve fraction of the WF (d = 1.45 g/cm^3) showed an aspect ratio between 5 and 10 and a particle size between 70 and 150 μ. The particle size distribution was obtained from a sieve residue analysis according to DIN 53734. The sieve residue was 0.5 wt % at mesh 10, 60 wt % at mesh 25, and 95 wt % at mesh 80. The lignin (d = 1.35 g/cm^3, M_n = 800 g/mol, M_w/M_n = 3) was a fine, dark brown powder (20–40-μm particle size) with a glass-transition temperature of 111°C. The soluble and moldable lignin was supplied by Alcell Specialty Products Inc. (Canada). The polymer and the initiator were used as received. The WF was dried at 100°C in an air-

circulating oven for 24 h prior to use. The lignin was dried at 50°C under vacuum for 24 h prior to use. The moisture content of the wood and lignin was less than 1 wt %. Maleic anhydride and cyclohexane were obtained from Aldrich and were used as received.

Processing

A Werner & Pfleiderer ZSK 25 twin-screw extruder with intermeshing corotating screws was used to prepare the compounds and the compatibilizers. The *L/D* ratio was 42/1 (*D* = 25 mm). To prepare the PCL-*g*-MA compatibilizers, we preblended the PCL and maleic anhydride in a separate extrusion step. The obtained PCL/MA (10 wt % MA) master batch and the neat PCL were fed under a nitrogen atmosphere separately with a gravimetric feed system into the hopper of the extruder. The initiator was diluted with cyclohexane and fed gravimetrically into the second heating section of the extruder with a gear pump (Maag MZP) at a feed rate of 4 mL/min. The residence time was approximately 2:30 min at a processing temperature of 220°C, a mass flow of 5 kg/h, and a screw speed of 200 rpm. Each experiment was carried out two times, and the difference between the two batches was less than 0.05 wt % according to the maleic anhydride content in weight percent.

For the preparation of the compounds, the screw configuration was changed. The obtained PCL-*g*-MA compatibilizers and the PCL were mixed in a tumbling mixer. The WF and the lignin, respectively, as well as the prepared mixtures of PCL and PCL-*g*-MA, were fed separately with a gravimetric feed system. The residence time was approximately 1 min at a processing temperature of 160°C, a mass flow of 5 kg/h, and a screw speed of 200 rpm. Each compound experiment was performed once.

Injection Molding

The compounded and granulated compounds were injection-molded into test bars (DIN 53455) with a cross section of 10 × 4 mm^2 on a conventional machine (Ferromatik K40). The flow direction coincided with the longitudinal direction of the bar. Because of the high viscosity of the highly filled compounds, the injection had to be rapid (with a high injection pressure up to 1200 bar) to ensure a good mold filling. The melt temperature was 200°C.
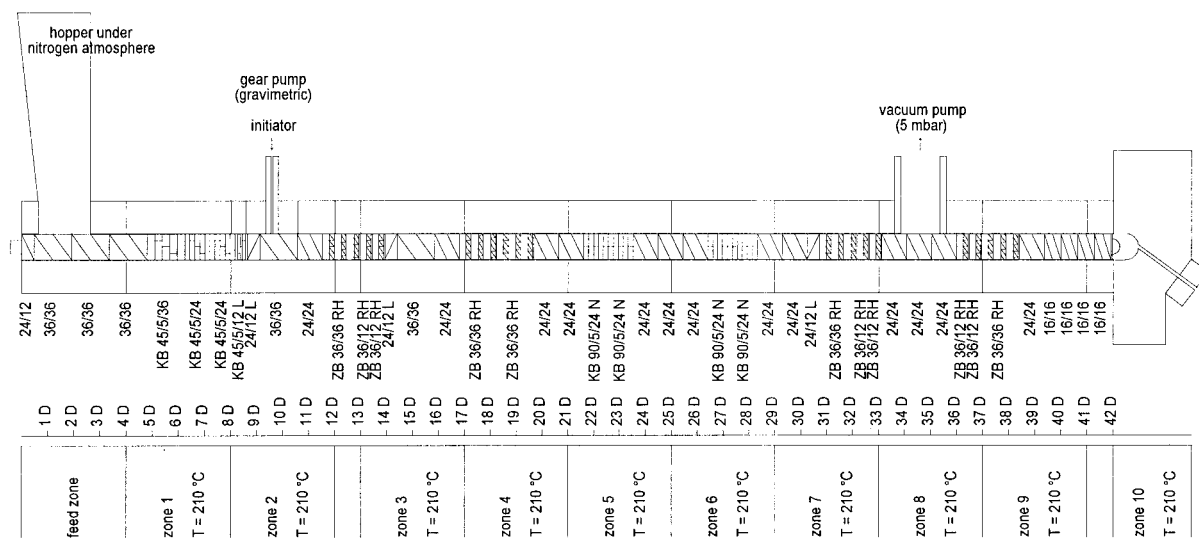
Figure 1 Screw configuration and temperature profile for the grafting of maleic anhydride onto PCL.

Mechanical Characterization

The tensile modulus of the compounds was measured with an Instron 4202 (ISO/DP 527), and the impact strength was measured with an impact tester from Zwick (model 5102; ISO 180/1A). The data were taken at room temperature without preconditioning of the samples. The statistical average of the measurements on at least five test specimens was taken to obtain the mean values and standard deviations for all tests.

Chemical Characterization

A 2-g portion of the grafted polymer was dissolved in hot toluene and precipitated into cold methanol. The precipitated polymer was washed with fresh methanol and dried in a vacuum oven at 50°C for 72 h. The polymer dissolved completely in the toluene. Any unreacted maleic anhydride was removed during the extraction procedure. The anhydride content of the grafted polymer was determined via titration. Typically, 200 mg of the dried sample was dissolved in 80 mL of tetrahydrofuran. The solution was titrated against $0.01N$ methanolic KOH with an automatic titration line from Schott (Titronic TA110). The end point of the titration was calculated from the second derivation of the titration curve with the evaluation program TR660 from Schott. The titration was carried out three times for each sample. The average of these three results was used to calculate the maleic anhydride content in weight percent. The standard error was found to be less than 2%.

The precipitation of the polymer into cold methanol was performed once.

Size Exclusion Chromatography (SEC)

SEC measurements were performed with a refractive-index detector to analyze the molecular size of the grafted polymer. A Knauer Mikrogelset A21 was used for separation, and HPLC-grade trichloromethane was used as the mobile phase. The experiment was carried out at room temperature and a solvent flow rate of 1 mL/min. The refractive index versus the elution volume was obtained for each sample and correlated with the calibration curve obtained from the polystyrene standard. The values obtained for the PCL samples were multiplied by 0.65 according to instructions from the manufacturer.

ESEM

An ElectroScan 2020 environmental scanning electron microscope was used to study the morphology of the WF composites.

TEM

The morphology of the samples was examined with TEM. For TEM measurements, ultrathin sections were prepared at −80°C with an Ultracut E ultramicrotome (Reichert & Jung) with a diamond knife. The measurements were carried out on a LEO 912 Omega (120 kV).

Table I   Initial Concentration of MA and Initiator 2,5-Dimethyl-2,5-di-(*t*-butylperoxy)-hexane (L101) Related to the Polymer Mass Flow

Compatibilizer	MA (wt %)	L101 (wt %)	Flow Rate of the Initiator Solution (mL/min)	Polymer Mass Flow (kg/h)
C0	4.0	0	0	5
C1	4.0	1.0	4	5
C2	4.0	0.5	2	5
C3	2.0	0.5	2	5

Biodegradation

The biodegradability of the samples was tested by their burial in natural soil. After 4 weeks, the samples were cleaned of the soil with water and analyzed with microscopy.

RESULTS AND DISCUSSION

The preparation of PCL-*g*-MA with different graft contents was carried out on a Werner & Pfleiderer ZSK 25 twin-screw extruder with intermeshing corotating screws. The throughput was 5 kg/h, the screw speed was 200 rpm, and the residence time was 2.5 min. The screw configuration and the temperature profile for the reactive extrusion are displayed in Figure 1. The initial concentrations of maleic anhydride and initiator fed into the extruder are listed in Table I. The grafted products were completely soluble in toluene, indicating that there was no crosslinking reaction occurring during the grafting process. In Table II, the molecular weights and the maleic anhydride concentrations after the extrusion step are listed. The total maleic anhydride contents of the compatibilizers C1, C2, and C3 after the extrusion differed from the initial maleic anhydride concentrations because of a loss through the vacuum line

(5 mbar) at heating zone 8 of the extruder. The reference sample C0 was prepared without devolatization of the melt and without an initiator. Compatibilizer C1 showed the highest graft content of 3.12 wt % maleic anhydride and the highest grafting yield of 78%. Compatibilizer C2, which, compared with C1, was prepared with the same amount of maleic anhydride but with only half the amount of initiator, had a lower graft content of 2.37 wt %. Because of the lower initiator concentration, the loss of maleic anhydride (20 wt % of the initial concentration) caused by the vacuum was also higher. Compatibilizer C3 exhibited the lowest graft content of 1.44 wt % and a grafting yield of 70%. Compared with C1, compatibilizer C3 had the same ratio of maleic anhydride to initiator but a lower grafting yield. This indicated that the fed volume of the initiator (cf. Table I) played an important role. Because of the smaller volume, the mixing between the polymer and the initiator solution was not sufficient, and this resulted in a lower grafting yield and in a greater loss of maleic anhydride caused by the vacuum. The molecular weights of the grafted polymers determined via SEC depended on the concentrations of maleic anhydride and the initiator. During the grafting process, three main reactions were feasible: (1) the acid-catalyzed deg-

Table II   Molecular Weight and MA Content of PCL-*g*-MA Compatibilizers After the Reactive Extrusion: Results from Titration and SEC

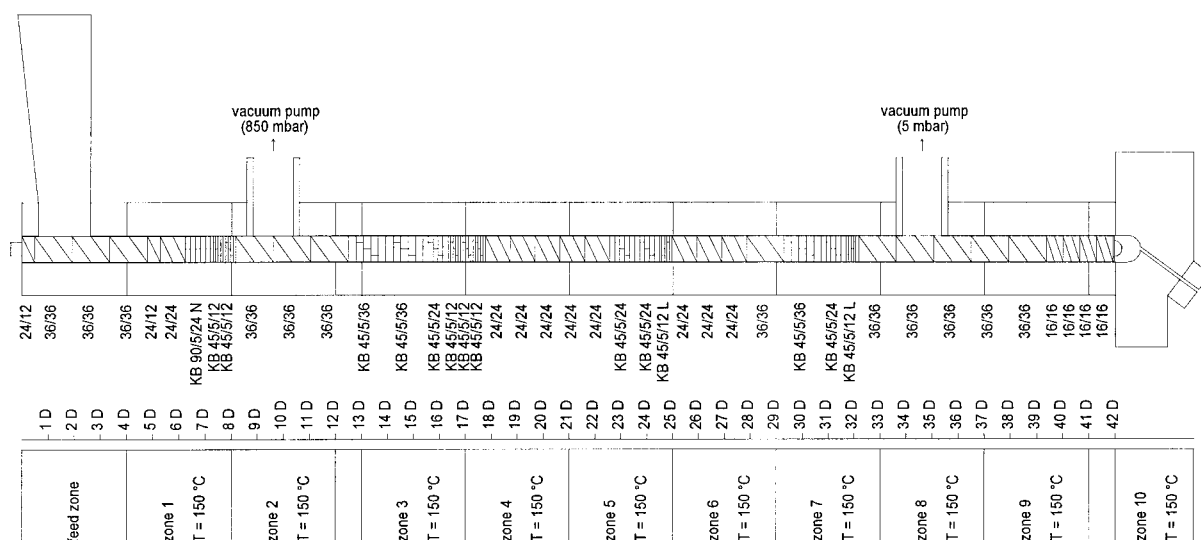| Compatibilizer	Initial MA Content (Before Extrusion; wt %)	MA Content Before Precipitation (wt %)	MA Content After Precipitation (Grafted MA; wt %)	Grafting Yield (%)	M_n (g/mol)	M_w/M_n
C0	4.00	4.00	0.00	0	15000	1.54
C1	4.00	3.86	3.12	78	21600	3.50
C2	4.00	3.18	2.37	59	24500	2.44
C3	2.00	1.86	1.44	70	62300	4.52

Figure 2 Screw configuration and temperature profile for the compounding of the PCL/WF and PCL/lignin compounds.

radation of the polyester through the maleic anhydride, (2) the grafting of the maleic anhydride onto the backbone of the polymer, and (3) the crosslinking of the polymer. For the reference sample C0, the molecular weight decreased from M_n = 69,000 g/mol (for the neat PCL) to M_n = 15,000 g/mol because of acid-catalyzed depolymerization. For the compatibilizer C3, the molecular weight was only slightly lowered with respect to PCL, whereas the distribution was broadened. In contrast, for the compatibilizers C2 and C3, the molecular weights remained nearly the same but were much lower than that of PCL. This clearly indicated that the molecular weights of the grafted polymers depended on the initial concentration of maleic anhydride. The effect of the initiator concentration on the molecular weight was only marginal.

Table III   Mechanical Properties of the PCL/WF Composites

Wood Flour (wt %)	Type of Compatibilizer	Compatibilizer (wt %)	Young's Modulus (MPa)	Yield Stress (MPa)	Strain (%)	Izod Impact Strength (kJ/m^2)
0	—	—	400 (10)	14.5 (0.2)	> 520	21.4 (0.9)
10	—	—	615 (15)	16.8 (0.3)	320 (15)	7.9 (0.6)
20	—	—	880 (10)	19.0 (0.2)	15 (2)	6.9 (0.4)
30	—	—	1560 (45)	21.5 (0.3)	5 (1)	5.1 (0.5)
40	—	—	2210 (55)	24.5 (0.3)	4 (1)	4.2 (0.4)
50	—	—	2830 (60)	27.3 (0.4)	3 (1)	3.5 (0.4)
10	C1	5	605 (25)	17.7 (0.2)	410 (15)	9.6 (0.5)
20	C1	5	910 (10)	21.4 (0.2)	21 (3)	9.2 (0.5)
30	C1	5	1470 (55)	26.8 (0.2)	16 (1)	8.1 (0.3)
40	C1	5	2320 (65)	31.4 (0.4)	8 (2)	6.5 (0.3)
50	C1	5	3090 (60)	31.9 (0.5)	4 (1)	5.0 (0.5)
40	C1	2.5	2305 (60)	31.7 (0.4)	8 (1)	5.2 (0.5)
40	C1	10	2310 (30)	32.1 (0.3)	10 (1)	5.0 (0.6)
40	C2	5	2220 (60)	31.0 (0.4)	8 (2)	6.6 (0.7)
40	C3	5	2180 (55)	31.1 (0.1)	9 (1)	4.8 (0.5)
40	C0	5	2230 (45)	23.8 (0.7)	4 (1)	4.1 (0.4)

Values in the parentheses are the standard deviations.

Table IV   Mechanical Properties of the PCL/Lignin Compounds

Lignin (wt %)	Type of Compatibilizer	Compatibilizer (wt %)	Young's Modulus (MPa)	Yield Stress (MPa)	Strain (%)	Izod Impact Strength (kJ/m^2)
0	—	—	400 (10)	14.5 (0.2)	> 520	21.4 (0.9)
10	—	—	385 (10)	15.0 (0.2)	> 520	4.3 (0.4)
20	—	—	410 (15)	14.1 (0.3)	> 520	3.4 (0.4)
30	—	—	425 (5)	13.3 (0.2)	> 520	2.9 (0.3)
40	—	—	490 (15)	13.1 (0.2)	> 520	1.8 (0.3)
50	—	—	630 (20)	12.9 (0.2)	190 (15)	1.6 (0.2)
60	—	—	940 (25)	13.1 (0.3)	13 (2)	1.3 (0.2)
70	—	—	1175 (30)	12.1 (0.2)	5 (2)	0.7 (0.5)
10	C1	5	410 (10)	15.9 (0.2)	> 520	5.0 (0.4)
20	C1	5	450 (15)	15.1 (0.3)	> 520	4.0 (0.4)
30	C1	5	505 (15)	14.5 (0.2)	> 520	3.3 (0.3)
40	C1	5	540 (20)	13.9 (0.3)	> 520	2.1 (0.2)
50	C1	5	670 (20)	16.0 (0.3)	70 (10)	1.3 (0.2)
60	C1	5	1020 (25)	16.4 (0.4)	4 (1)	1.0 (0.3)
70	C1	5	1570 (40)	9.3 (0.2)	1 (1)	0.5 (0.4)
40	C1	2.5	520 (20)	13.9 (0.2)	> 520	2.1 (0.2)
40	C1	10	545 (15)	13.6 (0.2)	> 520	1.9 (0.2)
40	C2	5	490 (25)	15.1 (0.3)	> 520	2.1 (0.2)
40	C3	5	490 (15)	13.9 (0.2)	> 520	4.8 (0.5)
40	C0	5	500 (20)	13.2 (0.2)	> 520	1.5 (0.2)

Values in the parentheses are the standard deviations.

Mechanical Properties

WF composites and lignin compounds of PCL containing various PCL-*g*-MA compatibilizers were prepared in a Werner & Pfleiderer ZSK 25 twin-screw extruder with intermeshing corotating screws by the blending of PCL, PCL-*g*-MA, and
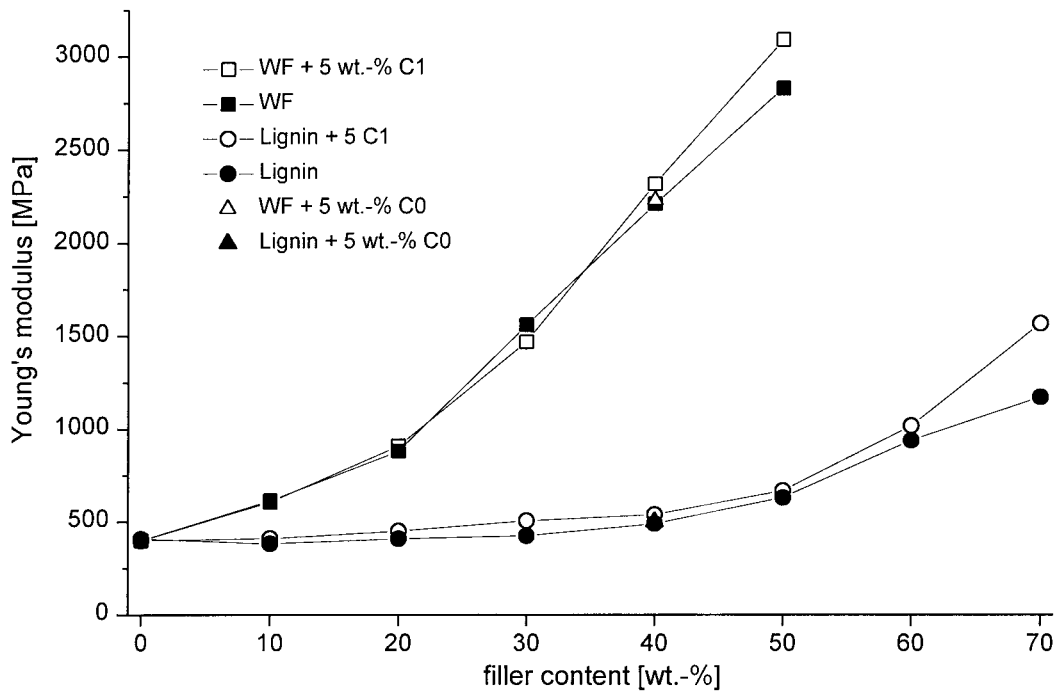

Figure 3   Young's modulus of the PCL/WF and PCL/lignin compounds in the presence and absence of compatibilizer.
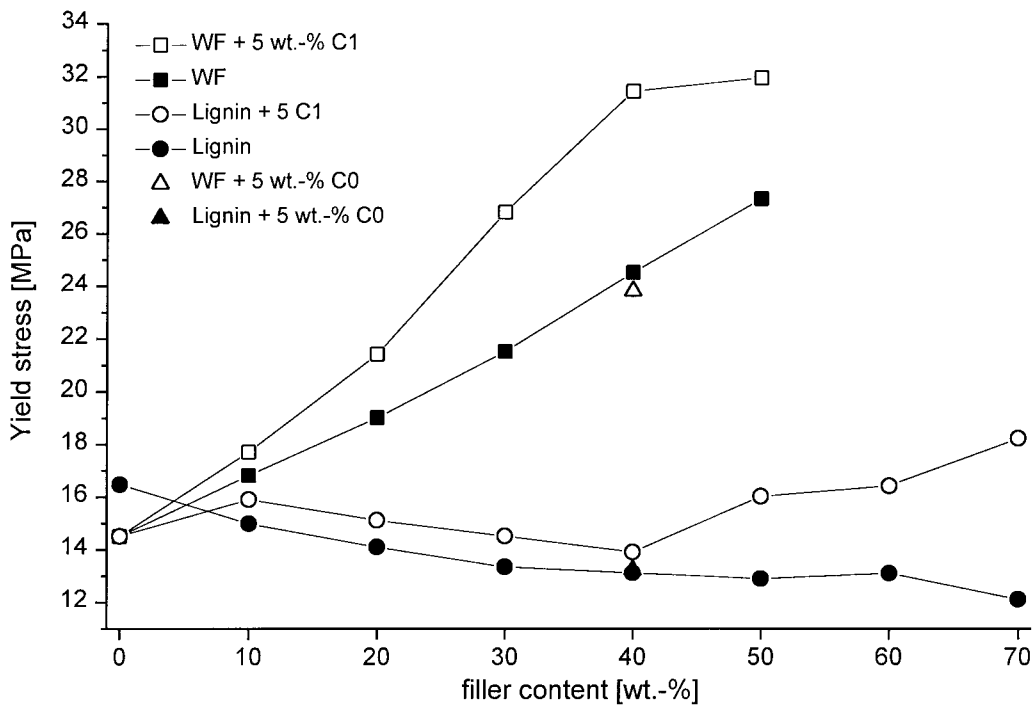
Figure 4 Yield stress of the PCL/WF and PCL/lignin compounds in the presence and absence of compatibilizer.

WF and lignin, respectively, at 160°C. The throughput was 5 kg/h, the screw speed was 200 rpm, and the residence time was 1 min. The screw

configuration and temperature profile are illustrated in Figure 2. The mechanical properties of the PCL/WF composites prepared in the presence
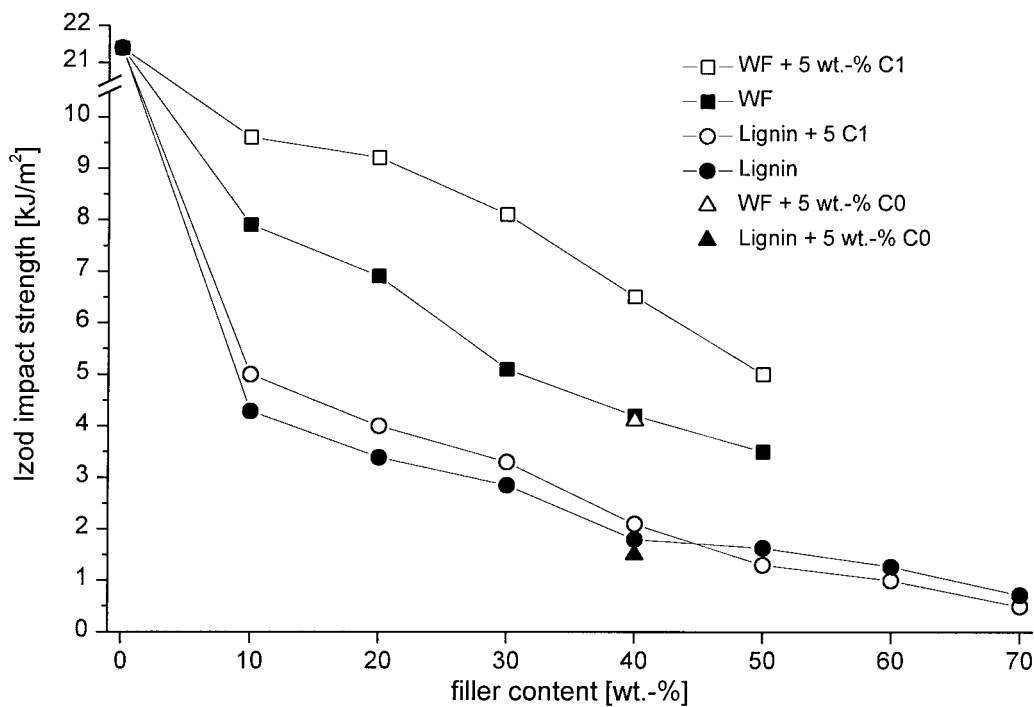

Figure 5 Izod impact strength of the PCL/WF and PCL/lignin compounds in the presence and absence of compatibilizer.
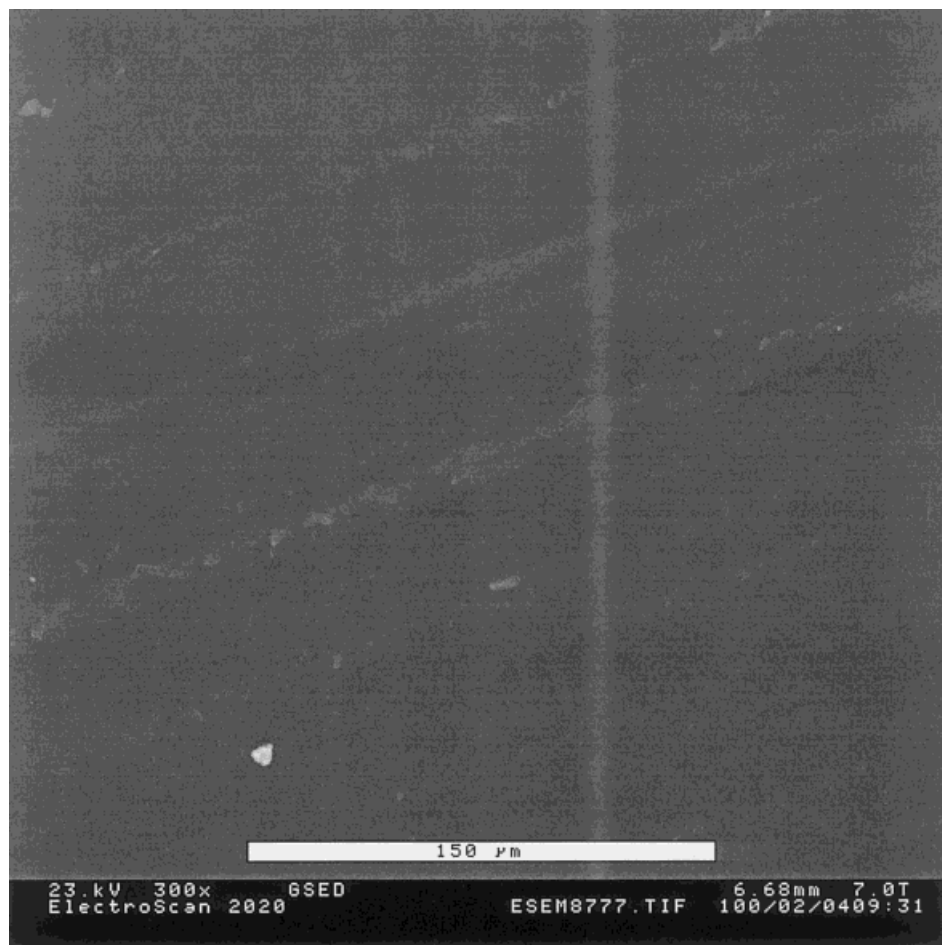
Figure 6   ESEM micrograph of a PCL film containing 10 wt % WF before biodegradation.

of the three maleic compatibilizers C1, C2, and C3 are listed in Table III. The data for the PCL/lignin compounds are listed in Table IV. Young's modulus, yield stress, and Izod impact strength of the PCL compounds with WF and lignin, respectively, in the presence and absence of compatibilizers are displayed in Figures 3–5. For the samples containing WF, the modulus increased drastically with increasing WF content. At a filler content of 40 wt %, the modulus of the composite without compatibilizer increased by 450% compared with that of bulk PCL. Furthermore, it is apparent from Figure 3 that for the compounds containing 5 wt % C1, a 10% higher modulus was only found for the sample containing 50 wt % wood. Because no significant differences in Young's modulus of the compounds containing 40 wt % WF and 5 wt % compatibilizer with different graft contents (C0, C1, C2, C3) were observed, it can be stated that the graft content had no significant influence on Young's modulus.

In contrast to the PCL/WF compounds, the corresponding lignin-based compounds exhibited much lower moduli. However, the moduli increased slightly with increasing lignin content. At greater than 40 wt % lignin content, the moduli increased drastically with increasing lignin content. At a filler content of 60 wt %, the moduli of the compounds, prepared in the absence of compatibilizers, increased by 130% compared with neat PCL. The influences of the compatibilizers, their amount, and their graft content on the moduli showed the same trends as those for the composites containing WF as filler.

As apparent from Figure 4, the yield stress of the WF compounds without compatibilizer increased with increasing filler content. The compound containing 40 wt % WF gave a 70% higher yield stress with respect to that of the bulk PCL. In general, the compounds containing the compatibilizer C1 showed higher yield stresses than the corresponding noncompatibilized compounds.
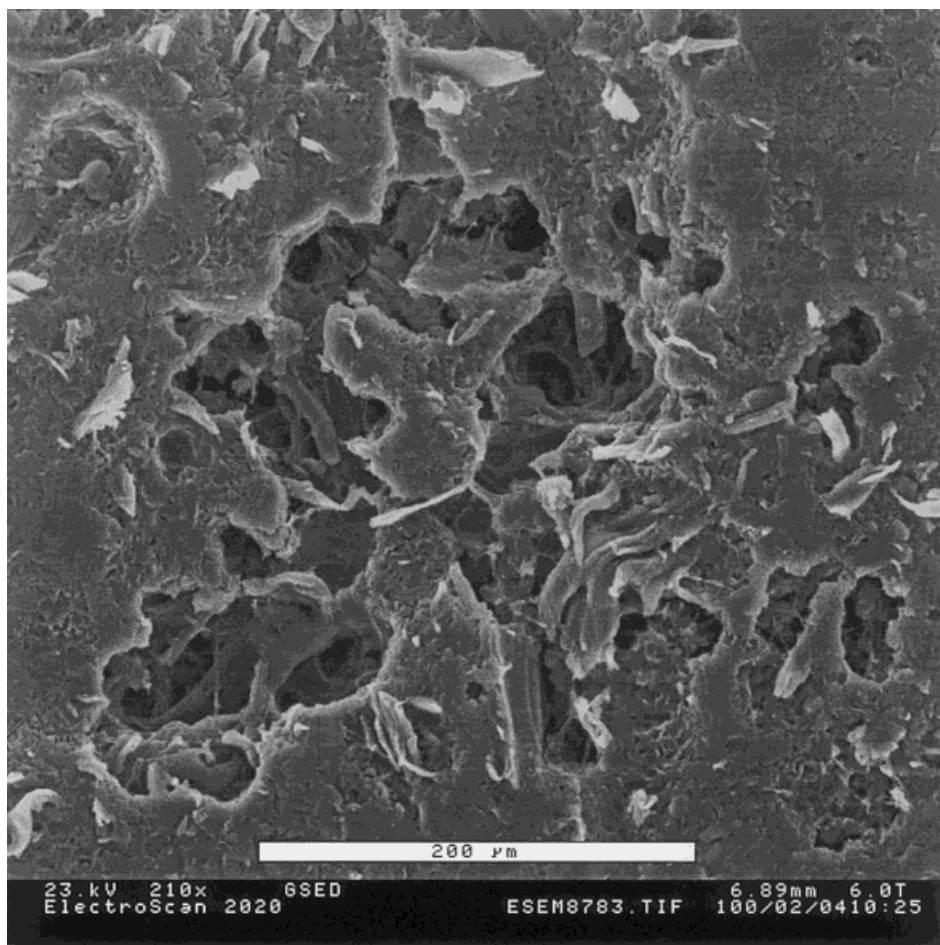
Figure 7 ESEM micrograph of a PCL film containing 10 wt % WF after 3 weeks in natural soil.

Hence, the compound containing 40 wt % WF gave 30% higher yield stress than that containing no compatibilizer. No difference in yield stress was observed for the compounds containing 40 wt % WF and the compatibilizers C2 and C3 (Table III). Almost the same yield stress as for the non-compatibilized system was found when the reference sample C0 was used as a compatibilizer. This indicates that a covalent bonding of maleic anhydride to the polymer backbone of the compatibilizer represented the prime requirement for further improvement of the mechanical strength. However, the content of the compatibilizers had no influence on the yield stresses. Whereas the lignin-based compounds gave much lower yield stresses, the yield stress of the samples without compatibilizer decreased with increasing lignin content. In contrast, compatibilizer-containing compounds gave higher yield stresses. The yield stresses of the compatibilized lignin compounds also decreased with increasing lignin content. However, at greater than 40 wt % lignin, a slight increase was observed. The content of the compatibilizers and the type of the compatibilizer had no influence on the yield stresses (cf. Table IV). The remarkable differences in yield stress between WF and lignin compounds were likely to be associated with differences in bulk properties and also differences in interfacial coupling reactions. In contrast to the corresponding WF compounds, lignin-based compounds exhibited much higher elongation at break. Even at a filler content of 40 wt % lignin, an elongation at break greater than 500% was observed. This is very unusual for a filled polymer because frequently less than 15 wt % of an inert filler is enough to adversely affect the strain properties of a material.

As apparent from Figure 5, the notched Izod impact strength decreased drastically for all samples with increasing filler content. The addition of
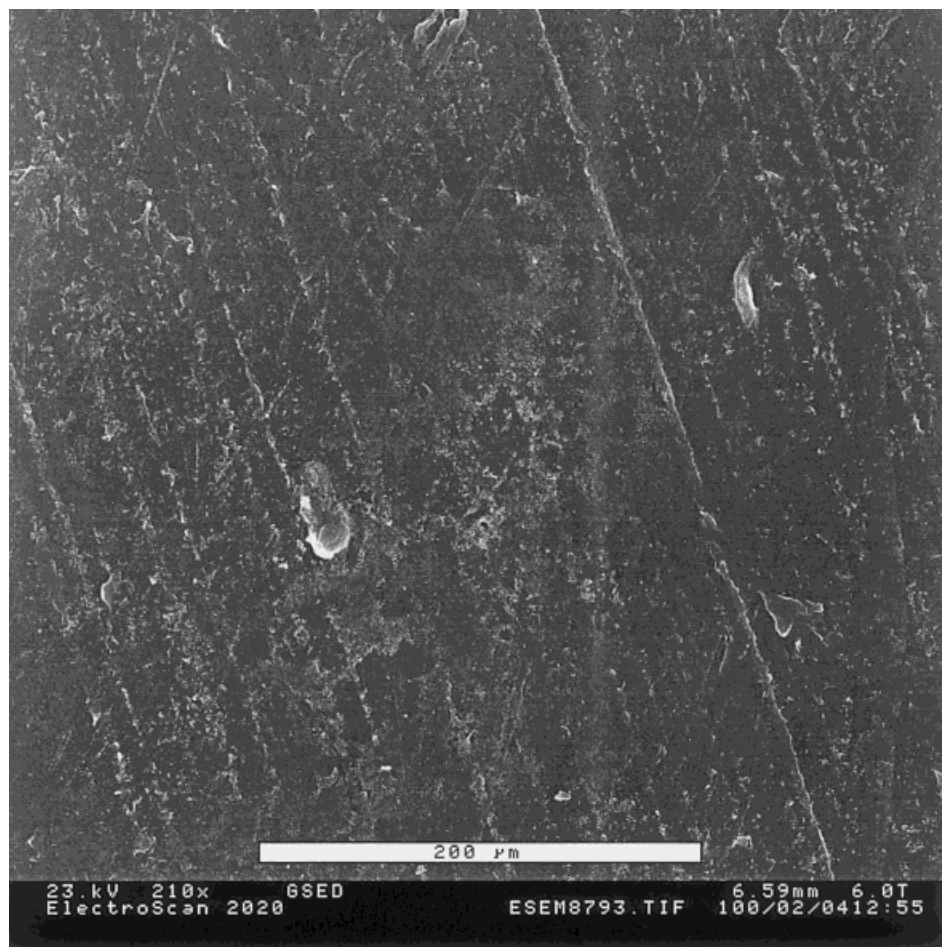
Figure 8 ESEM micrograph of a PCL film containing 30 wt % lignin after 3 weeks in natural soil.

more than 30 wt % lignin resulted in very brittle materials. However, the compatibilized compounds, up to a lignin content of 40 wt %, gave a slightly improved Izod impact strength. In contrast, the compounds containing WF as a filler exhibited a higher Izod impact strength than PCL/lignin compounds. Moreover, impact strength was improved when compatibilizers were added. For the sample containing 40 wt % WF and compatibilizer, an increase of 55% in impact strength was observed with respect to that of the noncompatibilized compound. Adding the compatibilizers C2 and C3 accounted for a similar impact strength. However, for the reference sample C0, the same impact strength was obtained as for the sample without compatibilizer. This finding provides additional experimental evidence that the covalent bond formation, resulting from the reaction of the maleic anhydride group with hydroxyl groups of the WF, improves the impact strength of the corresponding compounds.

Biodegradation and Morphology

To examine the origins of the unusual combinations of mechanical properties relating to effective PCL matrix reinforcement, we studied the morphology of the WF and lignin compounds and biodegradation via ESEM and TEM.

To investigate biodegradation, we buried compression-molded films in natural soil for 4 weeks and analyzed them with ESEM. Figure 6 shows the surface of a WF/PCL composite before exposure to soil. As apparent from Figure 7, biodegradation took place after 4 weeks. The WF was visible, thus indicating that the biodegradation progressed faster along the surface of the WF. This was likely to be associated with the presence of a rougher and larger surface exposed to the attack of microorganisms. Furthermore, it can be seen from Figure 7 that the biodegradation on the surface did not follow a regular pattern. This could be explained by the mechanism of biodeg-
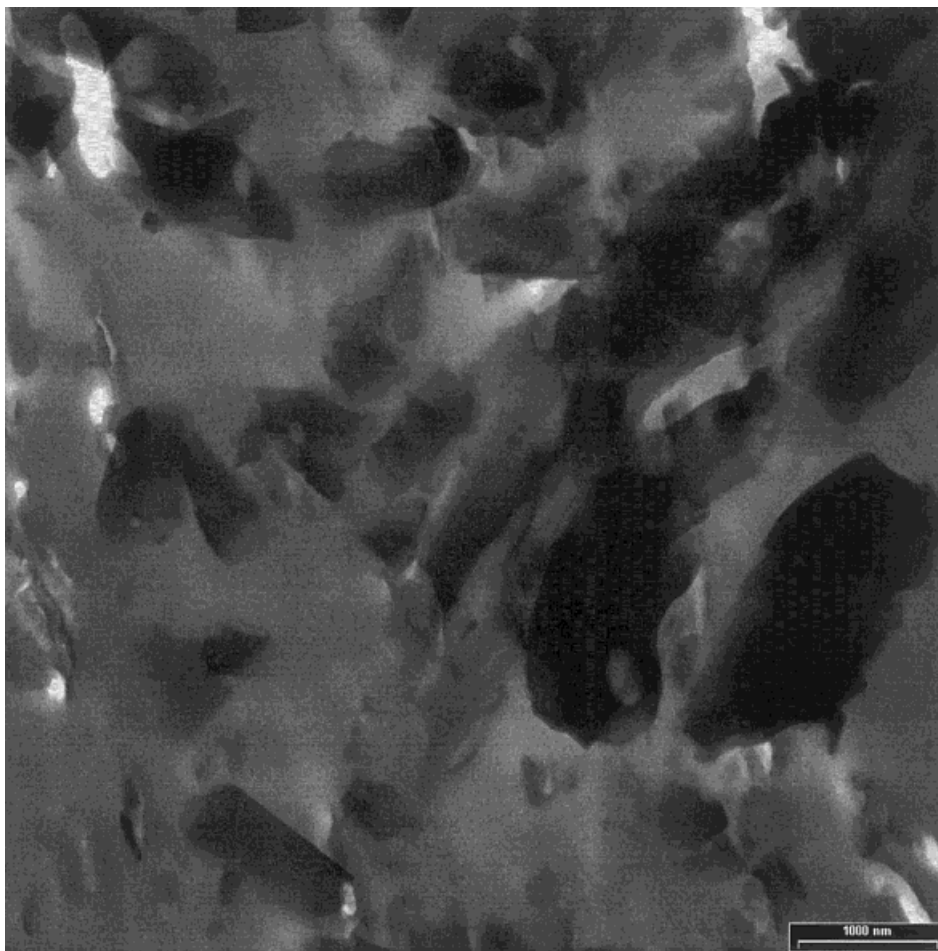
Figure 9 TEM micrograph of a PCL/lignin compound containing 50 wt % lignin.

radation. At the locations with low pH, the biodegradation started first and was promoted by the presence of water, which diffused into the compound through the WF particles. Figure 8 shows the surface of a lignin compound buried in natural soil after 4 weeks. No biodegradation took place. This was likely to be associated with the phenolic nature of lignin, which prevents attacks by microorganisms and acid formation.

A TEM micrograph of the compound containing 50 wt % lignin is displayed in Figure 9. The lignin particles were well dispersed in the polymer matrix, having a particle size of 200–1500 nm. This good and fine dispersion of the lignin explains why the PCL matrix tolerated such large quantities of lignin.

CONCLUSIONS

Melt grafting of maleic anhydride onto PCL was the key to PCL-*g*-MA compatibilizers, which en-

hanced the mechanical properties of reinforced PCL compounds based on WF and lignin. The grafting of maleic anhydride onto PCL was achieved in high yields with a twin-screw-extrusion process. Low concentrations of maleic anhydride and appropriate maleic anhydride/initiator ratios afforded PCL-*g*-MA. A low maleic anhydride content of PCL-*g*-MA (1.44 wt %) and a small PCL-*g*-MA addition (2.5 wt %) were sufficient to achieve attractive property combinations. For a PCL compound containing 2.5 wt % PCL-*g*-MA and 40 wt % WF, Young's modulus increased by 450% and the tensile strength increased by 115% in comparison with the properties of bulk PCL. In comparison to the results of Dalväg et al.[3] and Meyers et al.[4] in terms of PP wood-filled composites, we found at the same WF content much greater effects (fourfold) with increasing Young's modulus and tensile strength. The mechanical properties of the WF composites were better than those of the lignin-based compounds. More than 70 wt % lignin was added

without mechanical properties being impaired. Compositions containing 40 wt % lignin showed elongation at break exceeding 500%. This is exceptional for such high filler content. According to TEM analysis, very effective lignin dispersion was achieved within the PCL matrix. Biodegradation studies revealed that lignin addition enhanced the biostability of PCL compounds. In conclusion, lignin can be used as a weak and nontoxic biostabilizer to enhance the product lifetime of PCL compounds in outdoor applications.

REFERENCES

1. Joly, C.; Kofman, M.; Gauthier, R. J Macromol Sci Pure Appl Chem 1996, 33, 1981.
2. Felix, J. M.; Gatenholm, P. J Appl Polym Sci 1991, 42, 609.
3. Dalväg, H.; Klason, C.; Strömvall, H.-E. Int J Polym Mater 1985, 11, 9.
4. Meyers, G. E.; Chahyadi, I. S.; Coberly, C. A.; Ermer, D. S. Int J Polym Mater 1991, 15, 21.
5. Raj, R. G.; Kokta, B. V.; Daneault, C. Int J Polym Mater 1989, 12, 239.
6. Sain, M. M.; Imbert, C.; Kokta, B. V. Angew Makromol Chem 1993, 210, 33.
7. Oksman, K.; Clemons, C. J Appl Polym Sci 1998, 67, 1503.
8. Nitz, H.; Reichert, P.; Römling, H.; Mülhaupt, R. Macromol Mater Eng 2000, 276, 100.
9. Mani, R.; Tang, J.; Bhattacharya, M. Makromol Chem Rapid Commun 1998, 19, 283.
10. Koenig, M. F.; Huang, S. J. Polymer 1995, 36, 1877.
11. Warth, H.; Mülhaupt, R.; Schätzle, R. J Appl Polym Sci 1997, 64, 231.
12. Glasser, W. G.; Sarkanen, S. ACS Symp Ser 1989, 391, 452.
13. Rials, T. G.; Glasser, W. G. J Appl Polym Sci 1989, 37, 2399.
14. Ciemniecki, S. L.; Glasser, W. G. Polymer 1988, 29, 1030.
15. de Oliveira, W.; Glasser, W. G. Macromolecules 1994, 27, 5.
16. de Oliveira, W.; Glasser, W. G. J Appl Polym Sci 1994, 51, 563.
17. Rösch, J.; Mülhaupt, R. Polym Bull 1994, 32, 361.
18. John, J.; Tang, J.; Yang, Z.; Bhattacharya, M. J Polym Sci Part A: Polym Chem 1997, 35, 1139.
19. John, J.; Tang, J.; Bhattacharya, M. Polymer 1998, 39, 2883.