Effect of Processing Additives on (Bio)degradability of Film-Blown Poly(ε-caprolactone)

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ABSTRACT: Poly(ε-caprolactone)s (PCL) with slip masterbatch, Erucamide, SiO_2 and Erucamide + $CaCO_3$ as low-molecular-weight processing additives, were film-blown in a single screw extruder. The films and recycled PCL without additives were exposed to composting, anaerobic sewage sludge (37 and 55°C), pure fungal culture, and chemical hydrolysis at two pH (7 and 10.5) and at two temperatures (room temperature and 50°C). Recycling and addition of processing additives resulted in a slightly slower degradation rate compared with the degradation of pure PCL. The degradations in biotic environment were generally faster than in abiotic environment. Higher degradation rates are observed in more complex environments (composts and anerobic sewage sludge) due to synergism between high temperature and a richer fauna of microorganisms. In the biotic environments, faster reductions in number-average molecular weight ($\bar{M}_n$) than in weight-average molecular weight ($\bar{M}_w$) were observed. A decrease of $\bar{M}_n$ with up to 75–80% was estimated for composted pure PCL, while similar samples in anaerobic sludge at 55°C were completely degraded in 50 days. The mechanical properties of the samples subjected to composting exhibited a more rapid enbrittlement compared to the samples subjected to abiotic hydrolysis. The observed increase in crystallinity with increasing degree of degradation is explained by crystallization made possible by chain cleavage in the amorphous phase. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 61–74, 1998

Key words: PCL; additives; biodegradation; chemical hydrolysis

INTRODUCTION

Poly(ε-caprolactone) (PCL) is a biodegradable polymer with very good mechanical properties. The biodegradation of PCL of different molecular weights by *Pullularia pullulans* showed that samples with low molecular weight were degraded more quickly than samples with higher molecular weights.[1] Biodegradation of an aliphatic polyester with the same reduced viscosity as PCL, but produced from 1,4-butanediol and adipic or sebacic acids, also showed a higher degradation rate.[2]

Blends of PCL with corn starch granules in different amounts were biodegraded by *Rhizopus arrhizus* lipase and *Bacillus subtilis* α-amylase.[3] The amount of corn starch did not affect the degradation caused by the lipase, which will cleave PCL chains randomly, while the starch content had a positive effect on the degradation from the amylase. PCL has also been mixed with destructurized starch, which is commercialized by Novamont under the name Mater-Bi.[4] In blends between PCL and poly(ethylene terephthalate) (PET), transesterification reactions and insertion of PCL segments in the PET chain occurred dur-

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Table I Description of PCL with Processing Additives

Sample Name	Polymer	Additives
PCL-V	Tone 787	None
PCL-SMB	Tone 787	3.0 wt % Slip master batch
PCL-R	Tone 787	None, recycled
PCL-ER	Tone 787	0.2 wt % ER[a]
PCL-S	Tone 787	0.5 wt % SiO_2[b]
PCL-EC	Tone 787	0.2 wt % ER[a] + 1.0 wt % $CaCO_3$[c]

[a] Erucamid (primary amide) Crodamide ER produced by Croda Universal Ltd.
[b] SiO_2 Cab—O—Sil M5 produced by Cabot Corporation, U.S.A. (pH 3.5–4.2, 4%).
[c] $CaCO_3$ Omyacarb 2-GU produced by OMYA AB, Sweden (pH ca 9).

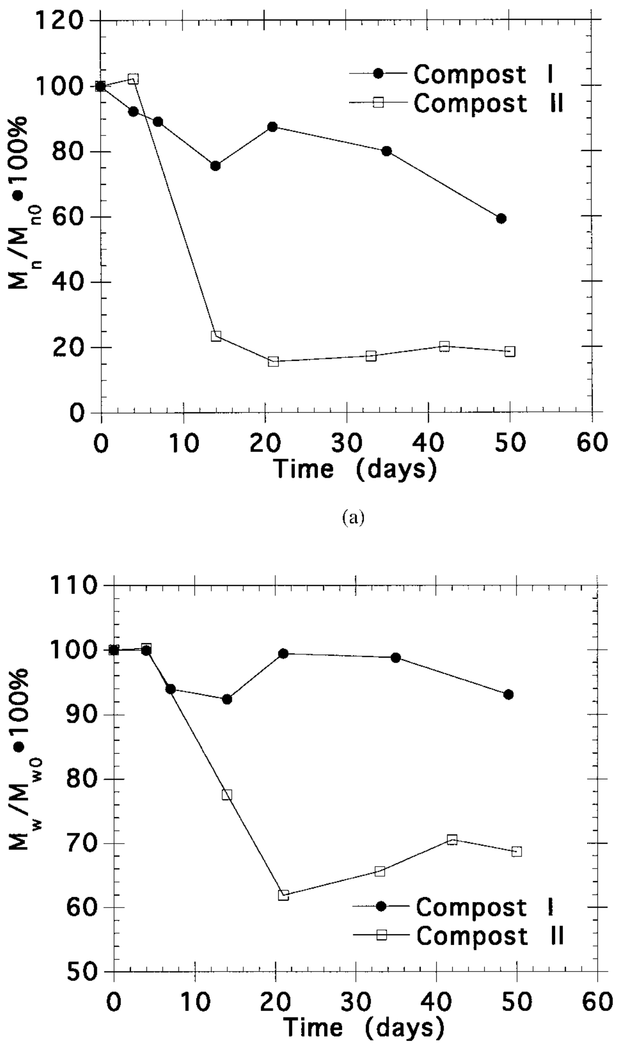
ing mixing.[5] The samples were tested in full-scale composting, soil burial, accelerated aerobic degradation, and exposure to different fungi and esterases. The biodegradation detected from the samples was well below what would be expected from the chemical structure of the individual components as well as the behavior of individual homopolymers under similar environmental conditions. It was concluded that the presence of PET as the major component in PET–PCL blends reduces the ability of PCL to degrade. Pure PCL and PCL blended with poly(vinyl alcohol) (PVAl) were incubated with microorganisms isolated from an industrial compost.[6] The pure PCL was completely assimilated over periods of 600–800 h, while the blends, on the other hand, showed no signs of degradation, not even the PCL-rich ones. This was explained by adsorption of PVAl on the PCL films, which makes the PCL film inaccessible for microorganisms.[7]

Like many polyesters, PCL is sensitive towards chemical hydrolysis. The hydrolytic behavior of blends of PCL and poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) showed that the rate of degradation was found to be influenced by a complex set of factors, including temperature, pH, and the PCL content.[7] When comparing the degradation of PCL mixed with PLA (polylactide) and their block copolymers in phosphate buffer at 3 different temperatures, it was found that the rate of degradation increased with increasing PLA content in the copolymer.[8] The fastest rate of degradation was obtained when the ratio between caprolactone and lactic acid equaled 32/68. The biodegradability of PCL as well as it's utility has been reviewed.[9]

Although PCL is not degraded as fast as polyhydroxybutyrate (PHB), it has been found that both PHB- and PCL-degrading microorganisms are distributed over many kinds of environments. PHB- and PCL-degrading microorganisms were found in landfill leachate, compost, sewage sludge, forest soil, farm soil, paddy soil, weed field soil, roadside sand, and pond sediment. From total colony counts, it was found that the percentages of PHB and PCL degrading microorganisms were 0.2–11.4% and 0.8–11.0%.[10] When the degradation of PCL by mixed and pure cultures of bacteria and yeast was compared, the mixed cultures showed a more complete degradation of the breakdown products than the pure cultures did.[11] The degradation by pure cultures of different strains of *Fusarium* was investigated, and the results showed that PCL was degraded and used as a carbon source and that the *Fusarium* PCL depolymerase was cutinase.[12] The rate of mixed culture degradation of PCL with PLA, PHB, PHBV, Mater-Bi, cellulose acetate (CA), and cellulose esters were compared.[13] PCL had completely disappeared after 14 days, as had CA, with a degree of substitution less or equal to 2.06 and PHBV 90/10.

Antiblock and slip agents are frequently used as additives in film production. The former, for example, silica, are added in order to roughen the film surface to prevent the film surfaces to stick together when pressure is applied, that is, blocking, by separating the film surfaces at a microscale. In addition, nonsmooth film surfaces promote take-off of film from rolls during processing. Slip agents, for example, fatty acids and waxes, migrate to the film surface, producing a thin layer, which reduces friction, static buildup, and wear and ensures easy handling during the packaging processes. In addition to the effect on the finished product, slip agents improve melt flow (reduces energy consumption) and reduce wear during processing.[14,15]

The objective of this work was to evaluate the effect of processing additives on the (bio)degrad-



(a)

(b)

Figure 1 Changes in (a) $\bar{M}_n$ and (b) $\bar{M}_w$ for PCL-V degraded in compost I and II.

ability of PCL films. The additives change the surface properties of the films by migration and roughening, which, in turns, change the microenvironment for the degrading microorganisms. The results give, in detail, the susceptibility of PCL, with and without processing additives, to abiotic (chemical hydrolysis at different pH and temperature) and biotic (composting, aerobic fungi, and anaerobic sewage sludge) degradation.

EXPERIMENTAL

Material

The material used in this study was PCL, Tone 787 from Union Carbide. Table I presents the short form of the PCL samples with low-molecular-weight processing aids added to the polymer during processing.

Processing

The film blowing of PCL was carried out with a setup consisting of 2 18-mm Axon single screw extruders, L/D 30, and a 70-mm diameter die producing a two-layer film. The film was approximately 40 μm thick with a blow-up ratio of 2.9–3.4 : 1. The temperature profile of the extruder was set from 100 to 125°C at a screw speed of 50 rpm. The molding die was set to 100°C. The compounding of the samples was carried out with a Brabender Plasti-Corder PL2000 counter-rotating twin screw extruder DSK 35/9D (diameter/length) at 100°C.

Degradation Procedure

Composting

Small-scale composting was performed in a 270-L, turnable composting facility over a period of 49 (compost I) and 45 (compost II) days. The facility was isolated with 5-cm polyethylene foam with no external heating. The simulated household compost (compost I) consisted of 48% (v/v) dehydrated cow manure, 16% (v/v) sawdust, 35% (v/v) water, and 1% (v/v) dried bacterial starter (Bio Composter™). The temperature inside the compost varied between 3 and 34°C, and the moisture content was 75% by weight. The garden compost (compost II) consisted of typical garden waste, such as grass clippings and leaves. The highest recorded temperature inside the compost was 43°C, and the moisture content was 60% by weight. The large–scale composting (compost III) was performed at Hässleholm, Sweden, for 17 days. Compost III consisted of food residues and garden waste. The temperature was markedly higher (since the PCL partially melted) than in the small-scale composts.

Anaerobic Degradation in Sewage Sludge

Anaerobic degradation was performed in oxygen-free flasks. The flasks contained 0.8 g PCL and inoculum. Control flasks only contained the inoculum. The experiment was performed at 2 temperatures, 37°C (mesophilic) and 55°C (thermophilic). The production of gas was measured with a syringe. The volume of gas is defined as the gas volume produced from the flask with samples minus the gas volume from the control samples.

Table II Molecular Weight Changes of PCL-V Degraded in Compost I, II, and III Anaerobic Sewage Sludge (Mesophilic and Thermophilic)

Sample		$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	T_{ave} (°C)	T_{max} (°C)
Unaged	0d	117,100 ± 1900	202,300 ± 1500	—	—
Compost I	21d	95,200 ± 20,400	184,100 ± 15,400	14	33
Compost II	21d	18,400 ± 1100	125,300 ± 4400	20	43
Compost III	17d	35,800[a]	67,000[a]	NM[b]	60[c]
Anaerobic 37°C	22d	45,900 ± 4100	164,300 ± 2400	37	37
Anaerobic 50°C	22d	15,600 ± 700	89,400 ± 6200	50	50

[a] Single time measurement due to small amount of sample.
[b] NM = not measured.
[c] The maximum temperature in compost III is believed to be as high as 60°C due to the partial melting of the sample.

Chemical Hydrolysis

The hydrolysis was performed in a solution consisting of distilled water at pH 7 or 0.01*M* phosphate buffer solution at pH 10.5. Both solutions were kept at 2 temperatures, room temperature and 50°C. NaN_3 0.02% (w/w) was added to avoid the growth of microorganisms at room temperature. The pH was adjusted to the initial values after 3 weeks.

Degradation by Pure Microbial Culture

The microbial degradation was performed in 250-mL Erleyenmeyer flasks containing salt media and polymer samples. Each flask contained

Table III Thermal Properties of PCL Samples Degraded in Composts as Measured by DSC

Sample	ΔH_f^{1st} (J/g)	W_{Cr} (%)	T_m^{1st} (°C)	ΔH_f^{2nd} (J/g)	T_m^{2nd} (°C)
V CI 0d	75.6	54	60.2	59.3	55.4
V CI 4d	76.0	54	62.1	58.0	56.2
V CI 14d	77.4	55	62.0	58.8	56.1
V CI 49d	79.1	57	62.5	59.5	56.2
V CI 70d	77.3	55	62.5	60.0	55.7
V CII 4d	78.7	56	57.1	67.9	56.5
V CII 14d	80.4	58	62.6	61.4	56.4
V CII 33d	84.2	60	63.1	63.9	56.4
V CII 50d	90.9	65	63.2	65.4	56.3
V CII 84d	83.7	60	63.1	62.3	56.4
R CII 0d	77.1	55	62.9	58.6	56.4
R CII 4d	74.9	54	62.0	58.7	56.4
R CII 14d	76.4	55	62.6	59.0	56.7
R CII 33d	80.3	58	63.4	61.8	56.8
R CII 50d	83.0	59	63.4	61.8	56.5
S CII 0d	76.7	55	62.9	59.6	56.8
S CII 4d	75.0	54	62.0	59.2	56.9
S CII 14d	76.5	55	62.3	60.2	56.9
S CII 33d	79.7	57	62.9	60.8	56.7
S CII 50d	78.4	56	62.1	60.5	56.3
S CII 84d	85.0	61	63.1	63.6	56.8
EC CII 0d	75.6	54	62.9	58.6	56.5
EC CII 4d	75.3	54	62.5	58.6	56.9
EC CII 14d	79.0	57	63.0	60.6	56.5
EC CII 49d	83.3	60	63.3	62.8	56.8
EC CII 84d	79.2	57	63.3	59.7	56.5

V = PCL-V, no additives; R = PCL-R, recycled; S = PCL-S, 0.5 wt % SiO_2; EC = PCL-EC, 0.2 wt % Erucamide + 1.0 wt % $CaCO_3$.

0.3 g of polymer film (50 × 50 mm) and 150 mL of salt medium. The salt medium contained, per litre, the following: 5.0 g $(NH_4)_2C_4H_4O_6$, 1.0 g KH_2PO_4, 1.0 g $MgSO_4 \cdot 7H_2O$, 0.8 mL of a 1% solution of $FeCl_3 \cdot 6H_2O$, and 8 mL of a 1% solution of $ZnSO_4 \cdot 7H_2O$. The samples were inoculated at room temperature during a period of 49 days with *Aspergillus fumigatus* after the medium had been adjusted to pH 5.5 by the addition of HCl. After sampling, the polymer film was allowed to dry at room temperature after sterilization with 70% (v/v) ethanol in water. Sterile control consisted of 0.3 g of polymer film (50 × 50 mm) and 150 mL of salt medium (described above), pH was adjusted with HCl and with 5 mL 0.02% (w/w) NaN_3 solution added 3 times during the experiment.

Molecular Weight Determinations

The molecular weight was determined with a chromatography system consisting of a Waters 510 pump, a Waters WISP 712, and a Waters 410 RI detector. The system was equipped with 3 PLgel 10-μm mixed-B columns (300 × 7.5 mm) from Polymer Laboratories. The solvent during the analysis was tetrahydrofuran (THF). The sample injection volume was 200 μL. Calibration was performed with polystyrene standards in the molecular weight range of 2000–1,950,000 g/mol. Each sample was analyzed 4 times to get an appropriate average of the molecular weight.

Differential Scanning Calorimetry

The thermal properties of PCL samples were studied by a Perkin–Elmer DSC-7 at a heating rate of 10°C/min. The apparatus was calibrated with an indium standard. The values of the degree of crystallinity originate from the first scan, and the melting temperature from the second. The mass crystallinity was approximated by using the heat of fusion (ΔH_f^0) of totally crystalline PCL: 139.5 J/g.[16]

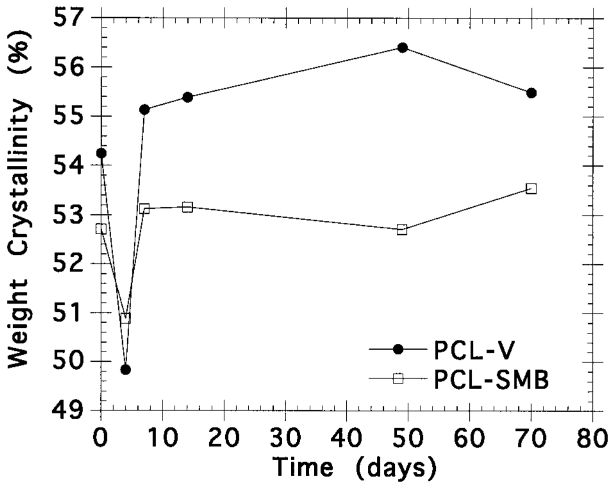
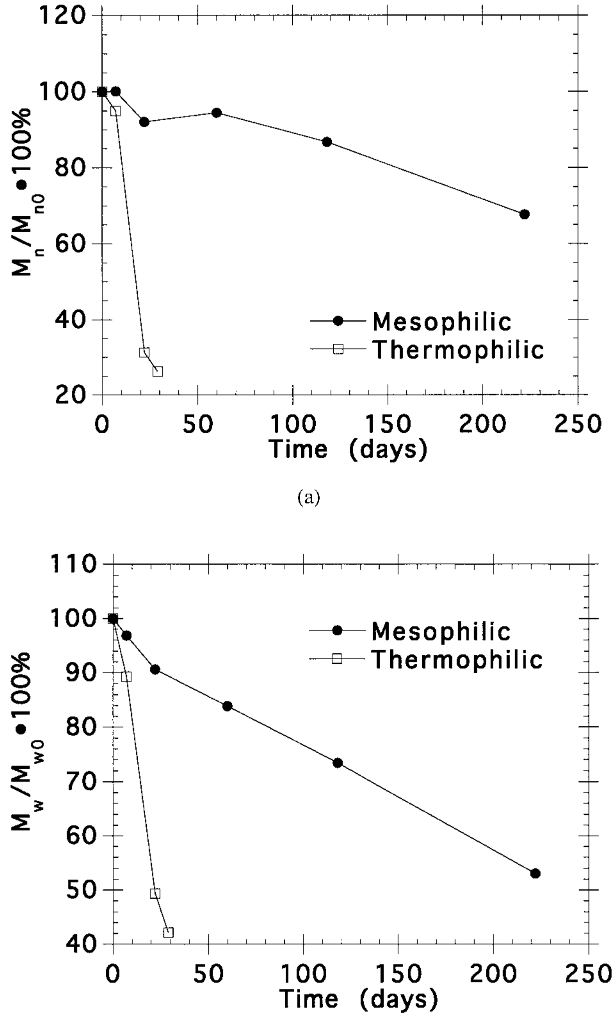


Figure 2 Degree of crystallinity of PCL-V and PCL-SMB in compost I.



(a)

(b)

Figure 3 Changes in (a) $\bar{M}_n$ and (b) $\bar{M}_w$ for PCL-V degraded in mesophilic and thermophilic sewage sludge.

Tensile Testing

The tensile testing was performed on an Instron 5566, equipped with a 2663 noncontacting video extensometer and pneumatic grips, controlled by a Dell 466/ME PC. The measurements were performed at a crosshead speed of 150 mm/min using a grip separation of 20 mm and a gauge length of

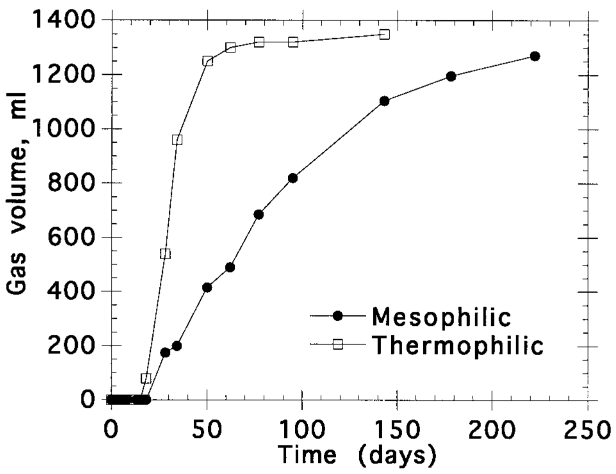


Figure 4 Evolution of methane and CO_2 from PCL-V in mesophilic and thermophilic sewage sludge.

10 mm. The test specimens were 15.5 mm wide rectangular strips that were conditioned prior to testing for 48 h at 50 ± 5% RH at room temperature. The data points were averaged from at least 5 measurements. Due to the high extensibility of PCL, the strain at break was calculated using crosshead separation.

RESULTS AND DISCUSSION

Biotic Environment

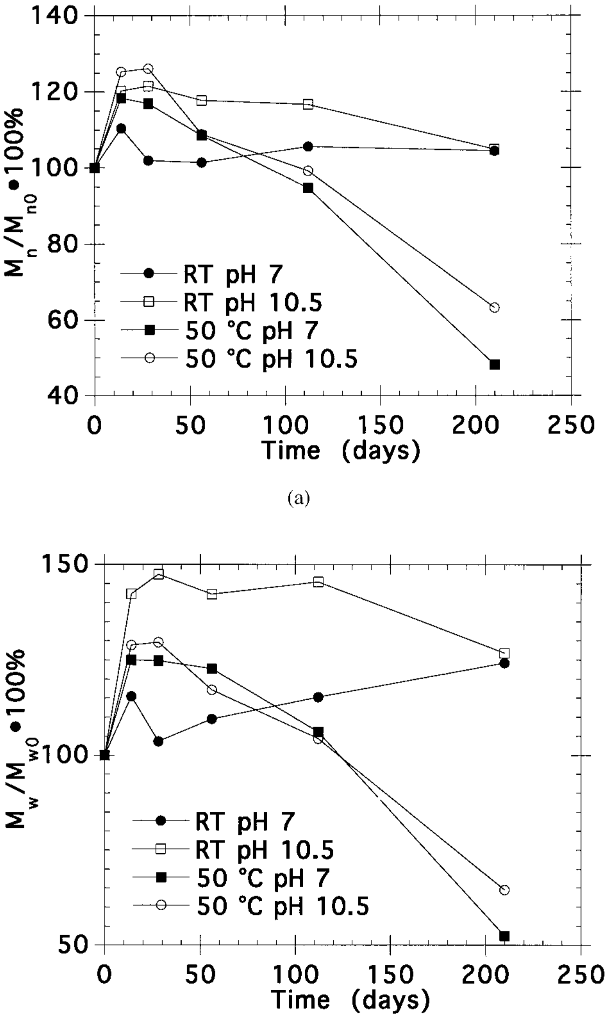
Figure 1 shows the changes in molecular weight for PCL-V in compost I and II. The samples degraded in compost II show a larger change in molecular weight than the samples from compost I. The number-average molecular weight ($\bar{M}_n$) changes to about 20% of its original value after 21 days in compost II [Fig. 1(a)]. No significant changes are seen thereafter. The $\bar{M}_n$ of samples in compost I is reduced to 70% of its original after 50 days. The samples in compost I hardly show any change in $\bar{M}_w$ [Fig. 1(b)], while the samples in compost II exhibit a 60% reduction in $\bar{M}_w$ after 21 days, whereafter a small increase can be noticed. An increase in polydispersity is thus noted for the samples.

A similar increase in polydispersity has also been observed for PCL degraded in soil for 6 months.[17] It was shown that $\bar{M}_w$ decreased only 15%, while $\bar{M}_n$ decreased 45%. At the same time, 60% weight loss was noticed. PCL films degraded in soil burial and composting demonstrated a 25% weight loss after 3 months of soil burial. The degradation in compost was faster since about 35% weight loss was noted after 2 months.[5] In another study, PCL disappeared completely in the compost within 14 days, even though it was added after the thermophilic phase.[13] ^{14}C-labeled PCL was subjected to composting.[18] The experiments were performed at 2 temperatures, 45 and 55°C, and about 20% of the samples had been transformed in CO_2 after 14 days. After more than 80 days, almost a total conversion was reached for the samples composted at the higher temperature.[18] When the degradation of PCL (Tone 767 and Tone 787) and Mater-Bi Z101U were studied during controlled composting and soil burial, the controlled composting showed the

Table IV Thermal Properties of PCL Films, Measured by DSC, Degraded in Anaerobic Sewage Sludge

Sample	ΔH_f^{1st} (J/g)	W_{Cr} (%)	T_m^{1st} (°C)	ΔH_g^{2nd}	T_m^{2nd} (°C)
V M 7d	81.2	56	62.7	61.3	54.9
V M 22d	79.3	54	64.0	58.1	55.5
V M 60d	82.0	56	65.1	61.9	55.7
V M 118d	86.9	60	66.2	63.4	56.3
V M 222d	91.1	62	66.2	65.9	55.6
V T 7d	81.9	56	65.1	61.5	54.9
V T 22d	98.8	68	66.1	68.7	54.7
V T 29d	103.8	71	67.3	70.1	55.2
V *A. fum* 49d	76.5	55	61.5	58.6	55.7
R *A. fum* 49d	75.2	54	63.6	58.9	56.3
E *A. fum* 49d	74.9	54	63.8	58.3	56.7
S *A. fum* 49d	79.3	57	64.3	61.5	57.5

M = mesophilic, T = thermophilic, and *Aspergillus fumigatus* (pure culture).



(a)

(b)

Figure 5 Changes in (a) $\bar{M}_n$ and (b) $\bar{M}_w$ for PCL-V degraded by chemical hydrolysis at pH 7 and 10.5 at 23 and 50°C.

fastest reduction in molecular weight as measured by changes in viscosity for the Mater-Bi samples.[19]

Table II shows the decrease in $\bar{M}_n$ and $\bar{M}_w$ of PCL-V degraded in compost III compared with compost I and II and the anaerobic sewage sludge experiments. A larger decrease in $\bar{M}_n$ than in $\bar{M}_w$ can be seen for the samples in the composts. In compost I, the polydispersity changes from 1.7 to 1.9. In compost II, the polydispersity ends up with a value of 6.8. According to reported calculations, a completely random degradation process would give a polydispersity close to 2.[20,21] It has been shown that if the process is nonrandom, the polydispersity would reach a value that is lower than 2 if cleavage near the center of the molecule is favored, while it would reach a value larger than 2 if cleavage near the chain ends is favored.[21] The degradation in the compost seems, therefore, largely to take place near the chain ends. However, it should be mentioned that other authors in contrast have concluded that the chain scission occurred in the middle of the chains, based upon the same observation of increasing polydispersity.[22]

Table III gives the results of the differential scanning calorimetry (DSC) measurements of the PCL-V films degraded in compost I and II. Figure 2 shows the degree of crystallinity of PCL-V and PCL-SMB in compost I. The degree of crystallinity measured as the heat of fusion during the first heating increased slightly after 50 days in compost I. The films degraded in compost II exhibited a more significant increase. After 50 days, the degree of crystallinity had increased by 20%, which agrees well with the fact that PCL samples in compost II were more degraded than samples from compost I at the same time. The increase in crystallinity is attributed to crystallization made possible by the chain cleavage in the amorphous phase.[23,24] The temperature of melting was unaffected during the degradation.

Figure 3 shows the molecular weight changes for PCL-V exposed to anaerobic sewage sludge at 2 temperatures, 37°C (mesophilic) and 55°C (thermophilic). A fast reduction in molecular weight could be seen for the samples degraded in thermophilic sludge. After 29 days, no more sample could be identified in the solution. The samples degraded in mesophilic sludge showed a slower reduction in molecular weight. The polydispersity increased for the thermophilic samples, indicating that cleavage near the chain ends are favored, while the mesophilic samples showed a decrease in polydispersity from 3.6 for the unaged material to 2.9 for the sample that was degraded for 220 days, thus showing a tendency of a value approximating 2, which is indicative of a random degradation process.[21]

Figure 4 shows the production of methane and CO_2 formed in the samples during exposure to anaerobic sewage sludge. The production of gas from PCL started after a lag period of about 20 days. The samples kept at 55°C showed a larger volume of produced gas and reached a maximum after 50 days. A similar lag phase, as shown in Fig. 4, has been reported for the biodegradation of PCL in activated sludge.[23] The authors reported a biodegradation of approximately 90% after 35

Table V Thermal Properties of PCL Chemically Degraded as Measured by DSC

Sample	ΔH_f^{1st}	W_{Cr}	T_m^{1st}	ΔH_f^{2nd}	T_m^{2nd}
V 23/7 0d	72.3	52	62.5	57.6	56.7
V 23/7 14d	75.0	54	63.1	57.5	57.3
V 23/7 28d	73.0	52	62.4	57.3	56.8
V 23/7 56d	75.9	54	63.0	57.5	57.0
V 23/7 112d	76.6	55	63.9	58.5	57.4
V 23/7 210d	76.5	55	63.8	58.0	57.4
V 23/10.5 14d	76.5	55	63.2	58.8	57.3
V 23/10.5 28d	76.2	55	63.7	58.6	57.6
V 23/10.5 56d	75.6	54	63.4	58.5	57.7
V 23/10.5 112d	76.0	54	63.7	58.7	57.8
V 23/10.5 210d	77.2	55	64.0	58.9	57.5
V 50/7 14d	79.1	57	69.6	58.5	56.8
V 50/7 28d	77.1	55	70.3	58.4	57.7
V 50/7 56d	81.3	58	70.8	59.3	57.2
V 50/7 112d	83.2	60	71.2	61.1	57.4
V 50/7 210d	94.2	68	71.9	70.3	58.4
V 50/10.5 14d	74.8	54	69.1	58.2	57.5
V 50/10.5 28d	79.5	57	70.8	58.6	57.2
V 50/10.5 56d	81.2	58	71.1	59.7	57.6
V 50/10.5 112d	83.8	60	71.2	61.7	58.2
V 50/10.5 210d	89.7	64	72.5	69.8	58.4
SMB 0d	73.6	53	62.1	58.1	56.1

V = PLC-V, no additives; SMB = PCL-SMB 3 wt % slip master batch.

days. The plateau reached for the thermophilic samples in Fig. 4 corresponds to the theoretical amount of produced gas from the amount of inoculated PCL. This also explains why no more material could be found for the thermophilic samples after 30 days, since almost ⅔ of the theoretical amount of methane had been produced at that time and soon thereafter reached it's plateau value, corresponding to complete conversion. The degradation of PCL and Mater-Bi in semicontinuous activated sludge (SCAS), both mesophilic and thermophilic, demonstrated only small changes in viscosity for the samples,[19] in contrast to the molecular weights presented in Figure 3. The mesophilic samples in the study by Bastioli et al. hardly displayed any changes at all, apart from the Mater-Bi samples, while the thermophilic samples show small changes. A weight loss of approximately 10% for the PCL sample with the same initial molecular weight as in this study was noted after 110 days for the thermophilic samples.

Table IV presents the results of the DSC measurements of the PCL-V samples subjected to anaerobic sludge. The degree of crystallinity increased by 45% after 29 days of degradation in the thermophilic sludge. In another study, an increase in crystallinity was noted for the PCL samples, although over a longer time period.[19] The samples aged in mesophilic sludge showed a more moderate increase of approximately 20% after 220 days of degradation, corresponding to less degraded PCL and the lower temperature. The heat of fusion and the melting temperature of the second heating increased for the films degraded in thermophilic sludge, which corresponded to the significant decrease in molecular weight (Fig. 3). The samples subjected to mesophilic sludge showed minor changes in the heat of fusion and the melting temperature of the second heating.

Abiotic Environment

PCL-V samples were exposed to hydrolysis at 2 different pH values, pH 7 and 10.5, and at 2 temperatures, room temperature (23°C) and 50°C. Figure 5 shows that hydrolysis at 50°C is faster than hydrolysis at 23°C, as expected. Although differences in pH have no significant effect on the molecular weight at 23°C, a small difference is seen for the samples at 50°C. Samples at 50°C exposed to hydrolysis at pH 7 show a

Table VI Molecular Weight Changes of PCL Samples Degraded in Compost I and Hydrolyzed at pH 7 at 50°C

Sample	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	Polydispersity
PCL-V compost			
control	108,900 ± 20,500	185,200 ± 15,300	1.74 ± 0.32
1w	97,100 ± 24,200	174,000 ± 15,800	1.97 ± 0.46
3w	95,200 ± 20,400	184,100 ± 15,400	2.00 ± 0.42
7w	64,500 ± 13,100	172,300 ± 15,500	2.76 ± 0.58
Hydrolysis (pH 7, 50°C)			
control	60,100 ± 10,000	130,200 ± 20,000	2.17 ± 0.13
2w	71,200 ± 7300	162,700 ± 14,800	2.30 ± 0.29
8w	65,250 ± 8900	159,800 ± 15,800	2.48 ± 0.41
30w	28,900 ± 3000	68,300 ± 8100	2.36 ± 0.20
PCL-SMB compost			
control	100,500 ± 32,200	189,600 ± 21,000	2.02 ± 0.56
1w	89,600 ± 28,100	185,100 ± 24,000	2.19 ± 0.53
3w	89,600 ± 18,400	188,600 ± 19,200	2.16 ± 0.40
7w	75,900 ± 15,900	183,800 ± 19,300	2.48 ± 0.37
Hydrolysis (pH 7, 50°C)			
control	55,500 ± 11,100	126,100 ± 23,200	2.28 ± 0.12
2w	69,600 ± 13,300	153,700 ± 22,900	2.23 ± 0.16
8w	60,500 ± 12,400	138,800 ± 19,400	2.32 ± 0.24
30w	35,100 ± 7000	78,400 ± 14,500	2.25 ± 0.13

larger decrease in molecular weight than samples exposed to pH 10.5. Previously, the chemical hydrolysis of injection molded pieces of PCL at 37 and 50°C (pH 2, 7, and 10.6) have been studied.[7] The hydrolysis at 50°C was shown to be faster than at 37°C. It was also found that the degradation under alkaline conditions was 2–3 times faster than under acidic conditions. The degradation of cylinders of PCL have also been studied hydrolytically at pH 7.6.[8] The study was performed at the following 3 different temperatures: 37, 45, and 55°C. The rate of degradation increased with temperature, which was similar to what was found in this study, where the temperature affected the extent of degradation during hydrolysis more than the pH (Fig. 5).

Table V gives the results of the DSC measurements of the films subjected to abiotic degradation. The degree of crystallinity increased continuously with increasing degradation time for the PCL samples. After 30 weeks, the degree of crystallinity has increased by about 6% at 23°C and 30% at 50°C. Data has been presented, which show a 10% increase of the degree of crystallinity after 30 weeks hydrolysis at 37°C, and a 20% increase at higher temperature during aging for longer periods.[19,25]

Our results did not reveal any significant difference between the different pHs. Thermograms taken from the second heating showed that, after 30 weeks, the heat of fusion for the samples degraded at 50°C exhibited approximately 20% higher values than the samples degraded at 23°C. The major increase occurred during the last 90 days, which corresponds to the reduction of the molecular weight shown in Figure 5, which is in accordance with the samples degraded in anaerobic sludge described above.

Effect of Processing Aids on the Degradation of PCL

In Table VI, the changes in molecular weight for PCL-V and PCL-SMB degraded in compost I and hydrolysis at pH 7 and 50°C are compared. The samples with slip master batch displays slightly

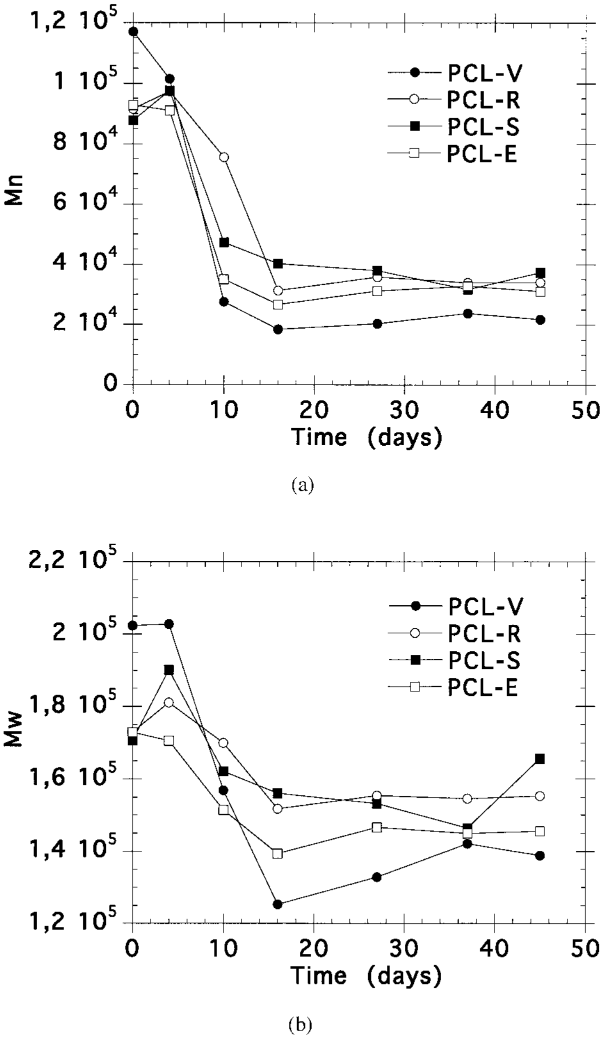


Figure 6 Changes in (a) $\bar{M}_n$ and (b) $\bar{M}_w$ for PCL-V, PCL-R, PCL-S, and PCL-E degraded in compost II.

higher molecular weight averages than the pure samples.

Figure 6(a) shows the changes in $\bar{M}_n$ of virgin PCL (PCL-V), recycled PCL (PCL-R), and PCL with processing additives (PCL-S and PCL-E), degraded in Compost II for 45 days. Virgin PCL degraded fastest, while recycled PCL and PCL with additives showed a slower degradation rate during composting. Recycled PCL shows a similar degradation rate as PCL with additives, which indicates that the additives do not affect the degradability of the films more than 1 extra processing does. Figure 6(b) shows the changes in $\bar{M}_w$ of PCL-V, PCL-R, PCL-S, and PCL-E. The same trend, as for $\bar{M}_n$, is observed. $\bar{M}_w$ of PCL-V, however, shows a larger decrease than of the others. For all samples, the initial degradation rate is rather fast, while after 16 days of composting, the molecular weight reaches a plateau and remains almost unchanged throughout the experiment.

Table III compares the results of the DSC measurements of the samples containing processing additives degraded in compost II. In general, films PCL-R, PCL-E, PCL-S, and PCL-EC exhibited the same increase of the degree of crystallinity during composting as film PCL-V (pure PCL). This behavior was also observed PCL-SMB in compost I and during abiotic degradation. The films degraded in thermophilic sludge, chemical hydrolysis at 50°C, mesophilic sludge, and compost II exhibited the highest degree of crystallinity, followed by the samples degraded in compost I.

Table VII shows $\bar{M}_n$, $\bar{M}_w$, and weight loss values of PCL with and PCL without processing additives degraded by *Aspergillus fumigatus* for 49 days at room temperature. Virgin (PCL-V) and recycled PCL (PCL-R) degraded faster than PCL containing additives. Weight loss values show correlation with $\bar{M}_w$ values. PCL-R has the lowest value of $\bar{M}_n$ and $\bar{M}_w$ after degradation. The polydispersity increased after the degradation, which is indicative of an increased cleavage at chain ends, as observed for the samples degraded in compost and thermophilic anaerobic sewage sludge. No significant changes in the thermal properties was detected, as shown in Table IV.

The biodegradation of PCL by *A. fumigatus* does not show the large changes in molecular weight, as was determined for the samples in Compost II (Table II). The changes in $\bar{M}_w$ are smaller than the changes in $\bar{M}_n$ were for the composted samples. In an early study, PCL of different molecular weights were exposed to different fungi, where one of them was a member of the *A. fumigatus* family (*A. fischerii*).[26] In that study, it was found that the dominating factor determining degradability was either polymer molecular weight or degree of crystallinity. However, when PCL in the form of powder with an average molecular weight of 10,000 (unknown if $\bar{M}_n$ or $\bar{M}_w$) was exposed to a fungi, *Paecilomyces lilacinus,* a 10% weight loss was noted after 10 days.[26] In another study,[22] PCL with the same molecular weight as used in this study was exposed to a consortium of five fungi, *Aspergillus niger, Penicillium funiculosum, Chaetomium globosum, Glicoladius virens,* and *Aerobasidium pullulans.* When the molecular weight was measured after 2 and 4 weeks, no difference in $\bar{M}_w$ between inoculated and sterile samples could be seen, though a

Table VII Molecular Weight Changes of PLC Degraded in Sterile Environments or by *Aspergillus fumigatus*

Sample	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	Remaining Weight (%)
PCL-V			
0d	117,100 ± 1900	202,300 ± 1500	100.0
49d *A. Fum*	58,000 ± 27,200	183,400 ± 6700	90.6
49d sterile	106,100 ± 2300	195,200 ± 900	100.0
PCL-R			
0d	91,600 ± 4000	172,900 ± 2300	100.0
49d *A. fum*	50,300 ± 3100	155,900 ± 1100	90.2
49d sterile	89,700 ± 4700	167,700 ± 3300	99.7
PCL-SIO			
0d	87,700 ± 6700	170,600 ± 2200	100
49d *A. fum*	72,700 ± 7600	167,400 ± 400	98.1
49d sterile	90,900 ± 2300	165,800 ± 1100	99.7
PCL-ER			
0d	92,800 ± 7100	172,900 ± 4600	100
49d *A. fum*	65,100 ± 1000	166,300 ± 2500	96.2
49d sterile	93,500 ± 1600	173,400 ± 900	100.3

significant reduction in $\bar{M}_n$ was noted.[22] The increase of the polydispersity was in accordance with our results with *A. fumigatus.* The same polymer in powder form was studied with 3 of the previously mentioned fungi, *C. globosum, A. pullulans* and *P. pinophilum,* for 28 days. A weight loss of about 10% was noted for *A. pullulans,* while smaller changes were noted for the other 2. No change in molecular weight as measured by viscometry was noted. DSC analysis did not reveal any changes in the thermal properties.[5]

Tensile Properties of the Samples Degraded in Biotic Environment

Table VIII presents the results from the tensile testing of the PCL films. The film containing mechanically mixed slip master batch (PCL-SMB) exhibited lower tensile modulus (*E*) and higher elongation at yield (ε_y) and break (ε_b) due to plastization. Comparing the results from tensile testing in Table VIII with previous measurements shows that the stress values are higher and the elongation at break is lower than those previously reported for injection-molded and melt-pressed PCL samples.[20,27] The difference could be explained by the orientation caused by the film blowing. After 3 weeks of degradation in compost I, the ultimate properties were significantly reduced. The ε_b was reduced significantly to about 10%, which was due to increased surface erosion. The stress at yield decreased to 90% of the initial value for PCL-V and 70% for PCL-SMB, which was similar to values reported previously for PCL degraded by fungi.[22] No further changes were seen after 7 weeks. At longer degradation times, the films were too brittle and perforated to test.

The mechanical properties of the compounded films were generally less affected than those for PCL-SMB described above. Though the ultimate properties of the film containing erucamide (PCL-E) were higher compared with the others, SiO_2 reduces σ_y, ε_y, and σ_b slightly. It was obvious that the samples degraded in compost II lost their mechanical properties more rapidly compared to the samples subjected to compost I. This behavior was clear for sample PCL-V, which showed significantly poorer elongation properties in compost II (Table VIII) compared with compost I. After 4 days of degradation, no tensile testing could be performed on the samples from compost II due to

Table VIII Mechanical Properties of PCL Samples, as Given By Tensile Testing, Degraded in Compost I and II

Sample	E (MPa)	σ_y (MPa)	ε_y (%)	σ_b (MPa)	ε_b (%)
V 0d	549 (38.8)	20.3 (1.6)	8.0 (0.9)	49.7 (20.0)	576 (244)
V CI 4d	615 (39.0)	19.6 (1.1)	4.3 (0.3)	50.7 (12.5)	423 (67.6)
V CI 7d	636 (77.5)	20.7 (1.5)	7.0 (0.8)	35.4 (10.4)	340 (102)
V CI 21d	577 (52.7)	19.9 (0.6)	6.9 (1.8)	14.6 (3.4)	11 (15.2)
V CI 49d	432 (86.0)	9.0 (0.8)	7.5 (4.4)	6.4 (2.4)	8 (7.7)
SMB CI 0d	433 (41)	19.5 (0.8)	12.5 (1.2)	38.1 (4.7)	637 (91)
SMB CI 4d	452 (39)	19.4 (1.3)	11.6 (1.1)	38.6 (8.8)	926 (169)
SMB CI 21d	483 (78)	17.0 (1.7)	8.4 (0.7)	14.2 (4.6)	19 (22)
SMB CI 49d	446 (37)	14.8 (1.1)	8.5 (1.4)	8.9 (2.5)	35 (21)
V CII 4d	606	21.4	6.2	12.7	41
R 0d	406 (27.2)	18.9 (0.5)	15.3 (1.0)	45.0 (8.9)	617 (224)
R CII 4d	406	17.1	13.9	14.0	261
E 0d	415 (31.7)	18.8 (0.3)	14.8 (1.4)	60.5 (12.9)	1207 (287)
E CII 4d	461			10.8	53
S 0d	444 (41.9)	17.4 (1.5)	11.3 (2.7)	35.3 (12.5)	698 (353)
S CII 4d	555	17.3	9.6	13.5	262
EC 0d	433 (33.6)	18.9 (0.6)	13.8 (1.8)	51.3 (8.6)	780 (184)
EC CII 4d	445	19.6	8.7	16.0	584

After 14 days in compost II, the films exhibited holes, and, consequently, no tensile testing was performed.

V = PCL-V, no additives; R = PCL-R, recycled; E = PCL-E 0.2 wt % Erucamide; S = PCL-S 0.5 wt % SiO_2; EC = PCL-EC 0.2 wt % Erucamide + 1.0 wt % $CaCO_3$.

extensive degradation. The deterioration in mechanical properties were caused by emerging cracks and holes.

Tensile Properties of the Samples Degraded in Abiotic Environment

Table IX gives the results from the tensile testing of the samples (PCL-V and PCL-SMB) subjected to chemical hydrolysis at room temperature (23°C) and 50°C, pH 7 and 10.5. During hydrolysis, the modulii values increased slightly but the ratio between the samples remained the same. The elongation at break (ε_b) for sample PCL-V at 23°C was reduced to 15% of the initial value after 16 weeks at pH 10.5, and the same level was reached after a total of 30 weeks at pH 7. PCL-SMB showed a more moderate decrease, not reaching more than 85% of the initial value after 30 weeks at pH 10.5. Consequently, PCL-V embrittles more rapidly than PCL-SMB, and high pH accelerates the decrease in ε_b. The embrittlement is probably caused by chain scission of tie chains, considering that the average molecular weight did not change significantly at 23°C.

The PCL-V samples degraded at 50°C showed minor changes, though a slight reduction in the stress at yield (σ_y) could be reckoned. Sample PCL-SMB at 50°C showed larger differences with an increase of ε_y, ε_b, and σ_b. In addition, the modulus decreased slightly. At longer degradation times, the samples sintered together, and sufficiently large pieces could not be provided for further tensile testing.

Effect of Recycling on the Degradation of PCL

During reprocessing (recycling), $\bar{M}_w$ of PCL decreases about 15–16% and $\bar{M}_n$ about 21–25% (Table VII). Comparing films with the same blow-up ratio, the recycled film exhibited slightly lower tensile modulus and stress at yield, and higher strain at yield, strain at break, and stress at break. The latter 2 values show the largest differences compared with the virgin film. The degree of crystallinity was about 55% for both samples. When these samples are composted in a garden waste compost (compost II), the molecular weight of virgin PCL decreases faster than for reprocessed PCL (Fig. 6). Comparing the actual $\bar{M}_w$ values, all reprocessed samples reach a $\bar{M}_w$ plateau of 140,000–160,000 after 10 days, while the plateau of virgin PCL lies in the region of 120,000–140,000.

Table IX Mechanical Properties of PCL Samples, as Given by Tensile Testing, Chemically Degraded

Sample	E (MPa)	σ_y (MPa)	ε_y (%)	σ_b (MPa)	ε_b (%)
V 23/7 0w	543 (39)	20.9 (1.0)	8.2 (0.5)	30.6 (5.9)	466 (49)
V 23/7 2w	559 (31)	21.0 (0.9)	8.9 (0.8)	29.6 (4.1)	452 (54)
V 23/7 4w	564 (76)	21.6 (1.5)	7.2 (0.4)	20.3 (2.2)	237 (135)
V 23/7 8w	561 (44)	21.8 (0.3)	8.2 (0.3)	14.0 (5.9)	352 (175)
V 23/7 16w	567 (27)	21.8 (1.0)	7.2 (0.9)	18.5 (2.7)	279 (193)
V 23/7 30w	642 (48)	22.2 (0.8)	7.1 (0.7)	18.0 (1.2)	84 (103)
V 23/10.5 2w	562 (34)	20.9 (1.4)	8.7 (0.7)	26.6 (4.4)	428 (59)
V 23/10.5 4w	546 (46)	21.3 (1.0)	7.2 (0.8)	26.9 (7.2)	401 (95)
V 23/10.5 8w	532 (48)	21.2 (1.0)	7.5 (1.2)	18.8 (17.6)	330 (182)
V 23/10.5 16w	543 (33)	21.8 (1.3)	6.4 (0.4)	18.0 (0.5)	73 (53)
V 23/10.5 30w	627 (46)	22.0 (0.5)	7.0 (0.8)	18.7 (2.1)	84 (123)
V 50/7 2w	520 (37)	19.4 (0.5)	8.2 (0.5)	26.8 (3.1)	418 (45)
V 50/10.5 2w	511 (18)	19.7 (1.1)	8.2 (0.9)	34.2 (6.5)	488 (75)
V 50/10.5 4w	477 (23)	18.3 (1.0)	9.0 (0.9)	37.9 (10.2)	604 (158)
SMB 23/7 0w	456 (26)	19.2 (0.8)	12.6 (1.1)	28.1 (4.7)	548 (45)
SMB 23/7 2w	454 (22)	19.3 (0.5)	12.3 (0.7)	30.3 (10.1)	591 (101)
SMB 23/7 4w	416 (39)	18.7 (1.5)	12.9 (0.5)	29.1 (4.4)	600 (139)
SMB 23/7 8w	416 (29)	19.4 (2.2)	13.0 (0.6)	30.0 (12.4)	545 (195)
SMB 23/7 16w	423 (34)	19.7 (0.7)	12.7 (0.7)	26.8 (4.0)	534 (160)
SMB 23/7 30w	471 (40)	19.6 (0.5)	12.6 (0.5)	22.5 (6.5)	468 (213)
SMB 50/7 2w	456 (26)	19.2 (0.8)	12.6 (1.1)	28.1 (4.7)	548 (45)
SMB 50/7 4w	388 (46)	17.2 (0.2)	14.6 (0.5)	44.0 (18.5)	777 (259)
SMB 23/10.5 2w	499 (39)	19.7 (0.5)	13.1 (0.4)	41.6 (12.9)	685 (175)
SMB 23/10.5 4w	447 (52)	19.1 (1.0)	12.7 (0.8)	32.1 (16.7)	573 (227)
SMB 23/10.5 8w	437 (56)	19.0 (0.6)	12.7 (0.6)	26.3 (4.7)	564 (148)
SMB 23/10.5 16w	442 (26)	19.2 (0.4)	11.5 (1.6)	28.6 (2.3)	492 (135)
SMB 23/10.5 30w	510 (21)	19.7 (0.3)	12.7 (1.1)	22.3 (7.0)	400 (236)
SMB 50/10.5 2w	393 (36)	17.4 (0.7)	14.3 (0.7)	38.1 (14.1)	695 (231)
SMB 50/10.5 4w	411 (69)	17.4 (0.3)	14.3 (0.8)	34.5 (5.9)	649 (83)

V = PCL-V, no additives; SMB = PCL-SMB 3.0 wt % slip master batch.

CONCLUSIONS

The recycled films and films with processing additives showed a slower degradation rate compared to pure PCL. The chemical hydrolysis was slower than the biotic degradation. Biotic degradation with a single microbial strain gave lower degradation rates in comparison with the rate observed in the composts. In the biotic environment, a larger reduction in $\bar{M}_n$ was seen than in $\bar{M}_w$, in contrast to the samples that were degraded in abiotic environment. The difference was interpreted as a preference for degradation near the chain ends for the samples in the biotic environment. Temperature was seen to accelerate the hydrolysis in both abiotic and biotic environments. A higher temperature and a mixture of microorganisms, together lead to more severe degradation in the biotic environments in either a cumulative or synergistic way. In the abiotic environment, pH has less influence on the degradation rate than the temperature. The degradation at higher temperature resulted in an increase of the degree of crystallinity due to crystallization made possible by the chain cleavage in the amorphous phase. The samples degraded in biotic environments exhibited higher rates of embrittlement compared to the samples degraded in the abiotic environments.

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