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Biodegradation of poly(ε-caprolactone)/starch blends and composites in composting and culture environments: the effect of compatibilization on the inherent biodegradability of the host polymer

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Abstract

The biodegradability of poly(ε-caprolactone) (PCL) was studied in blends and composites of modified and granular starch. Four types of PCL–starch compositions were prepared: (i) PCL–granular starch blends; (ii) hydrophobic coating of starch particles by *n*-butylisocyanate (C_4 starch) and octadecyltrichlorosilane (C_{18} starch), followed by melt blending with PCL; (iii) PCL–starch blends compatibilized by PCL-g-dextran grafted copolymer (PGD); and (iv) PCL-grafted starch particles (PGS) as obtained by in situ ring-opening polymerization of caprolactone (CL) initiated directly from hydroxyl functions at the granular starch surface. Biodegradability of these materials was measured by monitoring the percentage of weight loss in composting and the rate of fungal colonization when samples were used as a sole carbon source for fungus (*A. niger*). Intrinsic viscosity $[\eta]$ of host PCL chains was measured after extraction of composted samples in boiled chloroform. SEM was used to study the surface morphology after compost incubation of the samples. The inherent biodegradability of host polymer was enhanced with surface compatibilization during composting for longer incubation. It was observed that the weight loss during composting increased with the decrease in interfacial tension between filler and polymer. In general, it was concluded that inherent biodegradability does not depend very significantly on the concentration of starch in the polyester matrix, but on the compatibilization efficiency. The effect of the PCL fraction in the graft copolymer, when used as compatibilizer, was also studied on the biodegradability of the host polymer.
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1. Introduction

The need for biodegradable plastics has increased during the past decades, not only due to increasing environmental concerns, but also for their biomedical applications.[1–4] The terms 'biodegradation' and 'compostability' are very common but are frequently misused. In biodegradation, the enzymes of the biosphere essentially take part at least in one step during cleavage of the chemical bonds of the material. Notably, biodegradation does not ensure that a biodegradable material will always degrade. In fact, degradation will only occur in a favorable environment, and the biodegradable material will not necessarily degrade within a short time. It is, therefore, important to couple the term biodegradable with the specification of the particular environment where the biodegradation is expected to happen, and of the time-scale of the process. In the family of synthetic biodegradable polymers, poly(ε-caprolactone) (PCL), which is a linear, hydrophobic and partially crystalline polyester, can be slowly utilized by microbes.[5–8] Its physical properties and commercial availability make it very attractive, not only as a substitute of non biodegradable polymers for commodity applications, but also for specific applications in medicine and in agricultural areas.[9,10] The main limita-

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tion of PCL is its low melting temperature ($T_m \sim 65$ °C), which can be overcome by blending it with other polymers[11–13] or by radiation cross-linking processes that result in enhanced polymer properties.[14] On the other hand, starch is the most abundant biopolymer that has generated an ever increasing interest as a component in plastic formulations to achieve the biodegradability. Griffin[15–17] was the first to develop formulations with granular starch and synthetic polymers with highly improved biodisintegratibility during microbial consumption. Otey and coworkers[18,19] used gelatinized starch, ethylene acrylic acid copolymer (EAA) and ammonia in the development of biodegradable starch–synthetic polymer blends. Starch with concentrations as high as 90 wt.%, forms the continuous phase,[20] but acceptable mechanical properties can only be obtained with lower starch content. Blends between starch and PCL have been well documented in the literature,[21–23] but their commercial production is not very popular due to the high production cost and variation in physical properties. Bastioli and coworkers[13,24,25] reported the enhanced biodegradation of PCL in the presence of starch by providing greater surface area for microbial attack. MaterBi® from Novamont is claimed to represent a commercially available and compostable product made of compatibilized aliphatic PCL–starch blends and is being used for thin films and sheets.[26] The main limit of PCL–starch composites is the weak adhesion between the hydrophilic polysaccharides and the hydrophobic polyester matrix. Although interfacial properties can be improved by introduction of polyether blocks, e.g., poly(ethylene glycol) (PEG) into the PCL,[27,28] the molar mass still decreases very slowly during biological degradation due to the presence of two separated phases. In fact, PCL-chain cleavage proceeds as slow as for the homopolymer by hydrolytic degradation.[29] More recently, compatibilization with phase continuity in PCL–starch blends as well as improved biodegradability during composting compared to neat PCL has been reported by using grafted pyromellitic anhydride as the compatibilizing agent.[30] PCL shows good biodegradability in the presence of soil,[31] landfill leachates, sewage sludge[32] and mixed microbes from river sediments,[33] where PCL ($M_w \sim 35,000$)[33] was kept as sole carbon source. Enzymatic studies have also been used to examine the biosusceptibility of starch[34] and PCL[35] under specified conditions. Composting is one of the most valuable methods to learn of the bioassimilation of polymeric material during the studies and many attempts have been made to know the compostability of PCL, either alone or in the form of blends or composites with other materials.[36,37]

In the present paper, we have studied the biodegradability of native and compatibilized PCL–granular starch blends in composting and culture conditions for different time periods. The aim of this study was to evaluate the practical applications of these composite materials as well as to study the effect of various compatibilizing techniques on inherent biodegradability of PCL.

2. Experimental

2.1. Materials

Commercial grade PCL CAPA 650 was kindly supplied by M/s Solvay S.A. Belgium. PCL number average molecular weight (M_n) was 49,000 with a polydispersity of 1.4 as determined by size-exclusion chromatography (SEC) in THF. Granular cornstarch, high-amylose cornstarch (HACS) and waxy maize cornstarch (MCS) with amylose–amylopectin weight ratios of 30/70, 70/30, 0/100, respectively, were supplied by M/s Bioplastics Inc. Their mean average diameters were 15.5, 13.9 and 18.7 μm, respectively, as determined in water suspension by laser-light granulometry using a Coulter LS 230 apparatus.

2.2. Blends preparation

2.2.1. PCL–granular starch blends. PCL–starch compositions were prepared by mechanical kneading on a two-roll mill at 130 °C for 15 min. Then, molten composite materials were molded first into 3 mm thick plates by hot pressing at 100 °C under 30 bars for 30 s and cold-pressing at 15 °C under 30 bars for 5 min for measurement of mechanical properties.

2.2.2. Hydrophobic coating of starch granules and melt blending with PCL. The hydrophobic coating of granular corn starch was performed by reacting the hydroxyl groups available at the starch surface with *n*-butylisocyanate in bulk without any solvent under microwave treatment at 400 W for 5 min in the absence of any catalyst.[38] These surface-treated starch granules are coined 'C$_4$ starch'. Another hydrophobic coating was achieved by reacting the surface by hydroxyl function with octadecyltricholorosilane ('C$_{18}$ starch'). Corn starch granules were suspended in THF, previously dried by refluxing over sodium–benzophenone radical-anion for 48 h and freshly distilled. Triethylamine (dried over BaO for 48 h and distilled) was added as a catalyst, and the reaction mixture was stirred at 50 °C for 1 week. Coated starch granules were recovered by filtration, washed with water and dried under reduced pressure until constant weight. FTIR spectroscopy was used to demonstrate the high grafting efficiency as determined from the decrease of the absorbance corresponding to hydroxyl functions at 3330 cm^{-1}.[39] After chemical modification, the coated starch particles were melt blended with PCL so as to reach final PCL–starch

compositions of 70/30 for C_4 starch and 60/40 for C_{18} starch.

2.2.3. Synthesis of PCL-grafted dextran copolymers and use as compatibilizer in PCL–granular starch blends.

The three-step synthesis and characterization of PCL-grafted dextran copolymers (PGD) have been reported in detail in a previous paper.[40] Typically, dextran T10 (from Pharmacia Biotech; $M_n = 6600$) was first partially silylated at 50 °C in DMSO–THF solution with 1,1,1,3,3,3-hexamethyldisilazane as the silylating agent. The material was recovered by precipitation in heptane, followed by filtration and drying. In a second step, the polymerization of ε-caprolactone (CL) was initiated in toluene solution at 60 °C from the hydroxyl groups remaining free along the partially silylated dextran after activation with triethylaluminum. The PCL-grafted silylated dextran copolymer was then recovered by precipitation in heptane, followed by filtration and drying. In a final step, deactivation of aluminum alkoxide growing sites and deprotection of silylated dextran hydroxyl groups were carried out by dissolution in THF and addition of dil aq HCl. The in situ precipitated PGD was recovered by filtration and drying. In this study, two PGD copolymers were used with the following molecular characteristics: PGD1 with $F_{PCL} = 0.60$, DP = 8 and Ng = 10, and PGD2 with $F_{PCL} = 0.89$, DP = 20 and Ng = 21 (where F_{PCL} is the weight fraction in grafted PCL, Ng is the number of polyester grafts per dextran chain and DP is the average degree of polymerization of PCL grafts). It is worth noting that PGD copolymers were precipitated at the surface of starch granules before melt blending with PCL at 130 °C. Precipitation of the copolymers onto cornstarch granules was carried out by dissolving PGD 1 or 2 copolymers into a toluene suspension of granular starch and then dropwise adding a poor solvent for the graft copolymers, i.e., heptane.

2.2.4. In situ PCL grafting onto starch granules and melt blending with PCL.

The PCL-grafted starch particles (PGS) were obtained by in situ ring-opening polymerization of CL in the presence of granular starch as previously described by some of us.[41,42] Typically, dried cornstarch granules and CL (50/50 by weight) were introduced in a round-bottom flask previously purged with nitrogen, added with 1 wt.% triethylaluminum and heated up to 90 °C for 10 min. The polymerization was terminated by fast cooling at room temperature (rt). Weight fraction in grafted PCL chains (F_{PCL}) was determined by gravimetry after selective extraction in toluene of the non-grafted PCL chains. F_{PCL} was 4% for a monomer conversion of 86% (PGS1). PGS2 was obtained by an alternative procedure in which starch and triethylaluminum were first reacted in toluene suspension at rt for 2 h, then the toluene was removed out by filtration under inert and dried atmosphere, followed by the addition of CL, allowing the polymerization to proceed. The surface-treated starch granules were recovered as aforementioned leading to a F_{PCL} equal to 24% for a monomer conversion of 96% (PGS2). PGS2 has been used without any extraction except for an aliquot that enables one to determine the number-average molecular weight of free/non grafted PCL chains ($M_n = 60,000$). In the next step, PGS1 and PGS2 have been melt blended with the PCL matrix in order to reach a final PCL–starch composition of 60/40.

2.3. Compost and culture incubation

All composite materials were molded between two Teflon sheets into thin films (~ 100 μm, 5×5 cm) at 55 ± 5 °C by applying 150 kg/cm² pressure for 30 s using a preheated hydraulic press. These films were quenched with tap water for 5 min. The constitution of compost[43,44] was (dry weight): 40.8% cow dung, 11.4% sawdust, 15.8% newspaper and computer paper, 2% white bread, 7.8% shredded leaves, 19.2% food waste (dry milk, potato, carrot, banana and other vegetables) and 3.0% urea. The composting bin was covered by small fragments of green grass, and the moisture content was maintained by periodic spraying of water. To avoid anaerobic conditions, the bin was constantly aerated with oxygen through a hollow tube. The temperature variation within the compost medium is shown in Fig. 1. It was dependent on the climatic conditions, and the temperature inside the compost chamber was always higher than that of the surroundings. The temperature of the compost increased rapidly during the last days of incubation after an extra addition of the same quantity of cow dung as had initially been added. The samples (three samples for each composition) were kept inside the compost at a depth of 3.5 feet. The biodegradability was determined by measuring the weight loss of composted samples after thorough washing with water and drying under vacuum until constant weight. Nu-
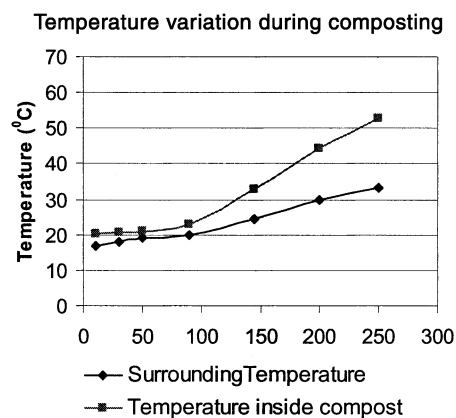

Fig. 1. Time dependence of the temperature in natural composting (the average of 5 values, ± 1.0 °C).

trient salt agar for test fungi was prepared by dissolving potassium dihydrogen phosphate (0.700 g), magnesium sulfate (0.700 g), ammonium nitrate (1.0 g), sodium chloride (0.005 g), ferrous sulfate (0.002 g), manganese sulfate (0.001 g) and agar 15.00 g in 1 L of distilled water. After sterilizing the medium at 120 ± 5 °C for 25 min, the pH was adjusted in the range pH 6.5–7.0 by the addition of (0.1 N) NaOH. For providing the solidified agar layer (depth 4–7 mm) nutrient salt was poured into sterilized petri dishes. The surface of test specimen (three samples for each composition) was inoculated by spraying the spore suspension. The petri dishes were incubated at 28–30 °C, after which they were sealed by wax to avoid contamination. The rate of fungal growth was estimated in accordance to ASTM G-2170 where the recorded parameter (S) is the fraction of the surface covered by fungus ($S < 10\%$ (+), $10 \leq S < 30\%$ (++), $30 \leq S < 60$ (+++) and $S \geq 60\%$ (++++)).

2.4. Characterization

Size-exclusion chromatography was performed in THF at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL/min), a Marathon autosampler (loop volume = 200 μL, solution conc. = 1 mg/mL), a PL–DRI refractive index detector, a LC1200 UV detector and three columns: a PL gel 10-μm guard column and two PL gel Mixed-B 10-μm columns (linear columns for separation of MW_{PS} ranging from 500 to 10^6 Da). Molar masses of PCL were calculated by reference to a poly(styrene) standard calibration curve, using the Mark–Houwink relationship $[\eta] = KM^a$ for PS and PCL ($K_{PS} = 1.25 \times 10^{-4}$ dL/g, $a_{PS} = 0.707$, $K_{PCL} = 1.09 \times 10^{-3}$ dL/g and $a_{PCL} = 0.600$). FTIR analysis was carried out with a Bio-Rad Excalibur FTIR spectrometer with a 0.2 cm^{-1} resolution. Spectra were recorded (from 4000 to 700 cm^{-1}) owing to a single reflection crystal system (Split Pea™ from Harrick) and a DTGS detector. The biodegradability of PCL–granular starch blends has been determined by measuring the weight loss of composted samples over 250 days (three replicates) after thorough washing with water and drying under vacuum until constant weight. Samples were extracted by boiling chloroform. This solution was filtered, and the soluble part was collected after evaporation. The soluble part was considered as PCL not consumed by microbes in composting. The intrinsic viscosity $[\eta]$ of the solute in chloroform was determined[45] at room temperature starting from a concentration of 0.1 wt.% by successive dilution. The thickness of the samples was measured as an average over 10 values. Scanning electron micrographs were taken on a gold-coated surface of the composted specimens after careful washing and drying by using a Leica Cambridge Stereoscan model 440. The

percentage weight loss was calculated by: $100 \times$ (Initial weight of component − Final weight of component)/ Initial weight of component.

3. Results and discussion

3.1. PCL−granular starch blends

The time-dependent weight loss is shown in Table 1 for PCL−granular starch compositions with starch content lower than or equal to 50 wt.% ($M_{nPCL} = 49{,}000$ and $M_w/M_n = 1.4$). Higher content of starch is responsible for the formation of very brittle materials that are highly difficult to melt process. It emerges from these data that PCL undergoes a slow degradation compared to the blends with starch (Table 1, entry 1). Increasing starch content in the blends favors the degradation rate as evidenced by an enhancement of weight loss as a function of time (Table 1, entries 2–6). In contrast, the percentage of weight extracted from composted samples is mostly independent of the initial PCL−starch composition. Therefore, considering that only PCL can be solubilized in boiling chloroform, it confirms that granular starch is rapidly degraded, while the host matrix is almost left unaffected in composting. The negligible change in PCL $[\eta]$ from 1.20 to 1.18 dL/g up to 120 days of incubation is another proof of the chemical inertia of the polyester under the investigated composting conditions. For longer composting time (250 days), $[\eta]$ decreases down to 0.85 dL/g which can either reflect a higher accessibility of PCL chains due to starch consumption or the gradual increase in composting temperature (see Fig. 1). In agreement with the latter assumption, a higher hydrolytic degradation occurs due to higher chain mobility at 35–40 °C together with an activation of thermophilic microbes.[37]

Replacing granular cornstarch by HACS and waxy MCS significantly reduces the degradation rate, at least up to 120 composting days (Table 1, entries 5, 7 and 8). In contrast, the weight loss after 250 days reaches a very similar value whatever the nature of the starch granules. Similarly, the fungal growth is slightly slower for the PCL−starch blends made of HACS and MCS until the 8th week, but reaches the same level of growth after 15 weeks (Table 2). Consequently, neither the amylose/ amylopectin weight ratio, nor variations in the mean average diameter of starch, are key parameters that determine the degradation kinetics and the fungal growth. Fig. 2 shows a scanning electron micrograph of a (60:40) PCL−HACS blend after 250 composting days. Many holes are observed randomly dispersed all along the surface, indicating the selective consumption of starch granules, leaving behind intact polymer matrix.

Table 1
Weight loss of PCL–starch blends during composting

Entry	Composition (PCL–starch blend)	Weight loss (%)			Weight loss of extracted fractions after 250 days composting (%)	
		90 days	120 days	250 days	PCL	Starch
1	100/0	0.8	1.1	45.6	–	–
2	90/10	1.6	2.2	56.5	51.9	98.3
3	80/20	1.8	2.3	61.4	52.3	97.9
4	70/30	2.8	3.5	66.1	52.4	97.9
5	60/40	11.1	11.3	70.5	52.8	96.9
6	50/50	11.7	13.3	75.8	53.7	97.9
7	60/40 HCS	2.8	5.6	72.0	54.9	97.6
8	60/40 MCS	3.2	6.3	72.9	55.6	98.8

Weight loss after 250 days composting was determined as follows:$100 \times$ (Initial weight of component − Final weight (recovered weight) of component)/Initial weight of component.
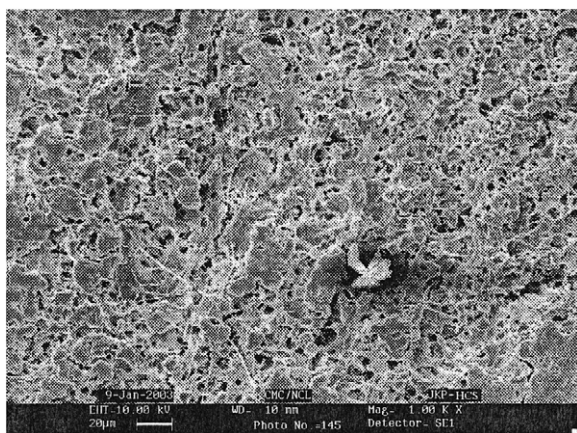

Fig. 2. SEM of 250 days composted (60/40 composition) PCL–HACS composition blend (Mag. 1.00 K ×).

3.2. Hydrophobic coating of starch particles

The mechanical properties of granular cornstarch-filled PCL compositions are improved by comptabilization.[38] Three strategies were investigated, including the hydrophobic coating of starch granules, the surface-localized addition of PCL-grafted dextran amphiphillic copolymers, and the use of PCL-grafted granular starch. The mechanical property changes were clearly related to parameters such as filler dispersion, interfacial tension, interfacial adhesion and reinforcement by PCL crystallization. As far as hydrophobic coating of starch particles is concerned, available hydroxyl groups at the starch surface have been reacted with n-butylisocyanate (C_4 starch) and octadecyltrichlorosilane (C_{18} starch). In both cases, mechanical properties were consistent with a better interfacial tension between the two phases, meaning that the material is more homogeneous, less brittle, but also less elastic. For instance, for the blends with C_4 starch, the strength (σ_r) and the elongation at break (ε_r) increase (from 16.1 to 17.1 MPa and from 437 to 528%, respectively) while a decrease is observed for the Young modulus (from 256 to 216 MPa). Table 3 shows the effect of the compatibilization by a hydrophobic coating of starch granules on the biodegradation of the composite materials.

Both of the hydrophobic coatings (C_4 starch and C_{18} starch) enhanced the degradation rate in composting. However, starch granules coated with a butyl shell

Table 2
Fungal growth onto the surface of PCL–starch blends

Entry	Composition (PCL–starch)	Fungal growth efficiency					
		1st week	3rd week	5th week	8th week	12th week	15th week
1	100/0	0	+	+	+ +	+ +	+ + +
2	90/10	0	+	+ +	+ + +	+ + +	+ + +
3	80/20	0	+	+ +	+ + +	+ + +	+ + + +
4	70/30	+	+	+ +	+ + +	+ + +	+ + + +
5	60/40	+	+ +	+ + +	+ + +	+ + +	+ + + +
6	50/50	+	+ +	+ + +	+ + +	+ + + +	+ + + +
7	60/40 HACS	+	+ +	+ +	+ + +	+ + +	+ + + +
8	60/40 MCS	+	+ +	+ +	+ + +	+ + + +	+ + + +

Table 3
Effect of the starch granules surface coating on the weight loss of PCL–starch blends during composting

Entry	Composition (PCL–starch blend)	Weight loss (%)			Weight loss of extracted fractions after 250 days composting (%)	
		90 days	120 days	250 days	PCL	Starch
1	70/30	2.8	3.5	67.2	52.4	97.9
2	70/30 C_4starch	4.1	5.6	77.2	67.9	98.9
3	60/40	11.1	11.3	70.5	52.8	96.9
4	60/40 C_{18}starch	12.8	14.1	75.1	60.1	97.5

showed the highest degradation. Indeed, the weight loss is significantly increased for the PCL–C_4 starch com-
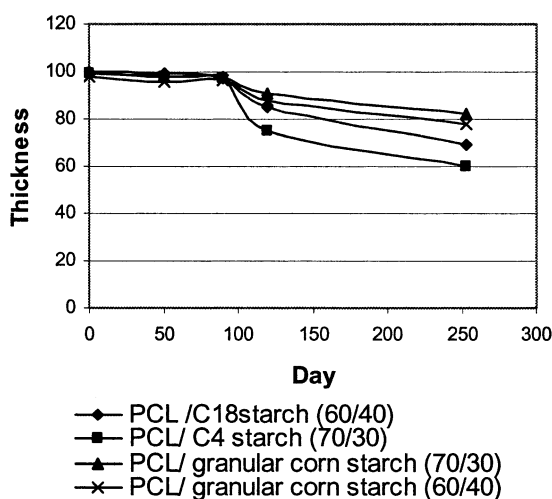
Fig. 3. Time dependence of the PCL–starch sample thickness (in μm) in composting. Effect of the surface coating of granular starch: PCL–C_4 starch (70/30), PCL/C_{18} starch (60/40) and PCL–granular corn starch compositions.
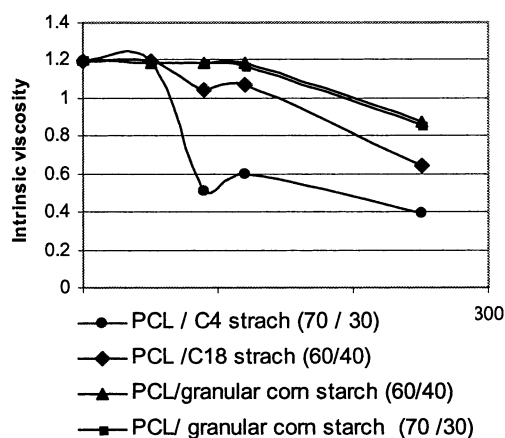

Fig. 4. Time dependence of the PCL intrinsic viscosity (in dL/g) for the PCL–starch samples in composting. Effect of the surface coating of granular starch: PCL–C_4 starch (70/30), PCL–C_{18} starch (60/40) and PCL–granular corn starch compositions.

position, and the amount of PCL that can be extracted was decreased. These observations are fully confirmed by the time evolution of the sample thickness and the PCL [η] (Figs. 3 and 4). There is a very similar relation between both sample thickness decrease and weight loss in function of biodegradation time, while [η] changes are clearly more pronounced for the PCL–C_4 starch blend. The slight increase in PCL [η] during the first 60 days
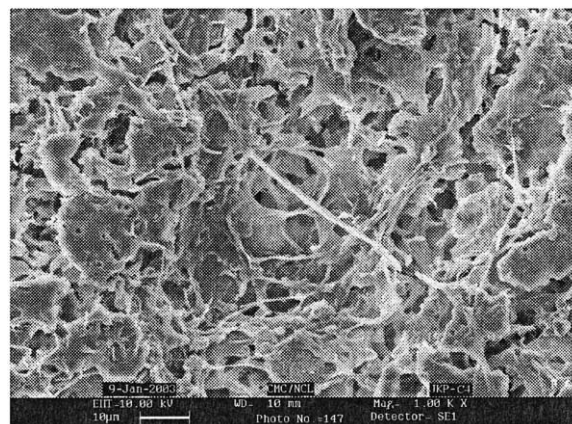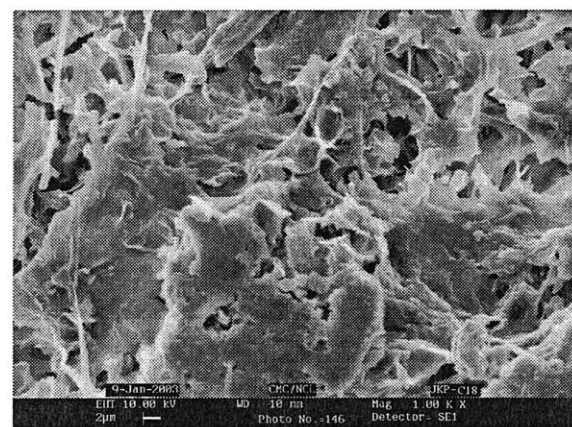
Fig. 5. (a) SEM of PCL/C_4 starch (70/30 composition) after 250 days composting (Mag. 1.0 K ×). (b) SEM of PCL/C_{18} starch (60/40 composition) after 250 days composting (Mag. 1.0 K ×).

Table 4
Weight loss of the PCL–starch blends, comptabilized with PCL-grafted dextran onto the granular starch surface during composting

Entry	Composition (PCL–starch blend)	Weight loss (%)			Weight loss of extracted fractions after 250 days composting (%)	
		90 days	120 days	250 days	PCL	Starch
1	60/40	11.1	11.3	70.5	52.8	96.9
2	60/40+PGD1	2.6	3.1	74.4	58.9	97.6
3	60/40+PGD2	9.0	11.1	76.5	63.0	96.9

can be explained by the selective diffusion of the shorter PCL chains out of the matrix and their eventual consumption by microbes in a similar way to what is observed during the hydrolytic degradation of polyester implants in aqueous media.[8] Scanning electron microscopy (SEM) does not show a clear difference between the degradation surfaces of PCL–C$_4$ starch and PCL–C$_{18}$ starch (Fig. 5a and b). However, the significant increase in PCL weight loss in PCL–C$_4$ starch compared to a 70:30 PCL–starch blend confirms that compatibilization and/or homogeneity of the two separated phases are in favor of the degradation of the host polymer.
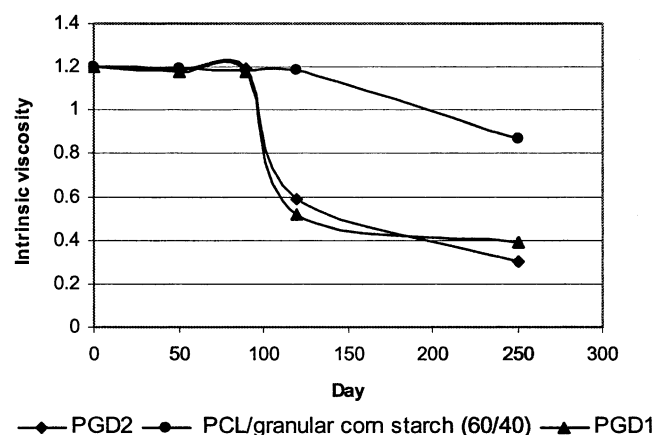

Fig. 6. Time dependence of the PCL intrinsic viscosity of the PCL/starch samples in composting. Effect of the precipitation of PCL-grafted dextran: PGD1 and PGD2 in comparison of (60/40 composition) PCL granular starch blend.

3.3. Addition of PCL-grafted dextran as compatibilizer

Two PCL-grafted dextran amphiphilic copolymers (PGD) have been used with different PCL fractions: PGD1 with $F_{PCL} = 0.60$, DP = 8 and Ng = 10, and PGD2 with $F_{PCL} = 0.89$, DP = 20 and Ng = 21 (where F_{PCL} is the weight fraction in grafted PCL, Ng is the number of polyester grafts per dextran chain, and DP is the average degree of polymerization of PCL grafts). It is worth recalling that both PGD have been precipitated at the surface of starch granules before melt blending them with PCL. From the mechanical properties point of view, a result is that the amphiphilic copolymers do not only promote a better dispersion and a lower interfacial tension, but also contribute to reinforcing the adhesion between the filler and the matrix.[37] Table 4 illustrates the degradation rate of the (60:40) PCL–starch blends added with 5 wt.% of PGD1 and PGD2, respectively. The location of PCL-grafted dextran at the interface between granular starch and PCL tends to decelerate the degradation for the initial period of composting as attested by the time dependence of sample weight loss. This is confirmed by a slow thickness decrease compared to that of a non-compatibilized 60:40 PCL–starch blend. Such behavior is in contrast with the significant increase of weight loss when the temperature as well as composting time is increased. The weight loss of extracted PCL is also drastically increased when comparing entries 1 and 3 (Table 4) with the time. These data clearly indicate that the difference in biodegradability must be due to the variation in weight fraction of PCL. Fig. 6 shows the PCL intrinsic viscosity change as a function of time. Compared to non modified PCL–starch blends, the addition of 5 wt.%
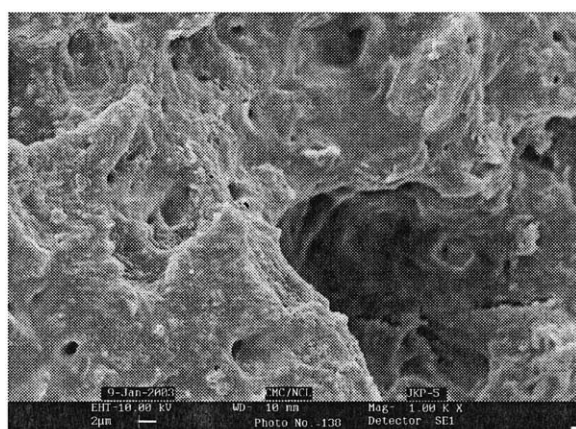
Table 5
Fungal growth onto the surface of PCL–starch blends comptabilized with PCL-grafted dextran onto the granular starch surface

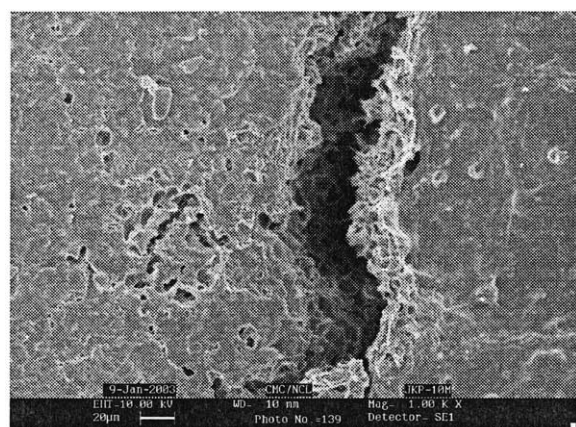| Entry	Composition (PCL–starch)	Fungal growth efficiency					
		1st week	3rd week	5th week	8th week	12th week	15th week
1	60/40	+	++	+++	+++	+++	++++
2	60/40+PGD1	+	+	++	+++	+++	++++
3	60/40+PGD2	0	+	+	++	+++	++++
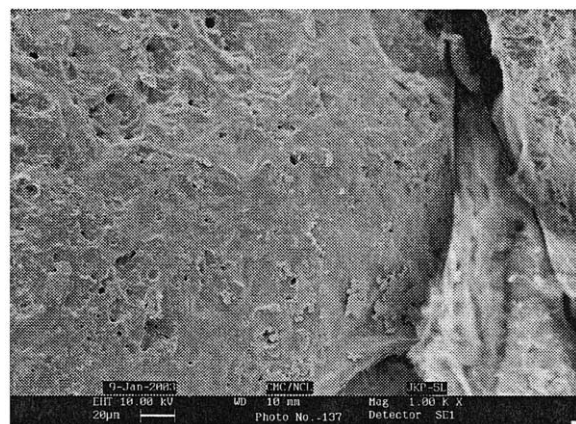
(a)

(b)

(c)

Fig. 7. (a) SEM of PCL–Starch (60/40 composition) compatibilized with PGD1 after 250 days composting (Mag. 1.0 K ×). (b) SEM of PCL–Starch (60/40 composition) compatibilized with PGD2 after 250 days composting (Mag. 1.0 K ×). (c) SEM of uncompatibilized (60/40 composition) PCL/starch blend after 250 composting (Mag. 1.0 K ×).

PCL-grafted dextran favors the degradation of the polyester chains. Remarkably, an increase in $[\eta]$ of PCL is observed between 60 and 90 composting days,

followed by a sharp drop occurring as the time of composting increases. The viscosity increase can be explained by the diffusion of shorter polyester chains and their eventual assimilation by microbes as already proposed for blends involving surface-coated starch granules. Fig. 7a–c show the SEM of (60:40) PCL–starch blends with and without compatibilization by PGD1 and PGD2. Based on the relative homogeneity and erosion of the surface, compatibilized compositions appear rougher and more degraded, particularly the sample prepared from PGD2. The fact that the surface of native PCL–starch blend is smoother may reflect a preferential consumption of starch granules to the detriment of the host matrix. The PCL weight fraction also affects the fungal colonization on the surface of these samples. Table 5 shows the slower surface coverage by fungus when PGD2 is substituted for PGD1. As a conclusion, dextran-grafted PCL copolymers enhance the degradation of the polyester matrix, particularly when PCL is the major component. In contrast, a high PCL weight fraction in the copolymer first disfavors the adhesion of fungus.

3.4. In situ PCL grafting onto starch granules

In this study, two compositions of PGS have been prepared that possess weight fractions in PCL of 4 (PGS1) and 24% (PGS2), respectively (Section 2). As the grafting efficiency is not quantitative but rather lies between 0.50 and 0.95 depending on the polymerization conditions, free/non grafted PCL chains contained in PGS1 have been selectively extracted by selective dissolution in toluene before melt blending with the PCL matrix. From the mechanical properties point of view, the grafting of PCL chains at the starch surface remarkably enhances both the rigidity and toughness of the composite materials (significant increases of both Young modulus and strength-at-yield from 295 to 365 MPa and from 9.6 to 13.0 MPa, respectively). It means that both interfacial adhesion and elasticity are increased as well as the crystallinity extent of PCL chains in the direct vicinity of starch granules.[37]

Tables 6 and 7 show the time dependence of weight loss and fungus growth of 60:40 PCL–starch compositions obtained by melt blending PCL with PGS granules. The composition added with PGS1 degrades faster than the one with PGS2 for longer composting. Similarly, fungal growth is easier with PGS1, although the presence of PGS slows down microbes adhesion onto the surface. Once microbes have been adsorbed, their penetration into the structure is rapid and they consume both starch and PCL. The morphological aspects of composted PGS1 and PGS2 containing compositions are shown in Fig. 8 (a) and (b), respectively. The cracked surface of PGS1 could be clearly seen even at lower magnification, and this sample was more biodegraded

Table 6
Weight loss of PCL−starch blends comptabilized with in situ grafted PCL onto starch granules, during composting

| Entry	Composition (PCL−starch blend)	Weight loss (%)			Weight loss of extracted fractions after 250 days composting (%)	
		90 days	120 days	250 days	PCL	Starch
1	60/40	11.1	11.3	70.5	52.8	96.9
2	60/40/PGS1	18.9	21.7	80.5	69.5	96.3
3	60/40/PGS2	4.7	7.0	78.0	64.5	98.3

Table 7
Effect of starch-surface grafting by PCL chains on the fungal growth at the surface of the samples

Entry	Composition (PCL−starch)	Fungal growth efficiency					
		1st week	3rd week	5th week	8th week	12th week	15th week
1	60/40	+	+ +	+ + +	+ + +	+ + +	+ + + +
2	60/40/PGS1	0	+	+ + +	+ + +	+ + + +	+ + + +
3	60/40/PGS2	0	+	+ +	+ +	+ + + +	+ + + +

than PGS2. This fact was fully confirmed by the higher decrease in thickness with PGS1. From Fig. 9, it can be seen that the [η] decreases sigmoidally for the composition added with PGS1, while the dependence of PCL−starch surface-treated with PGS2 is very similar to previous observations (hydrophobic coating and PCL-grafted dextran as compatibilizer). All these observations tend to demonstrate that the covalent grafting of PCL chains onto starch may play the role of a barrier reducing starch availability and delaying bioassimilation of both starch and PCL when the weight fraction in PCL reaches 24% and/or the PCL segments are able to crystallize. In contrast, when granular starch is poorly grafted by PCL (PGS1), the good dispersion, interfacial properties and adhesion, as well as the amorphous state of short grafted PCL segments are responsible for an increase in the degradation rate of both starch and PCL.

As evidenced by the present study, starch granules enhance the biodegradation of the composite materials in a uniform, linear and rapid way, providing a high surface area for microbial activity and easier microbial migration into the PCL matrix. It is all the more pronounced that starch granules are homogenously dispersed into the polyester matrix and that compatibilizing agents open the way to the entrance of microbes. When PCL chains are attached onto the starch surface through covalent ester bonds, they may crystallize in the direct vicinity of starch granules, limit the diffusion of PCL chains out of the material and restrict the penetration of microbes, at least at high-grafted PCL weight fractions, and in natural composting. As far as the biodegradation mechanism of PCL is concerned, it may either occur by an exoenzyme-catalyzed hydrolysis of
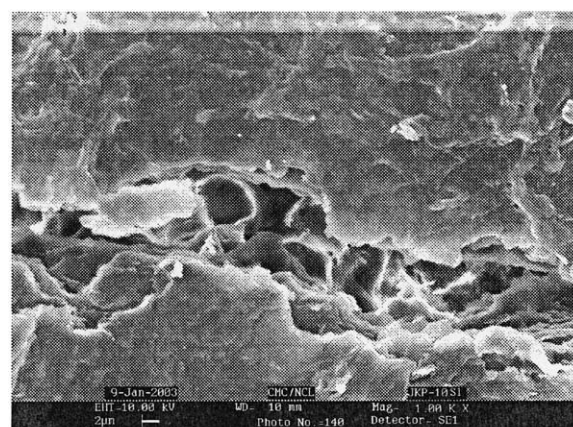
(a)
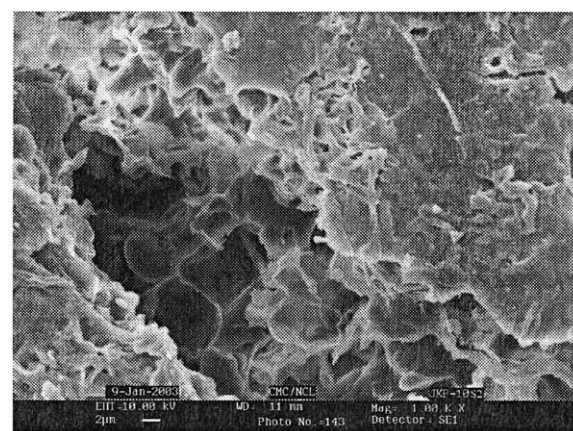
(b)

Fig. 8. (a) SEM of 60/40 PCL-g-starch composition (PGS1) after 250 days composting (Mag. 1.0 K ×). (b) SEM of 60/40 PCL-g-starch composition (PGS 2) after 250 days composting (Mag. 1.0 K ×).
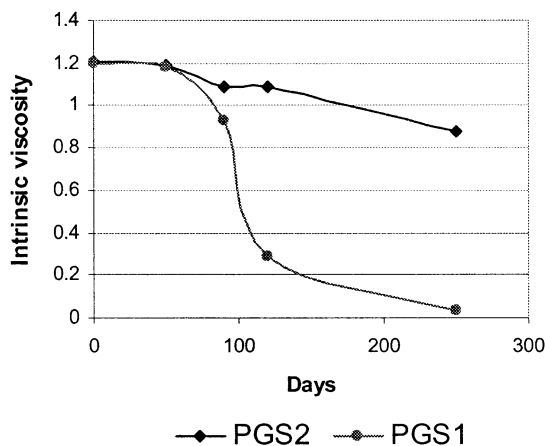
Fig. 9. Time dependence of the PCL intrinsic viscosity (in dl/g) for the PCL–starch samples during composting. Effect of the PCL covalent grafting onto the starch surface: PGS1 and PGS2.

ester linkages or by an oxidation process with the bio-assimilation of small fragments. The short chains are easily bioassimilated, and because of this surface erosion increases with the decrease in the thickness and viscosity.

4. Conclusions

The inherent biodegradability of the host polyester has been shown to increase with compatibilization within the PCL–starch compositions. In that respect, improving the dispersion of starch granules through a hydrophobic coating, and reducing the interfacial tension between PCL and starch owing to the starch–surface precipitation of PCL-grafted polysaccharide (dextran) proved to be very efficient. Grafting of PCL onto starch granules may suffer from an increase of PCL crystallinity in the direct vicinity of the starch surface, which reduces the accessability to microbes. It depends on the grafting efficiency and the weight fraction of grafted PCL chains. In other words, a balance might have to be found between the improvement of adhesion required for mechanical purposes and an acceptable degradation rate. Whatever the compatibilizing agent, the biodegradation of PCL–starch compositions starts with starch consumption and continuously increases with the content in natural filler. Monitoring sample thickness proved to be useful for the measurement of surface erosion, which is complementary to SEM.

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