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Preparation and characterisation of compatibilised polycaprolactone/starch composites

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Abstract

Polycaprolactone/high amylose starch blends were prepared by the adding of a proper compatibiliser constituted by low molecular weight PCL modified on the terminal groups by using pyromellitic anhydride. Thermal, mechanical and morphological analyses were performed in order to show the better performances of these blends compared to mechanical ones obtained without the use of the compatibiliser. Finally, the biodegradability of the materials, by a compost simulation test, was also tested to assess the influence of the compatibiliser presence on the whole biodegradation process of PCL. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polycaprolactone; High-amylose starch; Compatibilizing agent

1. Introduction

The aim of the present paper is to prepare and characterise starch-based materials using the polycaprolactone (PCL) as semi-crystalline matrix: PCL was chosen because of its good mechanical properties and because it is one of the more commercially available biodegradable polymers [1,2]. However, the main limit of the starch/PCL blends is represented by the lacking of adhesion between the polysaccharide and the synthetic polymer matrices owing to their different polarity giving consequently poor final properties. In fact, starch and hydrophobic polymers (as PCL) are immiscible and simple mixing produce blends with separate phase. To improve the compatibility and so the adhesion between the two immiscible polymers we introduced a reactive functional group (pyromellitic anhydride) on a PCL phase to increase the polar nature of the matrix and so to improve the adhesion between the components of materials. For this we utilised a PCL having a lower molecular weight (20,000 Da) with respect to that used as matrix (80,000 Da) owing to the fact that it posses lower viscosity and a major number of OH-terminals.

2. Experimental

2.1. Materials

Poly(ε-caprolactone), having a molar mass of 80,000 g/mol and a molar mass of 20,000 g/mol, were kindly supplied by Solvay.

Pyromellitic anhydride, Aldrich product, was used without further purification.

Starch (Amilomaize), having a high content of amylose (70%) was supplied by Cerestar.

The starch, before the use, was dried by lyophilisation until constant weight and kept in an desiccator containing silica gel dried.

2.2. Preparation of the PCL/starch composites

The composites were prepared by mixing in a Rheocord apparatus at 80°C for 15 min at 32 rpm. The PCL, starch and the pre-compatibiliser were added simultaneously in the machine, in different weight percentage. In Table 1 are reported the codes of the materials and their compositions.

3. Techniques

Wide-angle X-ray (WAXS) spectra were carried out by using a Philips powder diffractomer (PW 1050 model) operating at the CuKα wavelength of 1.542 Å.

Measurements of the diffracted intensities were made in the angular range of 4–40° (2θ), at room temperature and scanning rate 1°/min.

The infrared spectra were obtained by using a Perkin–Elmer Paragon 2000 FT-IR spectrometer.

The samples were investigated both in pressed disc mixed with powdered KBr and on deposited films from solution.

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The spectra were recorded at room temperature using 10 scans.

Thermal characterisation was carried out by using a Mettler TA-3000 differential scanning calorimeter. An empty pan was used as reference. About 10 mg of the samples were weighed accurately into aluminium pans and sealed hermetically. Two series of DSC experiments were performed. In the first the samples were heated from 0 to 200°C, cooled down to −100°C and then re-heated to 200°C at a rate of 10°C/min.

In the second the samples were heated from 0 to 200°C at a scan rate of 10°C/min, quenching down to −100°C at a rate of 50°C/min and a re-heated to 200°C at a rate of 10°C/min.

Tensile tests were performed on dumb-bell specimens, having thickness of 1 mm, by using an Istron machine. The deformation rate was of 10 mm/min. The procedure used for the calculation was in accordance to the ASTM (D256) standard.

Impact tests were performed at room temperature with an Instrumented Charpy pendulum on compression-moulded specimens (6 mm wide, 3 mm thick and 60 mm long) that were cut and notched with a fresh razor blade. The Charpy impact speed was 1 m/s.

Scanning electron micrographs were taken on an Au/Pd coated fractured surface of the dumbbell specimens using a Philips SEM 501.

The biodegradability of the polymeric mixtures was investigated by a compost simulation test. This test was a modification of the ASTM D5338 procedure of controlled composting (ASTM D 5338-1992. “Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions”). A 3-l reactor was filled with 2 l of mature compost and thermostated at 50 ± 2°C. The system was continuously aerated with previously water saturated and thermostated pressurised air. The specimens, having the same initial shape (i.e. the same surface to exposure to the biodegradation treatment), were buried inside the reactors. The samples were withdrawn from the compost reactors at different times, washed with distilled water and dried at 60°C to constant weight and the disintegration of the materials was evaluated (referred as % of weight loss). The mature compost used in this test was kindly supplied by Centro Ricerche Produzioni Animali (CRPA) of Reggio Emilia (Italy). It was produced at the Platform of the Composting Plant if Limidi di Soliera, Modena (Italy), from a mixture of residual sludge (municipal sewage treatment plant), grass and wood chips (maintenance of civic parks). The compost was stored indoors for several months. Prior to use, the compost humidity was adjusted to 60%.

4. Results and discussion

4.1. Synthesis and characterisation of the compatibiliser

Generally a required group can be incorporated into a

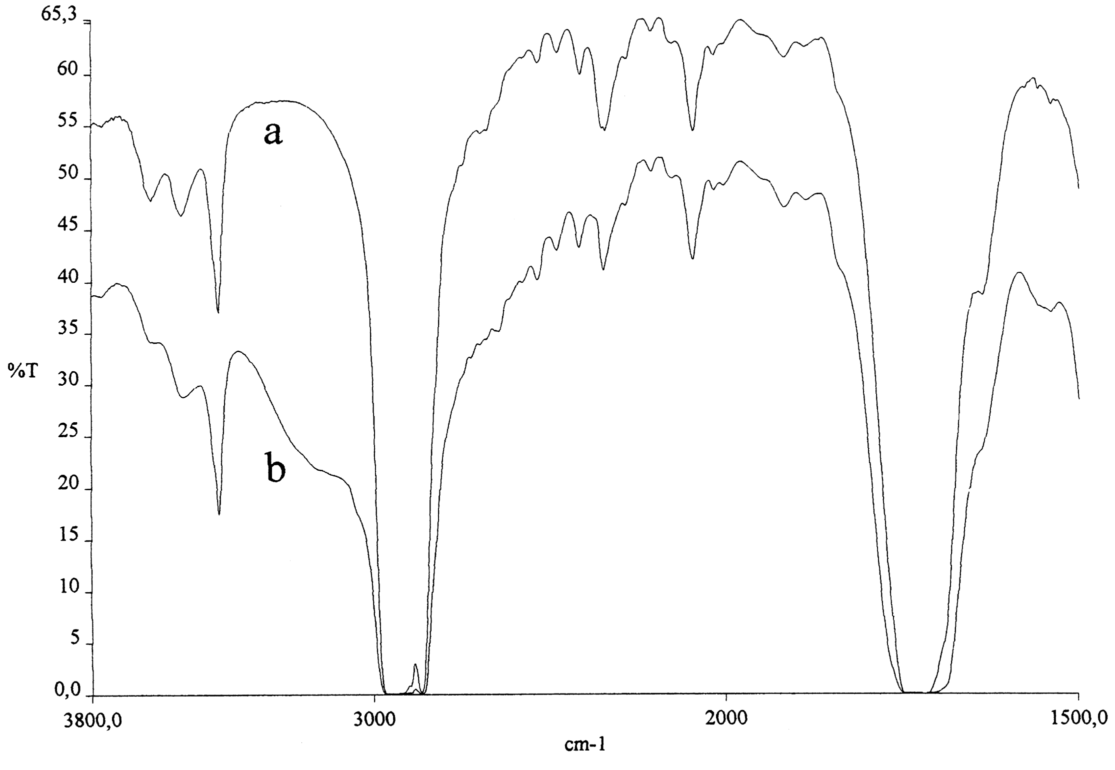
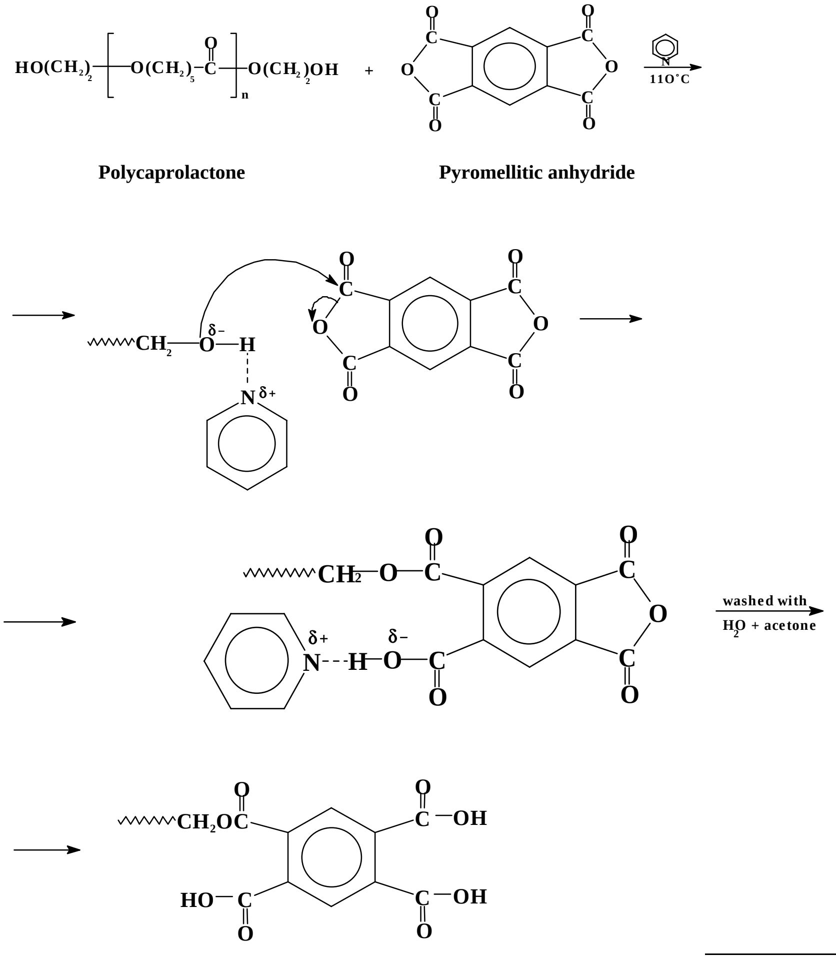


Fig. 1. Comparison between FT-IR spectra of neat PCL (a) and modified PCL (b).

polymer by chemical modification of pre-formed polymer through a variety of chemical reactions [3–9]. These chemical modifications may be carried out in solution, in the melt or even in the solid state. However, the modification of polymers during a melt-processing step has these advantages: it is not necessary solution removal, recovery and losses and there are few probabilities of contamination of final products.

In order to obtain a PCL end-capped with reactive groups able to react with the –OH groups of the starch, the PCL was modified by reaction with a dianhydride, namely pyromellitic anhydride, according to the following scheme of reaction:



To have a higher concentration of reactive hydroxyl end-groups on PCL, it was used for the above reaction a PCL having lower molecular weight (20,000). The reaction was carried out in bulk, with pyridine as catalyst. The temperature was set to 110°C as the viscosity of PCL is low enough to have a well stirrable system, and not too high to cause the scission of the ester linkage, which forms is thermoreversible. A large excess of dianhydride was used to allow high conversions and avoid undesirable chain-extension reactions between modified and unmodified PCL. The final product was purified from excess anhydride by repeatedly washing with a water/acetone mixture. A partial hydrolysis of the anhydride groups on end-capped chains may happen in these conditions.

The reaction has been monitored by IR spectroscopy. Samples have been periodically checked during reaction to control the degree of conversion; on the basis of IR analysis the total time of reaction has been set to 24 h. As shown in Fig. 1 the modification of PCL was accompanied by the decrease of the 3630 cm^{-1} band (stretching of hydroxyl end groups of PCL chains) and the appearing of a band at 3200 cm^{-1} due to OH stretching of carboxylic groups. The intensity of this latter band increased after the washing of the product reaction, owing to the opening of the anhydride rings unreacted.

The typical anhydride bands at about 1860 and 1780 cm^{-1} cannot be detected because of overlapping of very intense ester band of PCL at 1736 cm^{-1}.

4.2. Thermal analysis of the composites

Selective extraction of the components aimed to isolate a mixed PCL/starch phase have been carried out on the PCL 50M composite and on the PCL 50 composite as reference. Samples have been treated with chloroform. Emulsions were obtained in both cases; they were put in a cylindrical

Table 1
Description of composition of the composites and relative codes (Note 1. The symbols L (Low), M (Medium), H (High) refer to the content of the pre-compatibiliser)

PCL/starch composition (w/w%)	Weight percentage of the pre-compatibiliser (%)[a]	Code
100/0	0	PCL 100
90/10	0	PCL 90
70/30	0	PCL 70
50/50	0	PCL 50
100/0	2.5	PCL 100 L
90/10	2.5	PCL 90 L
70/30	2.5	PCL 70 L
50/50	2.5	PCL 50 L
100/0	5	PCL 100 M
90/10	5	PCL 90 M
70/30	5	PCL 70 M
50/50	5	PCL 50 M
100/0	10	PCL 100 H
90/10	10	PCL 90 H
70/30	10	PCL 70 H
50/50	10	PCL 50 H

[a] The percentage of the pre-compatibiliser is related to the weight of the PCL in the composites.

separator funnel and left at room temperature for long time to let the phases to segregate, according to a procedure known as “Molau test” [10].

A complete phase separation with a supernatant starch phase and a clear $CHCl_3$ solution is reached only in the case of the PCL 50 system, while in the case of PCL 50 M composite the solution was opaque even after several weeks, thus clearly revealing the emulsifying effect of the modified PCL. The supernatant starch phase was separated and the opaque $CHCl_3$ solution was evaporated; the recovered product was characterised by IR and DSC analysis. The above results do not give a clear experimental evidence of the formation of grafted starch/PCL molecules. As matter of fact, we cannot exclude that simple stronger polar interactions (hydrogen bonds) between hydrolysed anhydride end-groups onto PCL and starch could be responsible of the improvement in the interfacial compatibility between starch and PCL.

In Table 2 the thermal parameters (glass transition T_g, melting point T_m and content of crystallinity X_c), measured for all studied samples, are reported.

The PCL functionalised presents the same melting point of the unmodified polymer. Nevertheless it was noted an increase of glass transition temperature from −66°C (original polymer) to −55°C (modified polymer). T_g was supposed to increase because of reduced segmental motion of random coil chains in amorphous regions and increased free volume through the presence in the end-chains of the encumbering molecules of pyromellitic anhydride.

The content of crystallinity (X_c) was calculated as the ratio $\Delta H/\Delta H_\infty$ (where ΔH is the fusion enthalpy of PCL in the samples, while ΔH_∞ refers to the hypothetical perfect crystal of PCL ($\Delta H_\infty = 136$ J/g). It was observed that X_c increased as the content of compatibiliser enhanced and its value was independent on the content of starch. This behaviour was likely due to the lower molecular weight (20,000 Da) of the PCL modified. In fact, according to literature [11], polymers with low molecular weight, have a high content of crystallinity.

Table 2
Thermal analysis data

Composites	T_g (±2°C)[a]	T_m (±2°C)[b]	X_c (±2)[c]
PCL 100	−67	62	53
PCL 90	−66	60	52
PCL 70	−65	61	53
PCL 50	−65	59	52
PCL 100L	−67	61	57
PCL 90L	−68	61	57
PCL 70L	−68	59	56
PCL 50L	−67	59	56
PCL 100M	−66	63	64
PCL 90M	−67	64	62
PCL 70M	−66	64	64
PCL 50M	−64	62	63
PCL 100H	−67	62	66
PCL 90H	−69	62	67
PCL 70H	−69	61	66
PCL 50H	−68	60	68

[a] T_g = glass transition.
[b] T_m = peak melting point.
[c] X_c = degree of crystallinity.

Table 3
Tensile properties

Composites	E (MPa)[a]	σ_y (MPa)[b]	σ_b (MPa)[c]	ε_b (%)[d]
PCL 100	280	13.3	33.0	1328
PCL 90	337	10.7	26.1	1042
PCL 70	542	9.2	21.3	891
PCL 50	597	4.0	8.1	538
PCL 90L	277	11.7	31.5	1567
PCL 70L	402	11.2	14.7	833
PCL 50L	775	9.2	9.6	20
PCL 90M	369	12.9	28.6	1389
PCL 70M	548	12.8	18.3	658
PCL 50M	796	13.4	13.2	4
PCL 90H	487	14.2	21.6	739
PCL 70H	640	9.2	10.7	430
PCL 50H	994	8.8	9.3	3

[a] E = tensile modulus.
[b] σ_y = strength at yielding.
[c] σ_b = strength at break.
[d] ε_b = elongation at break.

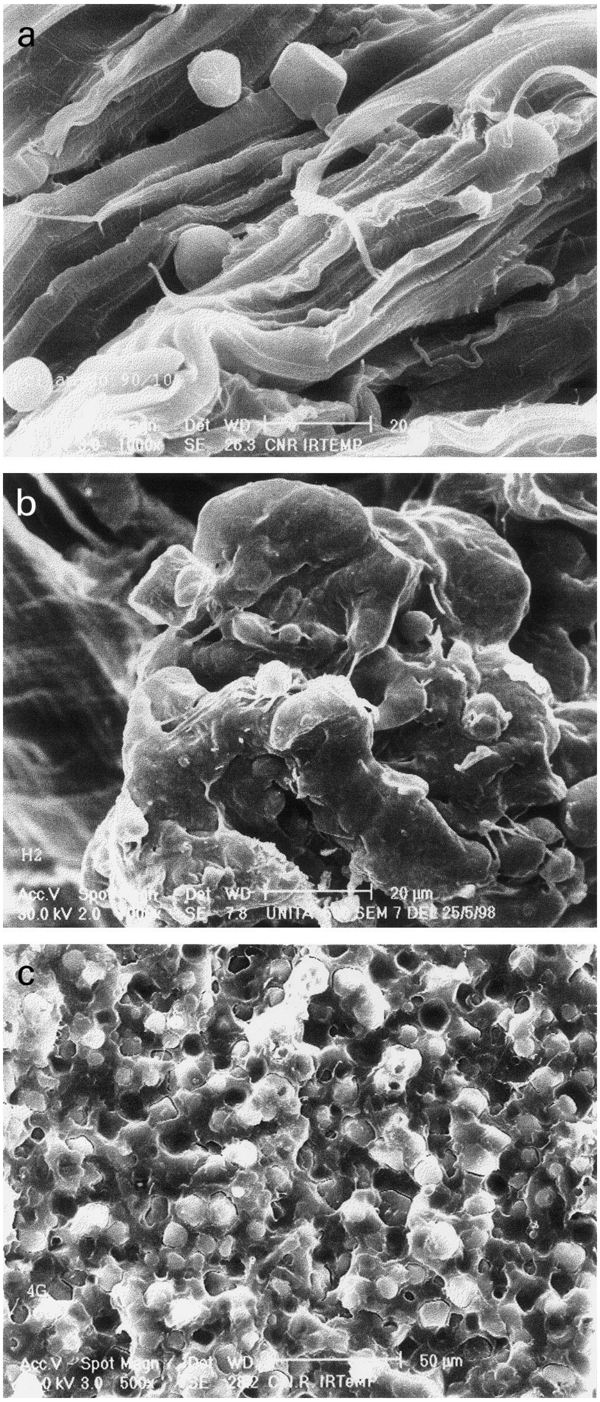


Fig. 2. (a) SEM micrograph of fracture surface of PCL 90 composite. (b) SEM micrograph of fracture surface of PCL 90 H composite. (c) SEM micrograph of fracture surface of PCL 50 H composite.

4.3. Tensile properties of PCL/starch blends and SEM analysis

Tensile properties such as tensile modulus (E), strength at yielding (σ_y), strength at break (σ_b) and elongation at break (ε_b) were evaluated from the stress–strain curves. The results are summarised in Table 3. From these data emerges that the PCL, as it well known, is a ductile polymer, able to undergo large deformations; unfortunately it posseses a relatively low modulus rendering it unable to be used for any applications where a high rigidity is required. Thus, the presence of starch phase in the mechanical blends can contribute to improve its modulus. As matter of fact it is observed that the addition of starch, also without the compatibiliser, acts as filler, increasing the Young's modulus of PCL until twice (597 MPa for the blend PCL/starch 50/50 against 280 MPa for PCL) having as consequence a reduction of all other mechanical parameters. This latter behaviour is due to the fact that the presence of starch granules that are not capable of being deformed prevent the fibres formation of PCL under cold-drawing.

Concerning the mechanical behaviour of PCL/starch blends containing the compatibiliser, they present a stronger increase of elastic modulus especially for the samples containing 50% of starch accompanied by higher strength at yielding with respect to neat PCL.

On the contrary, a decreasing of the elongation at break with the increase of starch amount it is observed. This finding is accentuated for the samples 50H and 50M where ε_b reaches values around 3–4%.

These results can be correlated to a better interfacial adhesion between the two phases: in fact it may, mainly in the region of linear elasticity of the matrix (low deformation), induce a minor ability of PCL chains to flow giving rise to a higher rigidity of the material. As matter of fact the presence of compatibiliser, increasing the interfacial adhesion between the starch granules and the polymeric matrix hinders the flow of PCL macromolecules even more under the cold-drawing.

A morphological analysis was also performed on the fractured surface of the samples after tensile tests. In Fig. 2a–c the SEM micrographs of PCL 90, PCL 90 H and PCL 50 H fractured surfaces are shown as examples, respectively.

It can be observed that the starch grains are well distributed and covered by PCL material in presence of compatibiliser (Fig. 2b), confirming a good interconnections between the two phases. On the contrary, the samples obtained without the addition of the compatibiliser show a poor interfacial adhesion (Fig. 2a).

Moreover, it can be easily observed that the samples having low starch content (10%) keep the ductile behaviour of PCL, while the composites having high content of starch (50%) seem to present a behaviour of a rigid material (Fig. 2c). These latter results are easily correlated to the elongation at break values.

4.4. Impact test and fractographic analysis

The values of fracture parameter Resilience (R), for neat PCL and the PCL/starch blends containing 0, 5 and 10% of compatibiliser, calculated according to the Linear Elastic

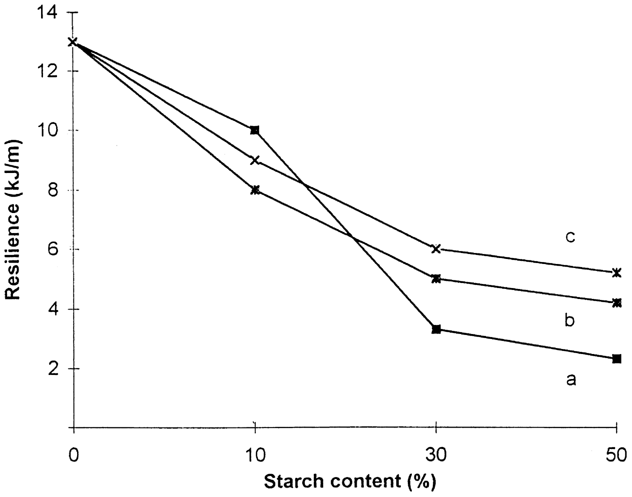


Fig. 3. Variation of resistance against percent of starch content (curve a: composites without compatibiliser; curve b: composites containing the 5% of compatibiliser; curve c: composites containing the10% of compatibiliser).

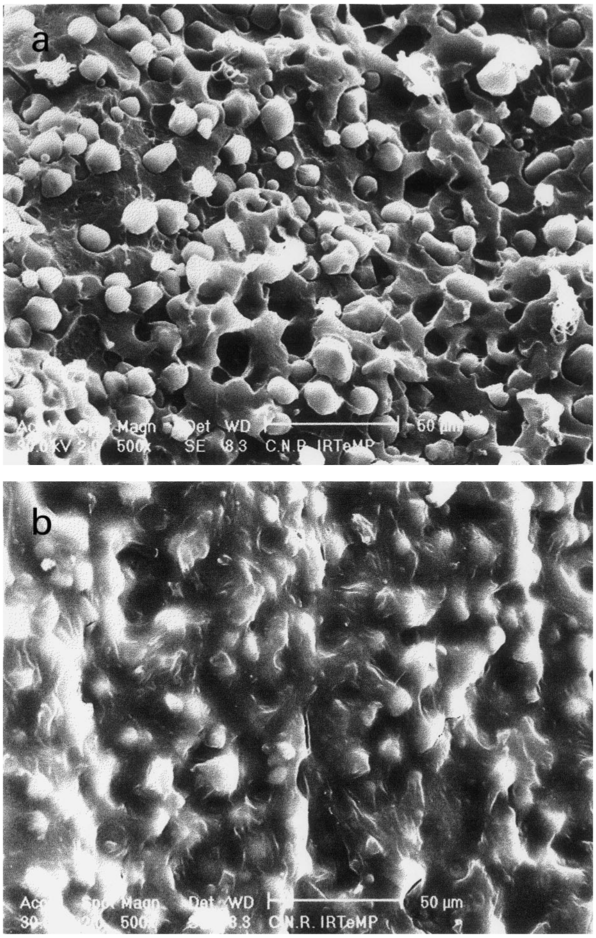


Fig. 4. (a) SEM micrograph of fractured surface of PCL/starch. (b) SEM micrograph of fractured surface of PCL/starch with compatibiliser.

Fracture Mechanics (LEFM) [12], as a function of starch content are shown in Fig. 3. From this figure a decrease of *R*, for all samples examined was observed. Nevertheless, for the samples having highest starch content (30–50%), it seems that the presence of compatibiliser slows down the drop of *R* value.

These results on the fracture behaviour can be interpreted on the basis of the fractographic analysis performed by SEM on the surface of notched specimens, the SEM micrographs were taken near the notch tip in the region of crack initiation. Fig. 4 show the fracture surfaces of PCL/starch blends prepared without (Fig. 4a) and with (Fig. 4b) the addition of the compatibiliser and can be easily noted the differences. In fact in the first case the presence of cavities and voids left by starch grains exhibits a poor adhesion between matrix and filler, while in the case of PCL/starch with the compatibiliser a fairly smooth fracture surfaces almost without pull out of starch particles owing to the better interfacial adhesion produced by the compatibiliser can be deduced.

The *R* lowering observed also in the blends containing the compatibiliser can be related to the Young's modulus improvement measured by low rate elongation tests (tensile measurements) where the stiffness of the material increases by the addition both of starch phase and of compatibiliser presence. As matter of fact the optimisation of mechanical properties of a material involves almost always a compromise between resilience and rigidity [13]. The PCL possessing low stiffness and high deformation capability is able to store deformation energy when a load is applied and thus is more difficult to break during the impact. The inclusion of the starch phase produces an increase of modulus decreasing the resilience values, while the presence of compatibiliser slows down this trend and this fact can be interpreted on the basis of alternative dissipated mechanism of energy owing to the higher interfacial adhesion between the two composite constituents and probably by a different crystallisation process.

4.5. Investigation on biodegradability

Polycaprolactone/starch specimens were submitted to the compost test and the percentage of the weight loss was evaluated at different times during the biodegradation process. Comparing the data reported in Table 4, it comes out that neat PCL exhibits a lower rate of degradation than PCL/starch mixtures. In fact, after 14 days of incubation all investigated mixtures were highly degraded and could be hardly extracted from the bioreactor. Moreover, the compost test performed on PCL/starch compatibilised blends indicated that the presence of modified PCL does not affect the biodegradability of the blends, at least at contents equal or lower than 10%.

SEM analysis of samples degraded at different extent, revealed that neat PCL undergone a homogeneous superficial erosion during the compost test. Instead, samples of PCL/starch appear to be degraded in heterogeneous manner

Table 4
Percentage of weight loss of neat PCL and PCL/starch mixtures in the simulating compost test. (The % of weight loss are the average of ten specimens.) (Samples completely deteriorated.)

Samples	7 days (%)	14 days (%)	23 days
Neat PCL	30	45	65%
PCL/starch 90/10	35	>65	–
PCL/starch 70/30	30	>75	–
PCL/starch 50/50	55	>75	–

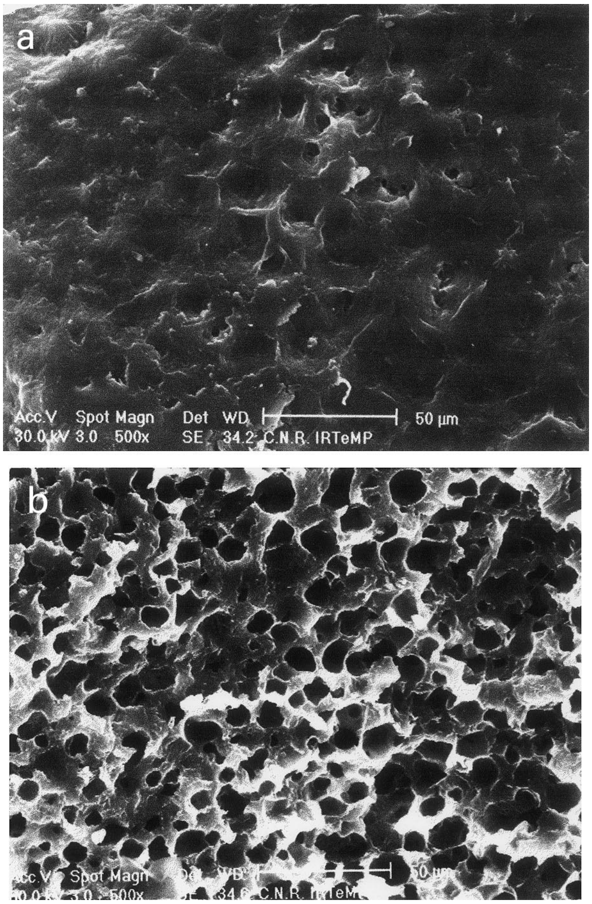


Fig. 5. (a) SEM micrograph of neat PCL after 23 days of biodegradation test. (b) SEM micrograph of PCL 50 after 23 days of biodegradation test.

and show an irregular surface with many holes in consequence of the preferential removal of the starch granules. As an example, the comparison between the surface of biodegraded samples of neat PCL and PCL/Starch after 23 days of incubation is shown in Fig. 5a and b, respectively.

5. Conclusion

From the above results, it can be deduced that the use of a compatibiliser (PCL-*co*-pyromellitic anhydride) in composites PCL/starch can improve the performances without changing their whole biodegradability. These environmentally compatible materials are characterised by less cost than the neat PCL and display all required qualities of a disposable plastic.

Moreover, it was shown that changing the amount of starch and compatibiliser, it is possible to tailor the properties of the composites for specific applications, otherwise requiring other polymers (as PE or PP) whose lack is a low biodegradability.

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