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Blends of biodegradable polyesters by reactive blending: preparation, characterisation and properties

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Blends of poly-ε-caprolactone (PCL) and poly-β-hydroxybutyrate (PHB) were prepared by mixing the two polymers in the presence of dicumylperoxide (DCPO) in solution of chlorobenzene. Similarly blends were obtained by mixing the two polymers with no peroxide added. The blends were prepared in a break of composition, from 85% wt PHB/15% wt PCL to 15% wt PHB/85% wt PCL, respectively. Also pure polymers were reacted with DCPO in the same way of the blends. Thermal (DSC), spectroscopic, mechanical (tensile tests) and morphological (SEM) analyses were performed on the blends and on the pure polymers. Significant differences were found in the chemical-physical characteristics of the blends with and without peroxide.

1. Introduction

Biodegradable polymers, since ’70, have been studied by academic and industrial research groups, in view of their several applications in biomedical field and in relation to environmental problems:

(A) In the field of reconstructing surgery, for example, the use of prostheses made of biodegradable and biocompatible materials has the advantage to avoid re-operating to remove the foreign element; at same time, the prosthesis supplies a frame for the damaged tissue [1]. Polymers used for this purpose must have particular qualifications, certified by specific commissions. Then the production is leant towards new materials obtained by copolymerisation or blending of already known and approved polymers [2, 3]. Polymers that are widely employed in biomedical field are poly-esters (poly-lactide, poly-glycolide, polycaproIactone), poly-anhydrides, polyaminoacids and natural polymers like collagen [4].

(B) Environmental problems concerning polymers arise from the heaping of hardly degradable plastic materials in environment. Though they form a limited fraction of solid urban wastes (between 2 and 5% in weight), polymers present serious problems in disposal. Then the research is leant either towards the study of the factors influencing synthetic polymers biodegradability and degradation mechanisms, or towards the planning and the synthesis of new biodegradable polymers for commodities application, able to realise low environmental impact when disposed off [5].

Poly-D(-)-3-hydroxybutyrate (PHB) is an optically active, high molecular weight, aliphatic polyester, biocompatible and biodegradable, produced by many types of micro-organisms; it was described first in 1925 by Lemoigne; first company to produce it on industrial scale was ICI [6].

PHB is a polymer of high crystallinity (more than 60%), with a melting temperature of 175–180 °C and a glass transition temperature between 4–7 °C, like those of polypropylene, but with very different mechanical properties.

Despite its biological origin, PHB is a thermoplastic polymer, then it can be extruded or spinned in the same plants of synthesis polymers; but its processability window is very narrow because the polymer degrades to crotonic acid through a β-scission reaction at temperature little higher than melting point.

Poly-ε-caprolactone (PCL) is prepared through the ring-opening process of ε-caprolactone, in the presence of an initiator/catalyst system [7]. It is a semicrystalline polymer, with structure similar to that of polyethylene. It has a low melting temperature (60 °C) and a low glass transition temperature (-60 °C). It can be easily spinned and used to yield fibres [8]. PCL biodegrades whether into the soil or for the attack of special micro-organism; the degradation times vary with the molecular weight, the crystallinity degree and the morphology [9].

Among the routes most followed to prepare new material, the blending is actually the most economic and versatile way [10–12], the main goal being likely the combination of the favourable properties of different polymers; anyway, due to the low combinatorial entropy of mixing, most binary polymer blends are immiscible, giving rise to a two-phase system generally characterised by an unstable morphology and a poor interfacial adhesion between the phases. These problems

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can be solved by modifying the interfacial properties of the blend phases using compatibilisation tools; the method is most often based on the use of suitable block or graft copolymer which, properly located at the interface between the phases, act as emulsifying agents. Alternatively, the compatibilisation can be achieved by direct formation of grafted species during blending, by using suitable grafting promoters.

In the sphere of this themes, the aim of the present work was to prepare multicomponent polymeric systems based on poly-β-hydroxybutyrate (PHB) and poly-ε-caprolactone (PCL) at different compositions, using reactive blending processes in solution, and to study the role of interfacial agents, such as graft copolymers prepared *in situ* by adding peroxides, on the morphology and the mechanical properties of the materials.

2. Experimental part

2.1. Materials

PCL, trademark CAPA 650, was kindly supplied by Solvay with reported $M_W = 55000$. PHB was kindly supplied by ICI (England) with $M_W = 790000$. Dicymilperoxide (DCPO) (Polyscience) was used as received. Chlorobenzene was used as received. Codes and composition of blends and homopolymers are reported in Table I. Note that the letters P and M stand for peroxide-treated and mechanical (i.e., not treated with peroxide) blends, respectively.

2.2. Typical blend preparation

PCLPHB 50/50 P5 was prepared by dissolving 10 g of PCL and 10 g of PHB in 200 ml of chlorobenzene. After complete dissolution, the two solutions were joined together in a flask equipped with a nitrogen inlet and a refrigerator, at 120 °C. After few minutes, 1 g of dicumylperoxide was added to the system; then after 24 h the reaction was stopped, the polymeric product was precipitated in methanol, repeatedly washed with methanol and finally dried in a vacuum oven.

The same procedure was used for the preparation of blends coded M but no peroxide was added during the mixing. Also homopolymers have been treated in similar way: PCL P5 was prepared by dissolving 10 g of PCL in 200 ml of chlorobenzene in a flask equipped with a nitrogen inlet and a refrigerator at 120 °C. After complete dissolution, 0.5 g of dicumylperoxide was added to the system. After 24 h, the reaction was stopped, the polymeric product was precipitated in methanol, repeatedly washed with methanol and finally dried in a vacuum oven.

TABLE I

Samples	PHB (% in wt)	PCL (% in wt)	DCPO (% in wt)
PHB	100	0	0
PHB P5	100	0	5
PHB P10	100	0	10
PCL	0	100	0
PCL P5	0	100	5
PCL P10	0	100	10
PHBPCL85/15 P5	85	15	5
PHBPCL70/30 M	70	30	0
PHBPCL70/30 P5	70	30	5
PHBPCL70/30 P10	70	30	10
PHBPCL50/50 M	50	50	0
PHBPCL50/50 P5	50	50	5
PHBPCL50/50 P10	50	50	10
PHBPCL30/70 M	30	70	0
PHBPCL30/70 P5	30	70	5
PHBPCL30/70 P10	30	70	10
PHBPCL37/63 5P	63	37	5
PHBPCL15/85 5P	15	85	5

2.3. Techniques

The viscosity measurements were performed at 25 °C with a Cannon-Ubbelhode viscometer. Concentrations of 0.005 g/cl in freshly distilled chloroform were used. The size-exclusion chromatography measurements were performed using two linear columns. Concentrations of 0.2 mg/ml in chloroform were used. Calibrations were carried out using 12 standards of Waters and Polymer Laboratories Polystyrene, with molecular weights from 3000000 to 580 amu. The flux was set to 1 ml/min.

Differential thermal analysis was carried out using a Mettler TA 3000 differential scanning calorimeter. Two series of experiments were performed: in the first one, the sample was heated from room temperature to 200 °C at a scanning rate of 10 °C/min, cooled at the same rate down to −100 °C and re-heated to 200 °C at 10 °C/min. In the second experiment, the sample was heated from room temperature to 200 °C at 20 °C/min, quenched down to −100 °C and re-heated to 200 °C at 20 °C/min. The NMR spectroscopy measurements were carried out on a Varian UNITY 400 spectrometer, at 298 K; concentrations of 20 mg/0.75 ml in deuthered chloroform were used.

Tensile tests were performed at room temperature with an Instron machine at 10 mm/min cross-head speed on dumbbell specimen of 1 mm thickness. The sample was cut from a compression molded sheet prepared by heating the powder at 180 °C for 3 min without pressure, then applying a pressure of 83 MPa for 3 min at the same temperature.

Scanning electron micrographs were taken on Au/Pd coated fracture surfaces of the dumbbell specimens using a Philips SEM 501 microscope. Moreover the smoothed surfaces were analysed, before and after exposition to the vapour of a selective solvent steams.

3. Results and discussion

3.1. Influence of peroxide decomposition on homopolymers

Generally speaking reactive blending is used for polymers with functional groups onto the backbone chain, able to promote exchange reactions, such as amide-amide and amide-ester interchanges and transesterification reactions [13].

Since PCL and PHB both have got the same functionality, the ester linkage, transesterification reactions could be used, in principle, to induce compatibilisation. Unfortunately, the extreme sensitivity to thermal degradation of PHB and the high temperature required for trans-esterification make such route to compatibilisation not practical. Previous work on PHB/PCL system mixed in the melt employing an organic peroxide showed that the decomposition of the peroxide in the bulk leads to the formation of gels that obstacle the rheology of the materials [14]. Nevertheless, the results on mechanical properties were encouraging to search different approaches to blends preparation.

On the basis of these results, we have prepared the blends from a common solvent in which also the peroxide is soluble; such route allows to create more homogeneous reaction environment and to avoid the cross-linking process.

After a first screening, we chose chlorobenzene as solvent, that is a high-boiling solvent, with no easy extractable hydrogen atoms, that might interfere with the radical reactions. The reaction is stopped pouring the solution in methanol: this allows all peroxide residues and polymer fractions soluble to be moved. Preliminary, the influence of peroxide has been checked on the homopolymers (see Table I).

Peroxides cause different effects according to the polymers and to their characteristics of stability: for example, molten polyethylene cross-links if treated with peroxides and for some applications it can be used as such, while molten polypropylene degrades upon peroxide attack because of the tertiary carbon atoms along the backbone chain [15].

With respect to PHB and PCL in molten state, it is reported, for PHB, a behaviour similar to that of polypropylene, i.e., degradation in the presence of peroxides [16], while formation of networks is predicted for PCL [17]. Experimentally, comparative analysis of the results obtained from viscometer tests and molecular weight determinations tests (by SEC) shows that, in our conditions, in dilute solution, the two polymers have different behaviour as far as peroxides action is concerned.

3.2. Viscosity and SEC measurements

Inherent viscosity values of PHB (Table II) drastically drop after treatment with peroxide already at peroxide content of 5% in weight, in agreement with the results of molecular weights distribution curve, as obtained by SEC (Fig. 1); increasing peroxide amount, no further decrease of molecular weights is observed.

PCL shows instead more diversified behaviour: increasing peroxide amount, inherent viscosity, after a slight diminution, is leant to grow (see Table II). This result fits the molecular weights distribution: in the case of PCL P10, the curve (Fig. 2) is broadened and shows a shoulder at higher molecular weights. This effect is punctually reflected in polydispersity value, that goes from 4.3 to 7.4.

TABLE II Inherent viscosity data for peroxide treated PHB and PCL

% DCPO	η_{inh} (dl/g) PHB	η_{inh} (dl/g) PCL
0	2.09	1.04
5	0.69	0.92
10	0.76	1.30

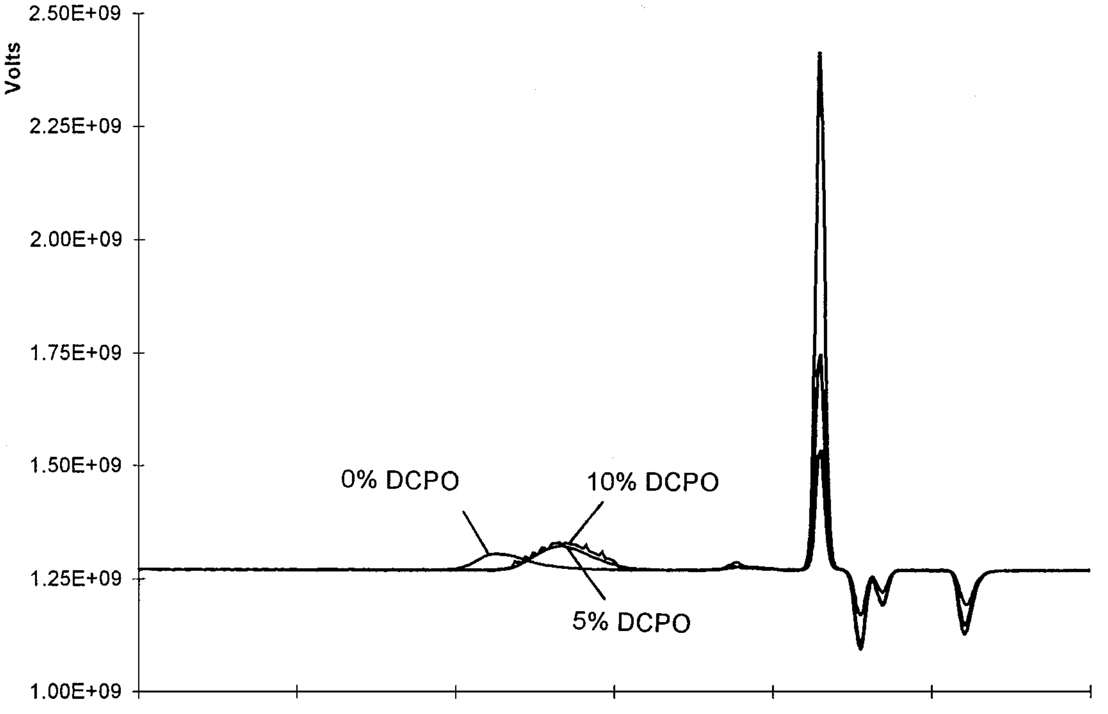


Figure 1 Elution chromatograms of pure PHB and PHB treated with peroxide.

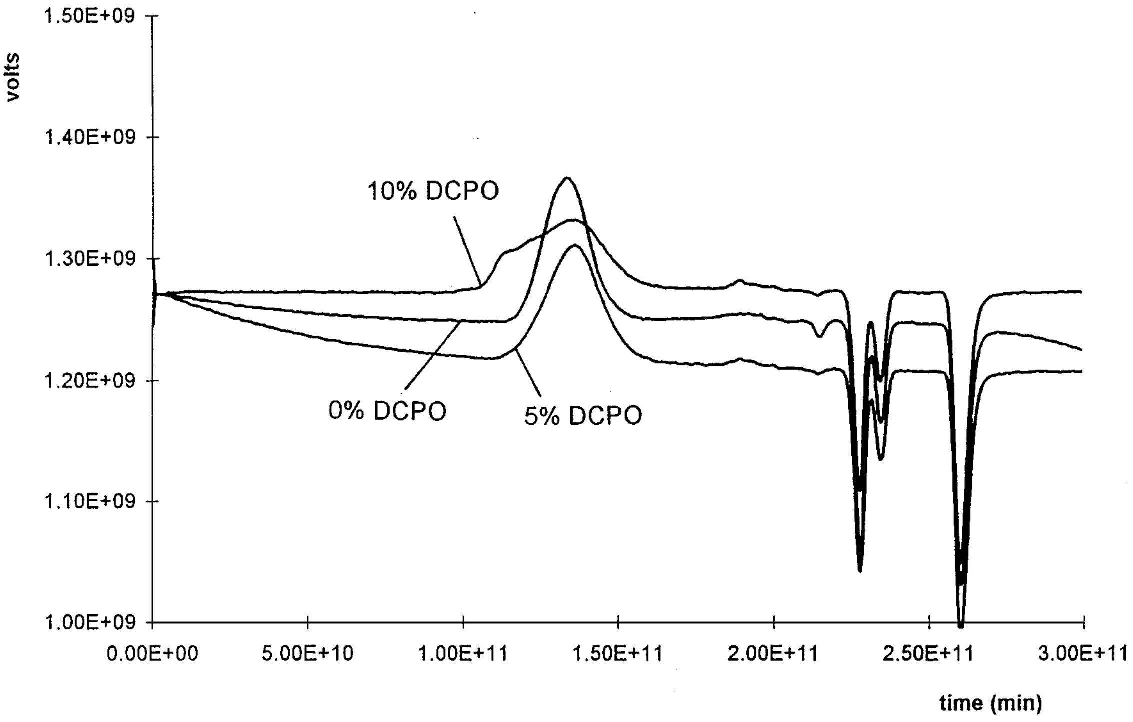


Figure 2 Elution chromatograms of pure PCL and PCL treated with peroxide.

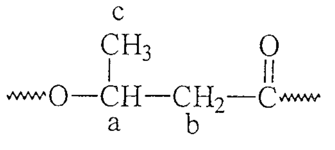
3.3. Structural analysis

To verify possible constitutional changes of polymers upon treatment with peroxide, we have carried out ^1H and ^{13}C nuclear magnetic resonance tests. Chemical shifts are reported in Tables III and IV, for PHB and for PCL, respectively.

Similarity of PCL and PHB spectra before and after peroxide treatment, together with data from viscosity and SEC measures, leads to the following interpretation:

- as far as PHB is concerned, there are no actual modifications in the spectrum in the way of a drop of polymer stereoregoularity;
- again in the case of PHB, we do not notice new chemical shift due to reactions with the peroxides. Hence the peroxide just causes a random scission of PHB backbone chain, similarly to what happens in the melt [18];
- the interaction mechanism between peroxide and PCL is again a chain random scission, then a molecular rearrangement, leading to molecular weight distribution amplification, can take over.

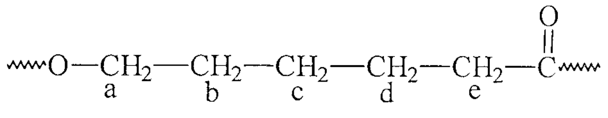
TABLE III Chemical shifts of PHB and PHB 10% DCPO



$$\sim O-\underset{a}{\overset{\overset{c}{CH_3}}{\overset{|}{CH}}}-\underset{b}{CH_2}-\overset{O}{\overset{\|}{C}}\sim$$

Nuclei	^1H (ppm)	^{13}C (ppm)
CH	5.26	67.59
CH_2	2.54	40.79
CH_3	1.28	19.77
C=O		169.09

TABLE IV Chemical shifts of PCL and PCL 10% DCPO



$$\sim O-\underset{a}{CH_2}-\underset{b}{CH_2}-\underset{c}{CH_2}-\underset{d}{CH_2}-\underset{e}{CH_2}-\overset{O}{\overset{\|}{C}}\sim$$

Nuclei	^1H	^{13}C
O–CH_2	4.06	64.11
CH_2–C=O	2.30	34.09
CH_{2b}	1.64	28.33
CH_{2d}	1.64	24.55
CH_{2c}	1.38	25.51
C=O		173.47

3.4. Blends analysis and characterisation

The main goal of the present work was to set up the conditions for the reactive compatibilisation of two very different polymers like PHB and PCL, in order to realise materials fundamentally different from the starting ones, with mechanical properties of wide spectrum and with modoulable degradation kinetics, according to the blend composition and to the peroxide content.

Since the two polymers are immiscible in the amorphous phase, we have attempted a chemical compatibilisation by preparing the blends in presence of organic peroxide, with the aim of develop radical reactions able to form a suitable copolymeric phase properly located at the interface. Chlorobenzene have been used as reaction medium (5% wt/vol overall concentration). For sake of comparison, for most of compatibilised blends, we have prepared the corresponding mechanical ones, that is with no added peroxide.

Blends are listed in the previously reported Table I.

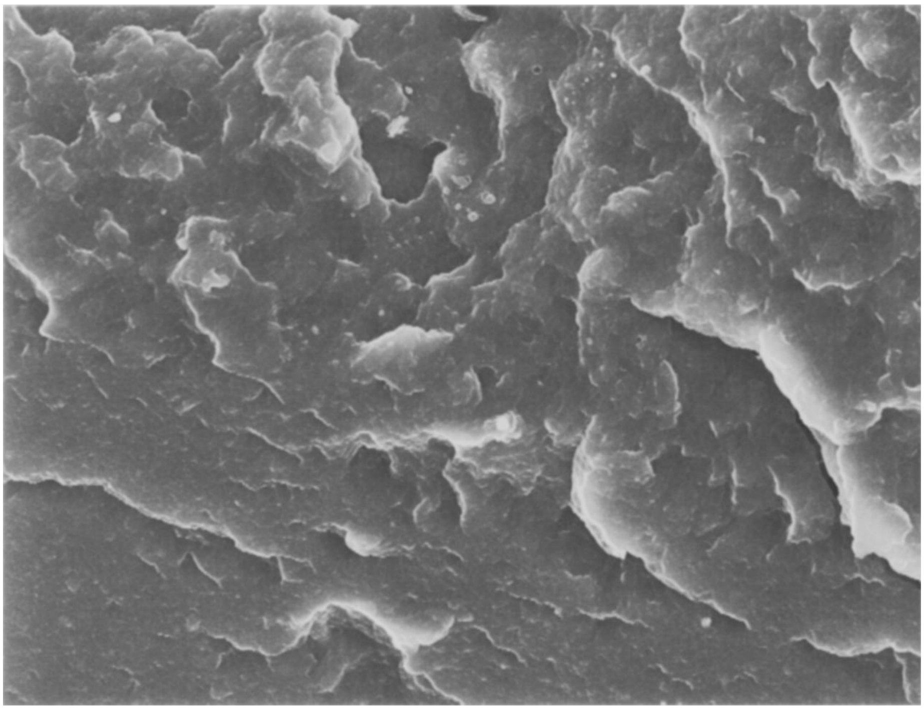


Figure 3 Fracture surface of PHB (500x).

3.5. Morphological analysis

SEM analyses was carried out to gather evidences on mode and state of dispersion of the components of the blends and to establish possible correlation between blends composition and corresponding morphology.

We have analysed fracture surfaces as obtained from the samples used in tensile tests, than the appearance of the surface depends on the deformation undergone by the samples. Furthermore, morphological analysis has been extended to the smoothed surfaces, before and after exposition to vapours of a selective solvent towards one of the phase. The used solvent, THF, is a very good solvent for PCL, while it is not found a solvent selective for PHB.

Homopolymers Fracture surfaces of the two polymers, as observed through electronic microscopy analyses, show very different morphological characteristics. Such analyses were carried out directly on the surface of specimens used for the tensile tests. For PHB, a stiff and rigid material, the fracture surface is sharp, with no evidence of plastic deformations (same observation holds for the specimens treated with peroxide) (Fig. 3). On the contrary, because of its high ductility, PCL samples are very plastically deformed and the micrographs

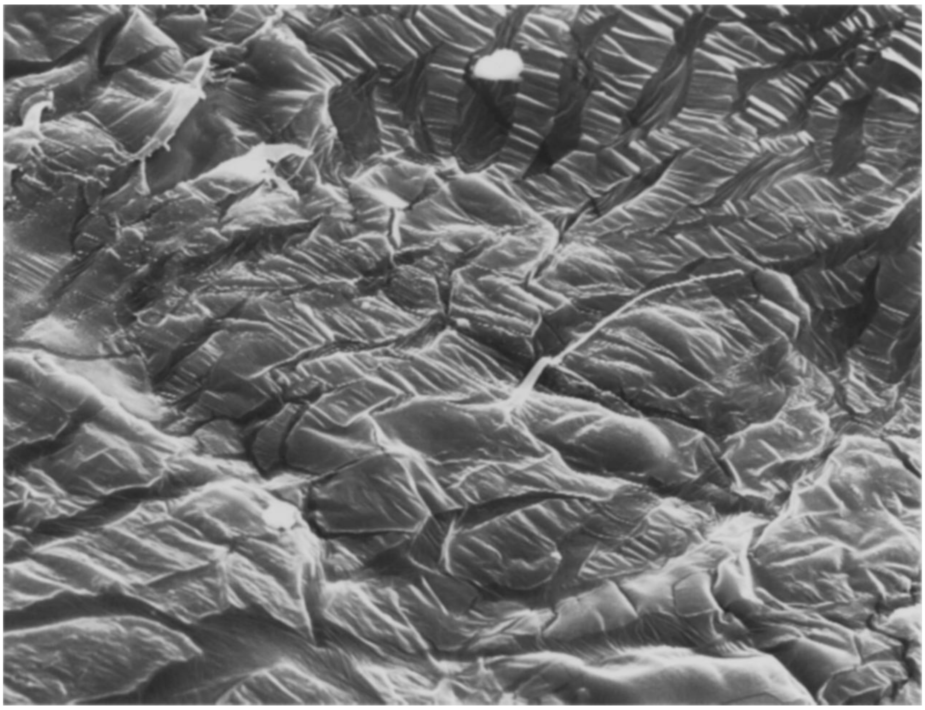


Figure 4 Fracture surface of PCL (500x).

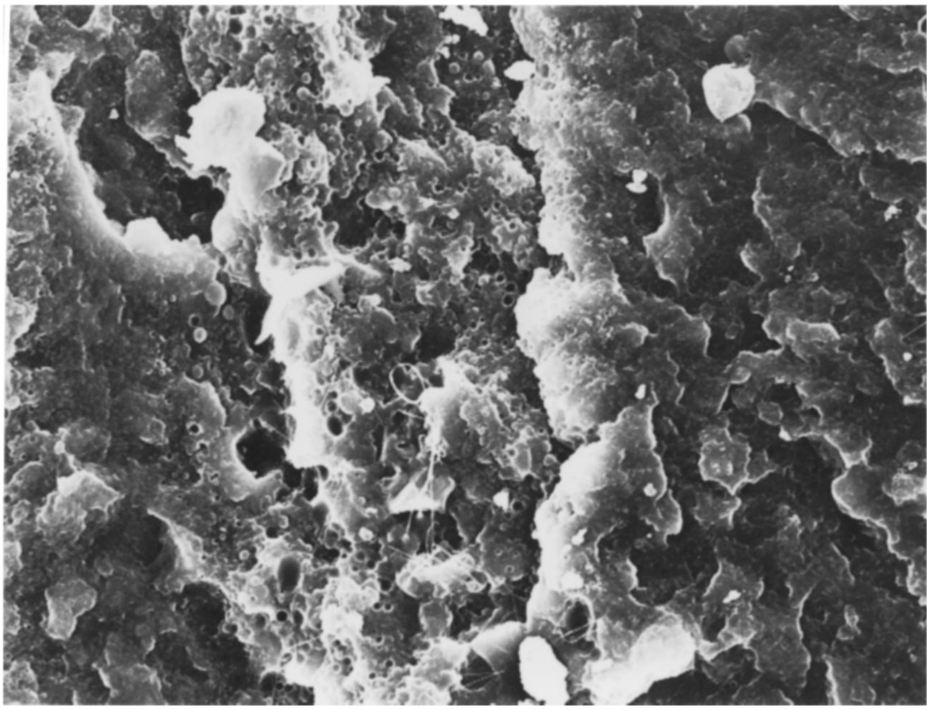


Figure 5 Fracture surface of PHB/PCL 70/30 M (500x).

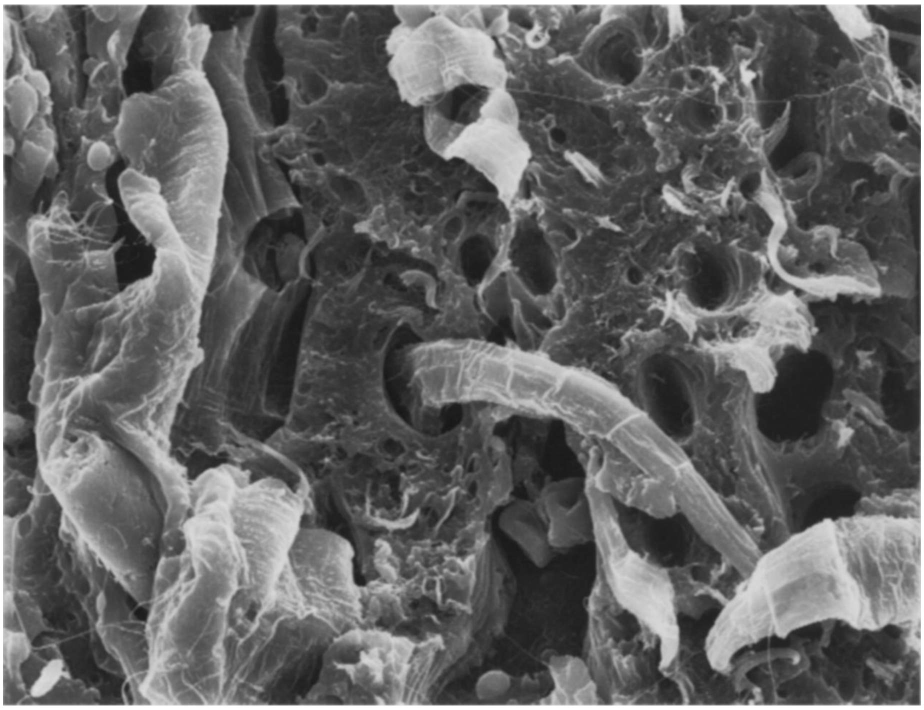


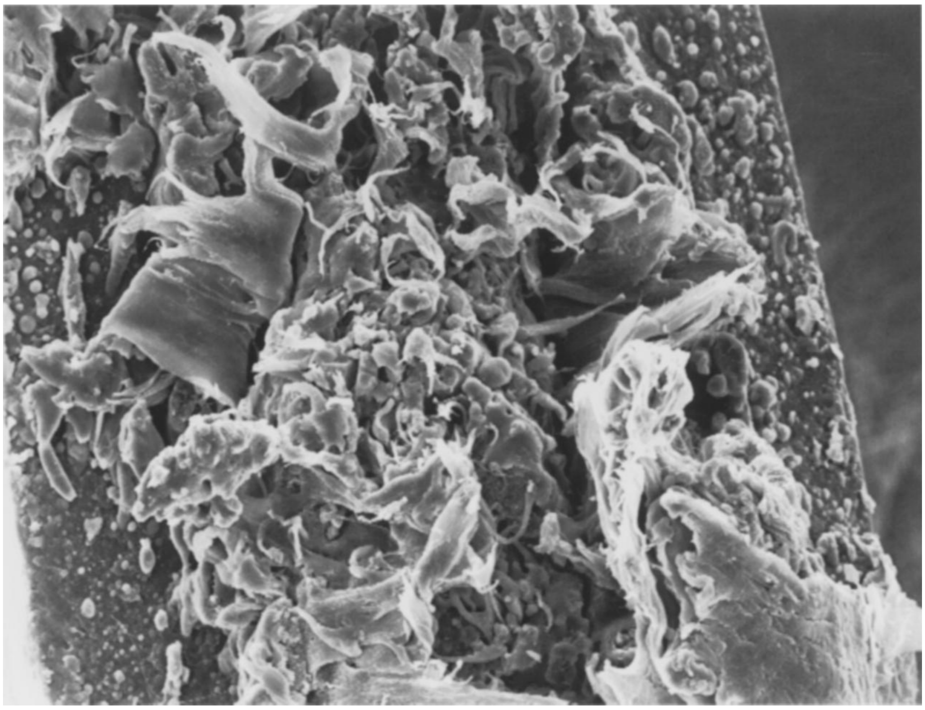
Figure 6 Fracture surface of PHB/PCL 50/50 M (500x).

show fibrous material protruding from the sample surface; similar behaviour is registered for the samples treated with peroxide (Fig. 4).

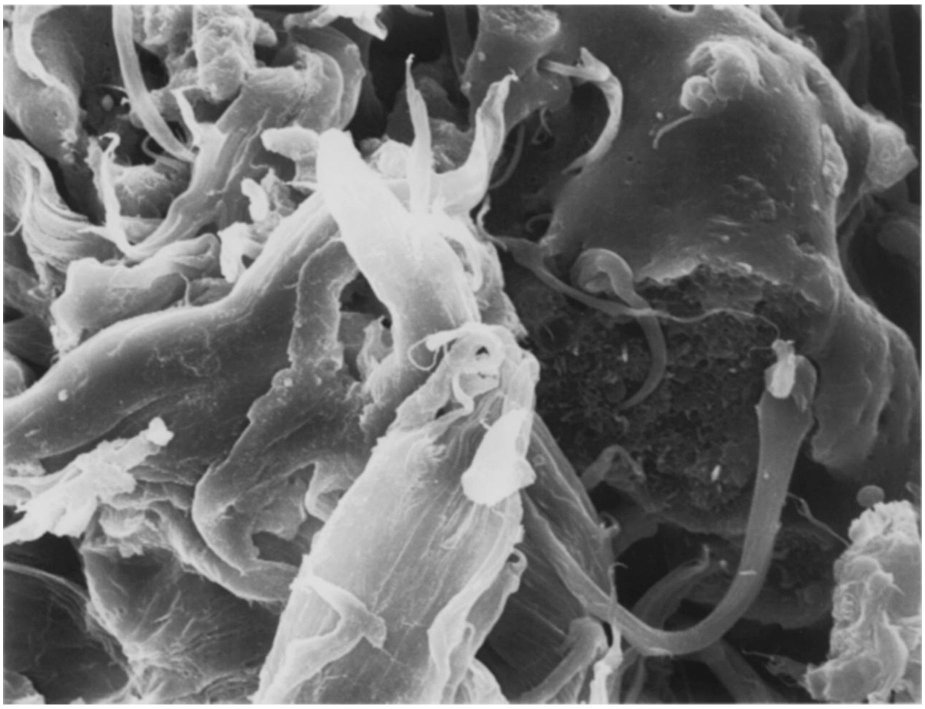
Mechanical blends Tensile fracture surfaces have been analysed from PHB-matrix to PCL-matrix blends. PHB-matrix blend 70/30 M (Fig. 5) shows a fragile fracture, with no evidence of plastic deformation of PCL domains, included as spheres, of about 5 μm size. Plastic deformations of PCL become evident only in the blend 50/50 (Fig. 6), where however they take the shape of elongated cylinders with poor adhesion to PHB-phase, that seems to possess enough continuity to act as matrix.

Strong plastic deformations of PCL can be noticed in the blend 30/70 (Fig. 7a and b). Even though it is present in 70% in weight, PCL actually seems to behave as a dispersed phase in a continuous matrix of PHB. This fact and the lack of adhesion among the phases give account for the poor mechanical tensile properties of the system (see below).

The above observations are confirmed by the analysis of the PHB-matrix blends after extraction of PCL



(a)



(b)

Figure 7 Fracture surface of: (a) PHB/PCL 30/70 M (100x) and (b) PHB/PCL 30/70 M (500x).

with THF. We see how PCL is dispersed phase also for contents of 50% in weight (Fig. 8). In the blend 70/30 (Fig. 9), PCL domains, totally separated from PHB, coexist with domains in which PHB spherulites have incorporated PCL domains during the crystallisation. The reason for the persistence of phase continuity of PHB also for contents of PCL more than 50% can be ascribed to the higher melt viscosity of PHB at the temperature of blends preparation (about 180 °C), while PCL, that melts at about 60 °C, has a much lower viscosity. This kind of result is reported too for other incompatible polymeric systems, and ascribed to similar factors [19].

Blends with 5% of peroxide Analysis of tensile mechanical behaviour, and then of the correspondent morphologies, of the blends treated with peroxide was done till extreme compositions (from PHB-matrix (85/15) to PCL-matrix (15/85) with 5% of peroxide). As general remark, peroxide-treated blends show more homogeneous fracture surfaces than mechanical blends. Particularly evident is the change of the fracture for the blends 50/50 and 30/70; in the former (Fig. 10), PCL domains

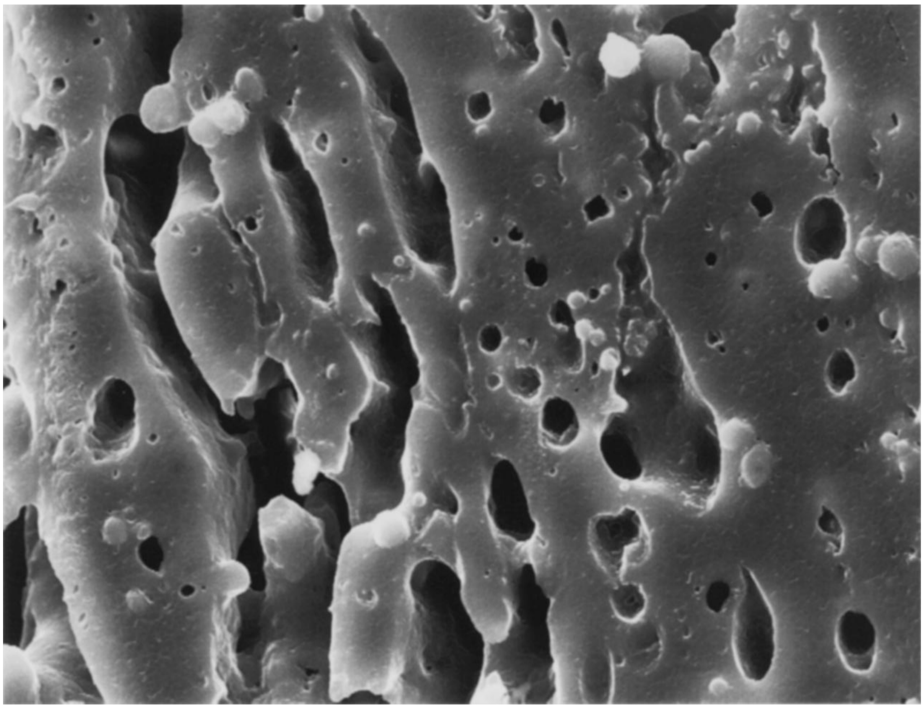


Figure 8 Surface of PHB/PCL 50/50 M after exposition to THF vapours (500x).

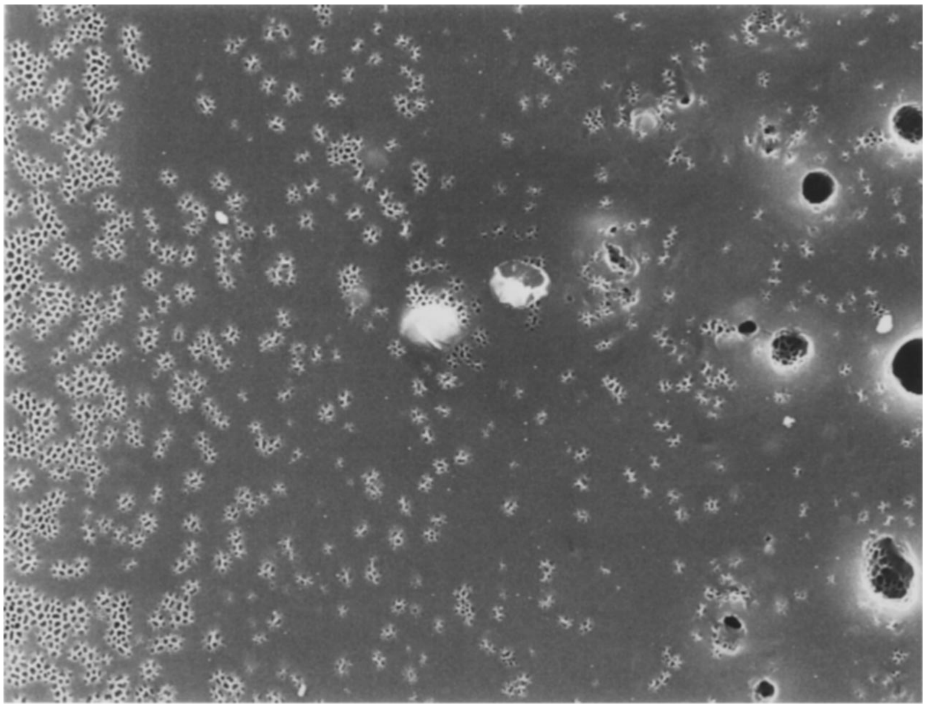


Figure 9 Surface of PHB/PCL 70/30 M after exposition to THF vapours (500x).

are strongly interconnected to PHB giving rise to plastic deformations widespread, even if of short range. In the latter (Fig. 11) the homogeneity of the fracture is such as to make indistinguishable the two phases, being the surfaces characterised by homogeneous plastic aspect.

In the two extreme compositions, the typical aspects of the fracture of the two matrices prevail, fragile the blend 85/15 (Fig. 12), very fibrous the blend 15/85 (Fig. 13). Extraction with THF of the PCL-phase shows the intrinsic morphology of the compatibilised blends. The more salient aspects of such analysis, for comparison with mechanical blends, are the following:

- at same composition, dimensions of dispersed phases, usually PCL, are reduced;
- PCL extraction, for same time of exposition to THF, is more problematic. Particularly, blend 50/50 (Fig. 14) shows elevated concentrations of microdomains strongly adherent to PHB surfaces, together with homo-polymeric phase of PCL;

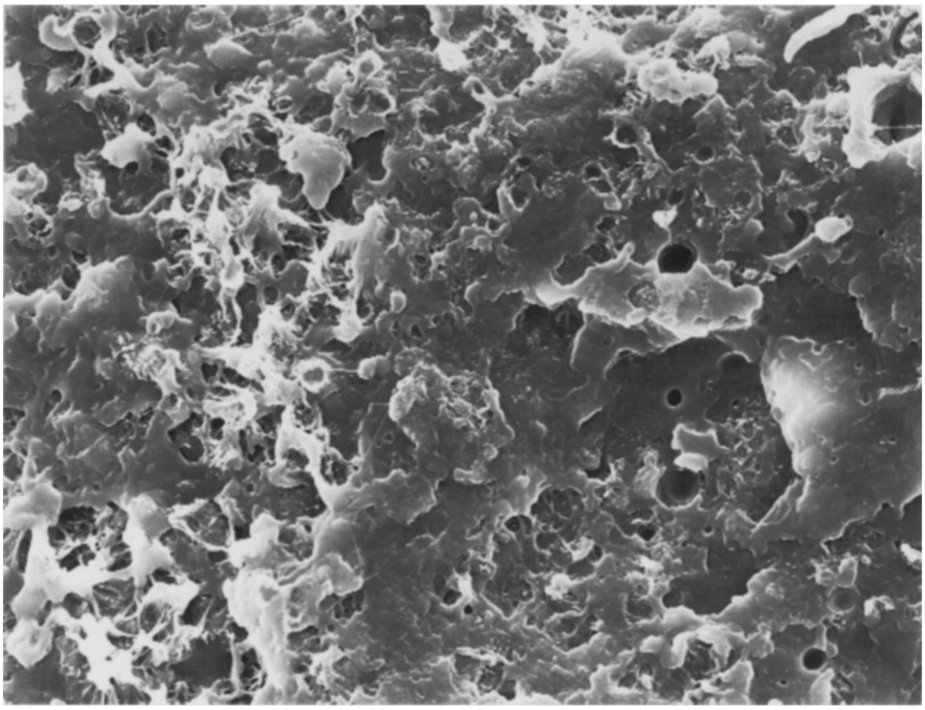


Figure 10 Fracture surface of PHB/PCL 50/50 P5 (500x).

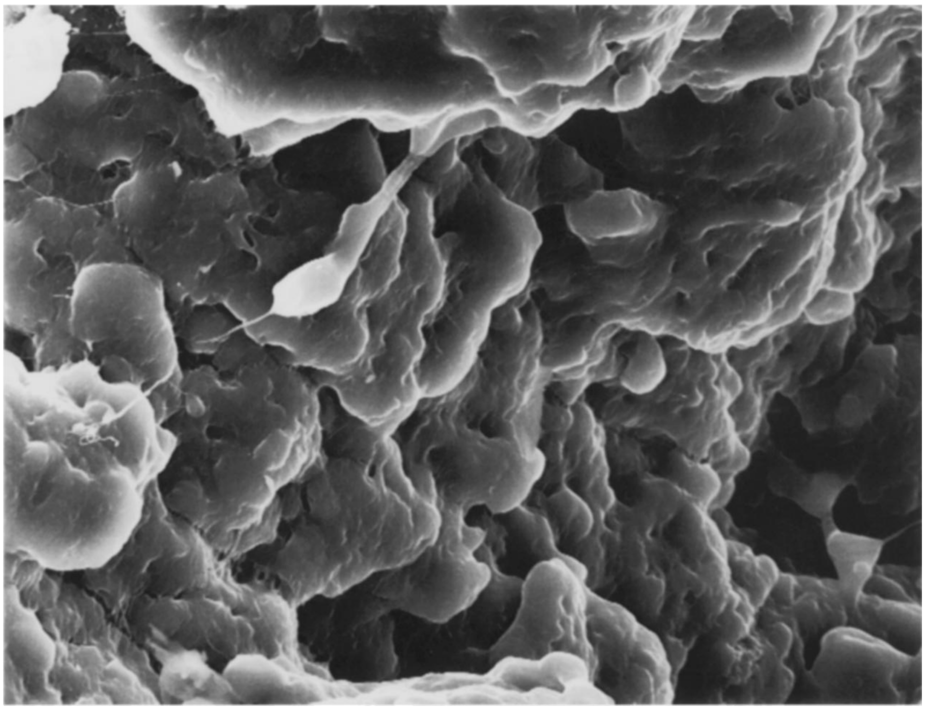


Figure 11 Fracture surface of PHB/PCL 30/70 P5 (500x).

domains of dimension between 5 and 15 μm, extracted by the solvent, are found.

3.6. Mechanical properties

Data from stress-strain trials carried out on the homopolymers and blends are shown in Table V.

The samples used for tensile tests were prepared by compression molding. In the case of PHB, a particular procedure is necessary in order to be sure that the equilibrium state is achieved, i.e., after molding, the sheets are left for at least 600 h to room temperature. The most relevant effect of the addition of peroxide to homopolymers is that the mechanical response of material not change dramatically. The changes are in agreement with molecular characterisation data, that show a trend to degradation for PHB and a simple rearrangement for PCL.

Mechanical behaviour of PHB and PCL is extremely different: PHB indeed shows a fragile fracture while

TABLE V Tensile mechanical properties

Samples	Young's modulus (MPa)	% Strain to yield point	Stress to yield point (MPa)	% Strain at break	Stress at break (MPa)
PHB	2452	—	—	1.44	14.10
PHB P5	—	—	—	1.99	28.75
PHB P10	—	—	—	1.23	19.22
PHBPCL85/15 5P	2099	—	—	2.64	13.26
PHBPCL70/30					
M	1920	—	—	1.35	11.25
P5	1717	—	—	2.49	13.10
P10	1842	—	—	1.64	13.66
PHBPCL50/50					
M	1379	—	—	2.77	9.47
P5	1320	—	—	3.89	11.16
P10	1318	—	—	5.48	11.70
PHBPCL37/63 P5	942	5.49	14.14	75.04	4.80
PHBPCL30/70					
M	828	—	—	4.33	5.68
P5	756	5.67	13.30	371.90	10.21
P10	919	—	—	6.46	9.60
PHBPCL15/85 P5	373	9.10	9.84	943.10[a]	26.36[b]
PCL	329	10.93	12.28	1192.0[a]	29.39[b]
PCL P5	340	9.79	11.23	848.0[a]	22.61[b]
PCL P10	329	11.00	12.73	786.0[a]	23.35[b]

[a] Not recorded since the specimen does not break; it is reported the value at maximum strain.

[b] As the specimen does not break, we mean the stress recorded at maximum deformation point.

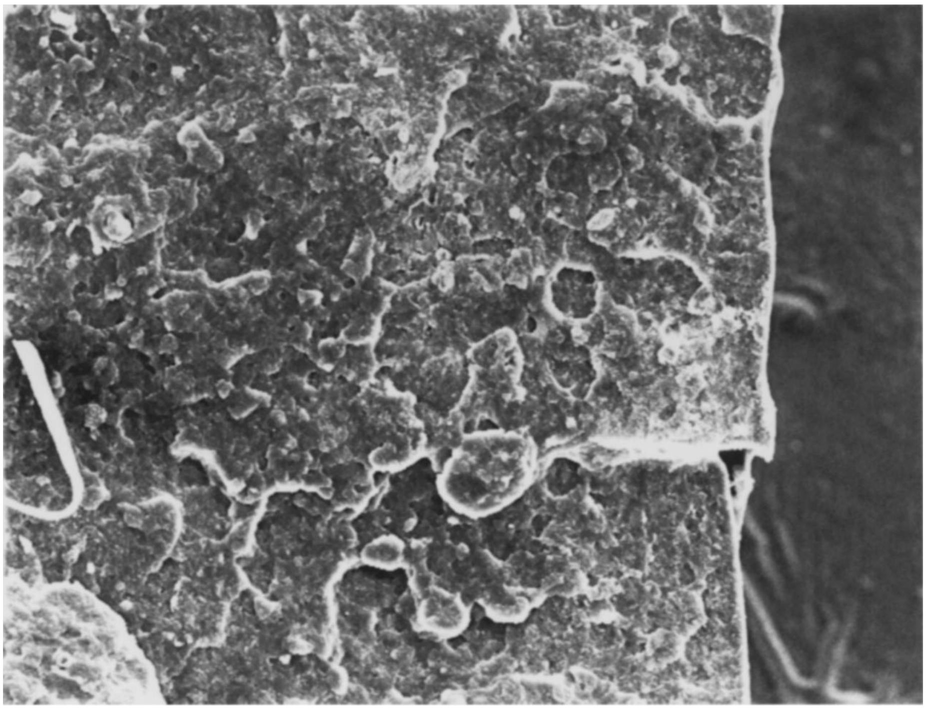


Figure 12 Fracture surface of PHB/PCL 85/15 P5 (100x).

PCL is a very ductile material and the stress-strain curve displays large necking region followed by full fibre orientation.

For the blends, curve outline changes according to which of the two polymers is working as the matrix. We have recorded necking formation only for the blends in which PCL characteristics prevail. Analysis of the mechanical properties has shown a substantial agreement with the morphologies found in the blends, that is mostly an improvement of some parameters, like yield stress and the correspondent stress at break in the blends with 5% of peroxide as to the correspondent mechanical one. This effect becomes particularly evident for the blend PHB/PCL 30/70 P5, in which the strain at break increases of two orders; this behaviour is even more clear in the correspondent stress-strain diagram (Figs 15 and 16).

Mechanical properties of the blends treated with 10% of peroxide have a less regular behaviour, probably because of the degradative modifications of the homopolymers contained in the blends.

Figs 17 and 18 show, respectively, the trends of the Young's Modulus and the stress at break as function of content of PHB in compatibilised blends with 5%

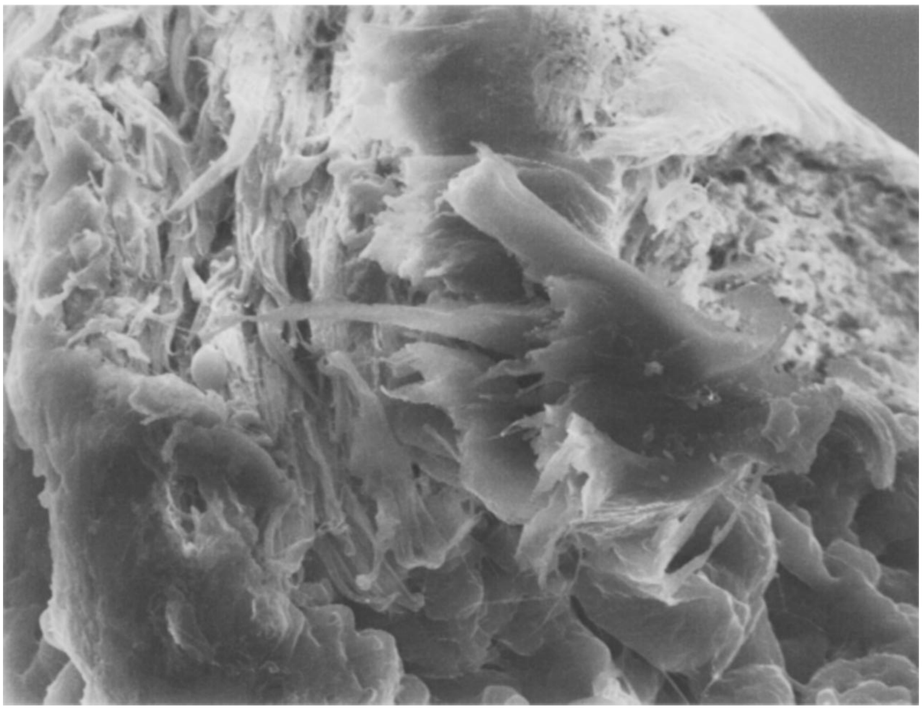


Figure 13 Fracture surface of PHB/PCL 15/85 P5 (100x).

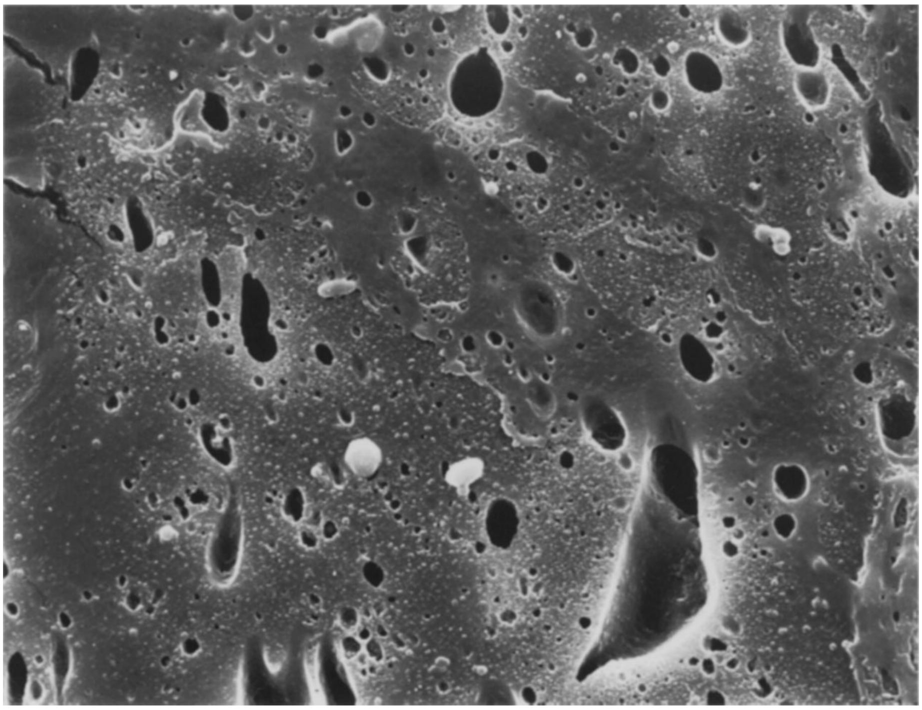


Figure 14 Surface of PHB/PCL 50/50 P5 after exposition to THF vapours (500).

of peroxide. As a matter of fact, the treatment with peroxide, and, hence, the formation of a graft copolymer, helps the system in two ways: first of all, we have a continuous PCL-matrix and, secondly, the PHB phase is regularly distributed and finely dispersed. Following this, the material displays finally the behaviour of a stiffer but ductile PCL matrix blend with regular inclusions.

This prove the assumption that, with procedures of reactive mixing of different polymers, we can prepare materials versatile in mechanical properties and with tailored end uses.

3.7. Characterisation of PHB-g-PCL copolymer

The main assumption of the present work is that the phase behaviour of PHB/PCL blends obtained in the presence of an organic peroxide is different from that of simple physical blends due to the formation of graft

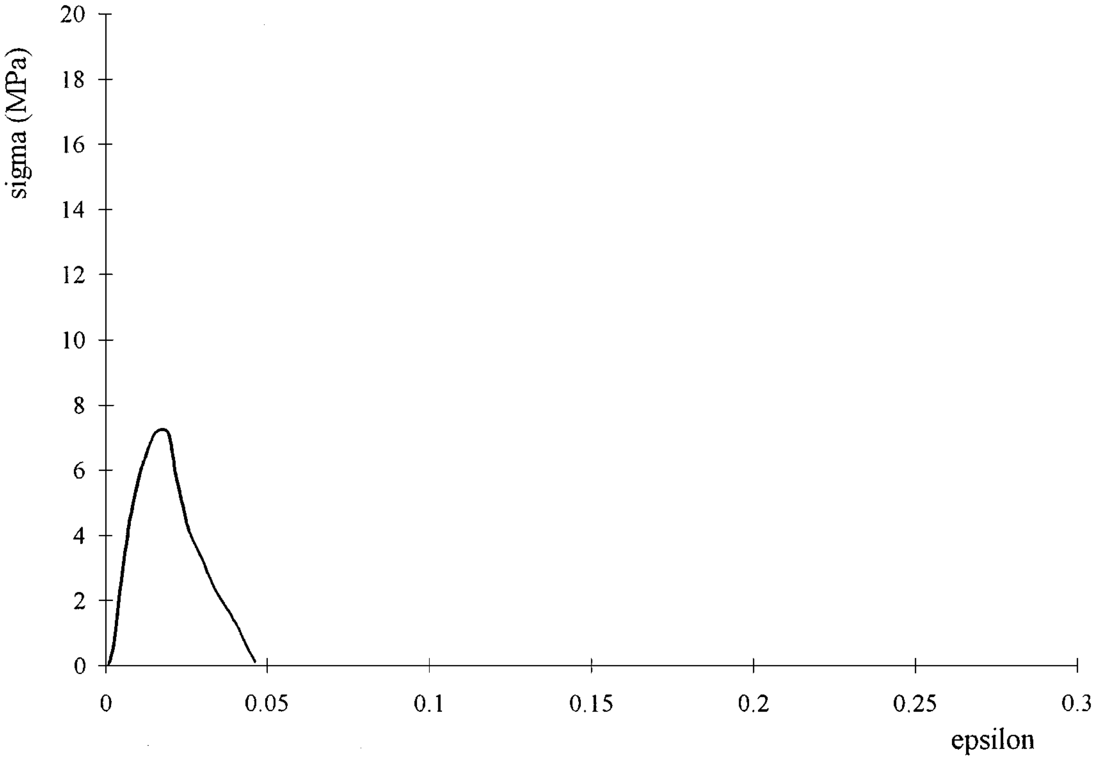


Figure 15 Stress-strain diagram of PHB/PCL 30/70 M.

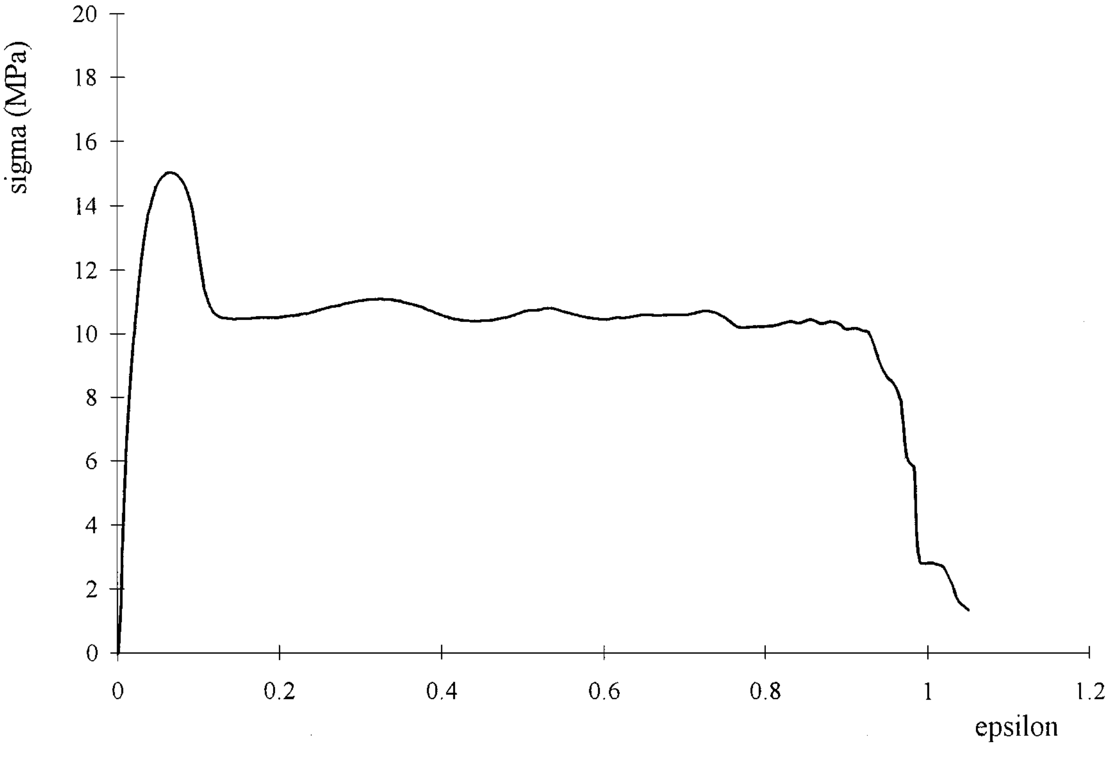


Figure 16 Stress-strain diagram of PHB/PCL 30/70 P5.

copolymers species. The existence of such species has been proved in previous papers, where the same blends were obtained by melt mixing [14]. It was noted that the fundamental chemical-physical characteristics of the blends remain unchanged. This is also the case of the present system. Particularly the thermal behaviour of peroxide treated blend does not differ from that of not treated blend. In the present experimental conditions, however, i.e., in diluted solution, it is not straightforward to extrapolate that a graft copolymer can form. So we have approached a selective solvent extraction of a PHB/PCL blend and the recovered species (average amount 5% of charged blend) have been analysed by DSC and NMR. DSC spectra (Figs 19a and b) show the presence of a double melting peak corresponding to that of PCL and PHB (PCL homopolymer $T_m = 58.6\,^{\circ}\mathrm{C}$, PHB homopolymer $T_m = 174.5\,^{\circ}\mathrm{C}$). A preliminary NMR investigation confirm that such

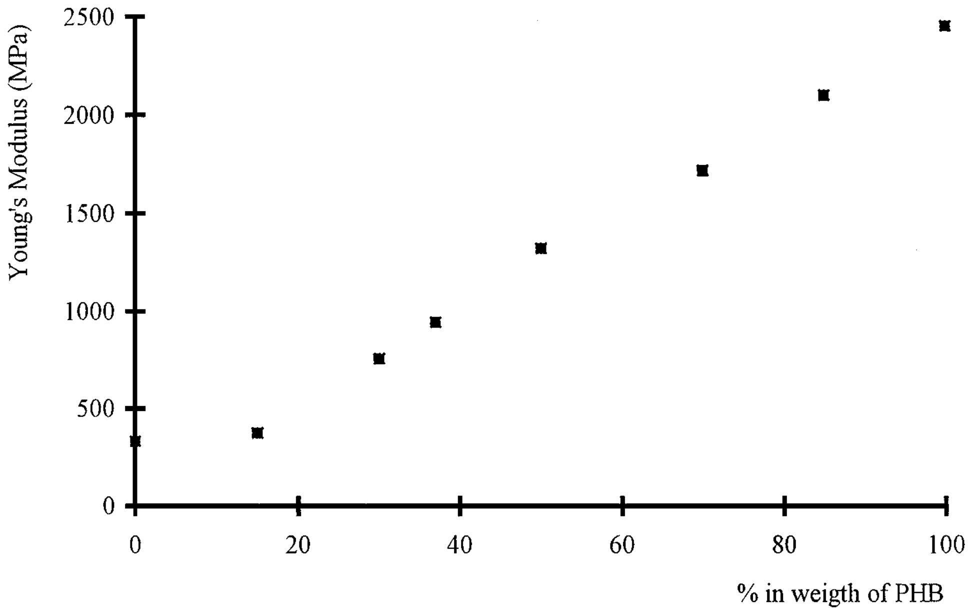


Figure 17 Young’s modulus as function of % of PHB.

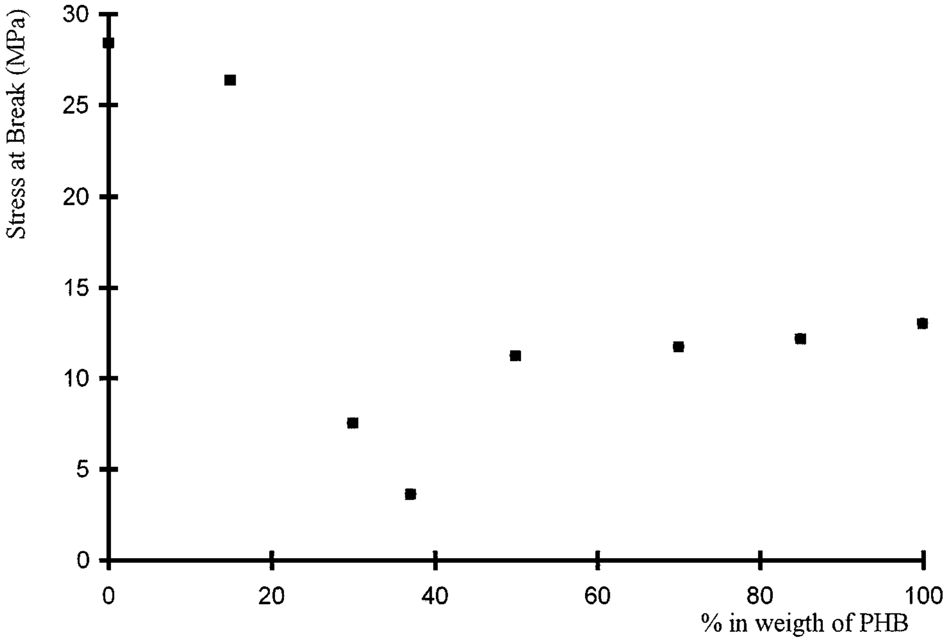


Figure 18 Stress at break as function of % of PHB.

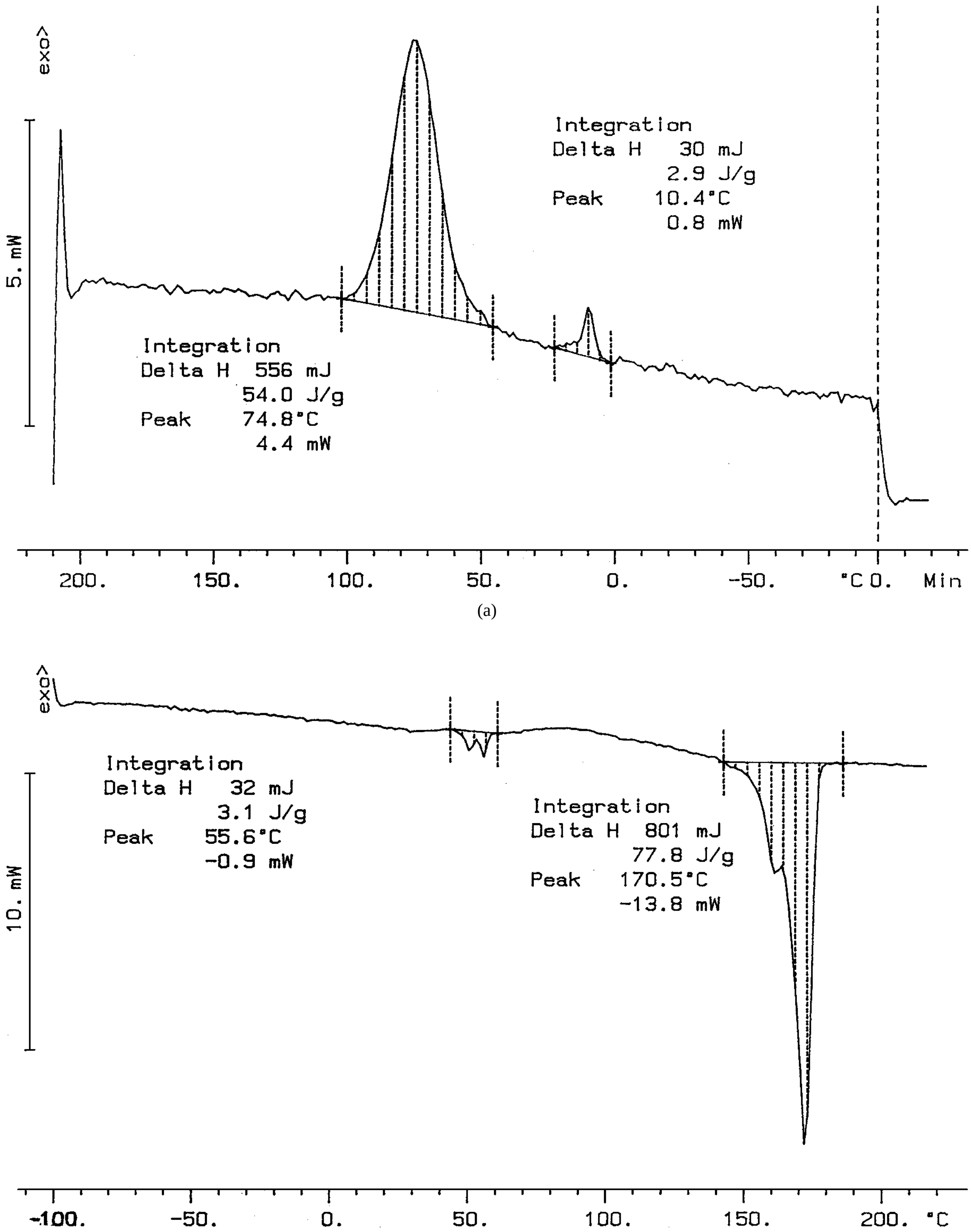
phase is constituted by grafted species containing both PHB and PCL segments, linked through a covalent bond between the tertiary C atom of PHB and one of the methylenic group –CH_2– of PCL. It is our intention in a forthcoming paper to report a more quantitative evaluation of the chemical composition of the obtained copolymer.

4. Conclusion

The preparation of multicomponent polymeric materials based on PCL and PHB was carried out using reactive blending processes in solution in presence of organic peroxide. The experimental procedure does not alter in dramatic way the homopolymers properties, molecular and structural, chemical-physical and mechanical, at least for peroxide content of 5% or below.

The interfacial agent formed by radical reactions initiated by peroxides exerts a compatibilizing action towards mixed polyesters, improving dispersion degree of the component and, at selected percentages, mechanical properties compared to the corresponding mechanical blends.

In the compatibilised blends, mechanical properties and morphology change with respect to the composition: in PHB-matrix blends, growing quantities of PCL improve plasticity of the material; in PCL-matrix blends, PHB contributes to increase tensile strength. The effect of the compatibilizer on mechanical properties becomes evident from the comparison between the



(a)

(b)

Figure 19 DSC thermograms of the copolymeric phase extracted by PHB/PCL compatibilised blend: (a) quenched and (b) second heating run (for details, see Section 2).

compatibilised blends and the mechanical ones, particularly for the composition PHB/PCL 30/70 M.

Biodegradability tests are being effected. Preliminary results seem to indicate that biodegradability in blends is maintained, although the kinetic is influenced by internal morphology.

Obtained data seems to show it is possible to prepare materials with programmed characteristics, that can be used for tailored purposes in biomedical and industrial field, by means of reactive blending methodologies.

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