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Reactive processing – property relationships in biodegradable blends useful for prosthesis application

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Reaction injection moulding of blend samples of poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (PHBV) and poly-ε-caprolactone (PCL) has been performed in the presence of peroxide. The blends are compared to mechanical PHBV/PCL blends obtained in the absence of peroxides. Differences in chemical–physical and mechanical properties are interpreted on the basis of intergrafted species present in the peroxide-treated blends. The obtained blends are proposed as versatile materials for applications for bioresorbable prostheses.

1. Introduction

Biocompatible and/or biodegradable polymer-based materials have been achieved in the last years with good clinical success in the internal fixation and stabilization of bone fractures [1–3].

The reabsorbable fixation device eliminates the need to remove the osteosynthesis materials with operation after the fracture has healed. The polymeric prosthesis must have the following properties: appropriate chemical and physical structures to satisfy the desirable useful life time in the body; absence of contaminant substance; possibility of being sterilized. Moreover, the polymers must not induce tumour formation, thrombus formation or inflammation in the surrounding tissues. All these requirements greatly reduce the number of polymers which are potential candidates for biomedical applications.

The purpose of the present study was to investigate the possibility of using novel polymeric blends as prostheses for implants. The proposed blends have been presented in previous works and are constituted by poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (PHBV) and polycaprolactone (PCL) polymers [4–5].

PHBV and PCL have been chosen because they are known to be biocompatible and biodegradable polymers [6–8]. Moreover, the two polymers possess different chemical–physical properties. Namely, PHBV is a high melting, relatively high glass transition temperature (T_g), stiff polymer, while PCL is a low melting, low T_g, very ductile material. PCL cannot be used for applications where there is a need of autoclaving of articles, as its melting temperature of about 60 °C prevents such a sterilization approach. The material resulting from blending operations might reach an optimal matching of morphological and mechanical properties particularly by using the "reactive blending technique" proposed by us [9–10]. Reactive blending might also affect the autoclavage ability of PCL.

In a previous paper [4], we described an approach to reactive blending, where the two polymers are reactively mixed in a mixing chamber of a Brabender-type apparatus, in the presence of peroxide. Upon thermal decomposition, peroxide originates radicals able to create bridges between the polymers by means of interchain cross-links formation. Two types of peroxides were used, namely dibenzoylperoxide (DBPO) and dicumylperoxide (DCPO), differing in the decomposition temperature. We have proved that the best results in terms of chemical interaction at interfacial level are obtained with DCPO, which decomposes during blend processing [4].

A drawback of such method was that the blends became less mouldable after peroxide decomposition, as consequence of the said chemical bridges between the homopolymer chains. In the present paper, we report on a modification of the above method, in which a pre-mixing step at lower temperatures is effected followed by the true melt blending. The peroxide then decomposes during final injection of the blend into a mould, to get the finished article. Morphological, structural, thermal and mechanical investigations are reported.

2. Experimental procedure

2.1. Materials

Polycaprolactone (PCL), trademark CAPA 650, was kindly supplied by Solvay (Belgium) with a reported

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M_w of 50 000. Poly(β-hydroxybutyrate-co-β-hydroxyvalerate) (PHBV) was kindly supplied by ICI (UK) and is reported to be a high molecular weight polymer ($M_w > 500\,000$) with a valerate content of 4 mol %. Dicumilperoxide (DCPO) was used as received.

2.2. Procedure of blend preparation

2.2.1. Reactive blending procedure

Following this methodology, blend components (PCL pellets and PHBV powder) are mixed in the proper ratio in the presence of DCPO (0.5 wt % of total blend weight) in the chamber of a Haake Rheocord at a mixer roller speed of 32 r.p.m. for 10 min at 100 °C. In such conditions, no decomposition of DCPO occurs, as verified by differential scanning calorimetry (DSC) analysis. After preparation, the mixture was quenched by a stream of compressed air.

It must be pointed out that the physical state of the blends at the end of such an homogenization step depends on the composition: PCL-based blends become macroscopically homogeneous, as the matrix polymer melts at around 65 °C, so the mixture needs to be re-pelletized before the next step. On the other hand, PHBV-based blends maintain a powder shape and can be directly processed.

The mixture was successively melt injected into a cylindrical mould to get rod-shaped specimens. The processing equipment is a home-made apparatus which essentially consists of a heating chamber where melting of premixed polymers occurs. Then a piston injects the materials into a multi-arm jacketed steel mould. The rods were used for all characterizations. The duration and temperature of injection moulding was chosen in order to assure the complete decomposition of peroxide. A typical processing cycle is as follows:

- heating from 30 °C to 170 °C in 25 min,
- holding at 170 °C for 5 min,
- cooling from 170 °C to 30 °C in 2 min.

2.2.2. Mechanical blending procedure

Blends, in the absence of DCPO, were prepared following exactly the same procedure as above. Table I shows a summary of the prepared blends. The codes include the blend composition (weight ratio on a basis of ten) and a letter which indicates whether the blends are prepared in absence (M) or in presence (P) of 0.5 wt % of DCPO.

TABLE I Summary of prepared blends

Sample	PHBV (wt %)	PCL (wt %)
PHBV P	100	–
PHBV M	100	–
PHBVPCL 91 P	90	10
PHBVPCL 91 M	90	10
PHBVPCL 73 P	70	30
PHBVPCL 73 M	70	30
PHBVPCL 55 P	50	50
PHBVPCL 55 M	50	50
PHBVPCL 37 P	30	70
PHBVPCL 37 M	30	70
PHBVPCL 19 P	10	90
PHBVPCL 19 M	10	90
PCL P	–	100
PCL M	–	100

2.2.3. Techniques

Differential thermal analysis was carried out by using a Mettler TC 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 rate of 10 °C min^{-1}, cooled at the same rate down to −100 °C and re-heated to 200 °C at 10 °C min^{-1}. In the second experiment, settled to visualize the glass transition temperature, the sample was heated from room temperature to 200 °C at 20 °C min^{-1}, quenched down to −100 °C and reheated to 200 °C at 20 °C min^{-1}.

Morphological characterization was performed on a Philips scanning electron microscope (SEM) 501; the samples of blends were smoothed with a LKB Ultramicrotome by means of a glass knife and etched with tetrahydrofuran (THF) vapour in order to remove the PCL phase.

Three-point bending specimens were used to perform flexural tests. The measurements were carried out on an Instron Apparatus, model 1122, at room temperature at a cross-head speed of 10 mm min^{-1}. Cylindrical samples 7.5 cm long and 3 mm wide were used.

3. Results and discussion

In a previous work [4], we have discussed the reactive blending of PCL and PHBV in a static mixer by means of the addition of peroxides. Intergrafted species are formed during the radical process responsible of relevant modifications in the morphology and in the mechanical properties. In fact similar blends obtained by mixing the two polymers without any peroxide added show very poor mechanical properties. The most severe limitation to a technological development of the process is the increased melt viscosity of the blends caused by the partial cross-link upon peroxide decomposition.

In order to avoid such a problem we used, in this study, a different processing procedure. In fact the blend components are premixed in the presence of peroxide in the mixing chamber of the Rheocord at a temperature below the temperature of peroxide decomposition. As stated in Section 2, the physical state of the blends at the end of the pre-homogenization step depend upon the blend composition. Successively, the premixed powder is melt-injected by a piston into a multiple mould to obtain the final desired shape of the prosthesis (in the present case, cylindrical rods). As matter of fact, we can assimilate the present methodology to a RIM (reactive injection moulding) process.

For comparative purpose the homologous blends have been prepared in the absence of peroxide according to same procedure.

All the characterizations which follow were performed on the final rods.

3.1. Thermal analysis

Two different experiments were designed to separately analyse the melting process and the glass transition. For melting, slow heating (I Run) followed by slow crystallization and second heating (II Run) were effected. Instead, to study the behaviour of glass transition temperature (T_g) two heating runs were performed at 20 °C min^{-1} with a very fast quenching stage between them.

The results on glass transition temperature (T_g) are reported in Table II. In this table, only the behaviour of peroxide-treated blends are shown, as no relevant differences are recorded for the mechanical blends.

The T_gs of minor components were not detectable in 90/10 and 10/90 blends. For the other blends, we can observe that the glass transitions of PHBV and PCL remain practically constant in the presence of the other component. This indicates, in our opinion, that the two polymers are essentially immiscible and that the chemical interaction, which occurs at the interfacial level, involves a minor portion of the blend components.

The influence of peroxide on melting behaviour is reported in Table III. The values of melting temperature (T_m) are taken from the first runs, due to the low crystallization rate of PHBV. While no regular trend is observed for mechanical blends (not reported), the melting temperature of PHBV stays almost constant and the melting temperature of PCL increases at very low content of PHBV (possibly as consequence of nucleation) and progressively decreases at higher content of PHBV, until reaches a value similar to plain PCL P.

TABLE II Glass transition temperature (T_g) of PHBV/PCL peroxide-treated blends and homopolymers (see text for details)

Sample	$T_{g\,\mathrm{PHBV}}$ (°C)	$T_{g\,\mathrm{PCL}}$ (°C)
PHBV P	0.6	–
PHBVPCL 91 P	0.6	– 55
PHBVPCL 73 P	0.4	– 55
PHBVPCL 55 P	1.6	– 55.4
PHBVPCL 37 P	1.9	– 55.2
PHBVPCL 19 P	–	– 55.6
PCL P	–	– 59.4

TABLE III Melting temperature of PHBV/PCL peroxide-treated blend and homopolymers (see text for details)

Sample	$T_{m\,\mathrm{PCL}}$ (°C)	$T_{m\,\mathrm{PHBV}}$ (°C)
PHBV P	–	164.3
PHBV7PCL 90/10 P	–	162.7
PHBV/PCL 70/30 P	66.6	165.9
PHBV/PCL 50/50 P	67.5	159.6
PHBV/PCL 30/70 P	69.5	162.0
PHBV/PCL 10/90 P	70.2	163.5
PCL P	66.4	–

3.2. Morphological analysis

SEM analysis has been effected to investigate mode and state of dispersion of components in mechanical as well as peroxide-treated blends. Prior to investigation, the surface of specimen blends and homopolymers have been smoothed at the microtome. Moreover, PHBV–matrix blends have been treated with boiling THF, which is able to etch away the PCL dispersed phase. No etching was effected on PCL-based blends, as no solvent is selective for PHBV. For this last blend, the analysis is nevertheless effected on the simply smoothed surfaces. We have in fact reported in a previous paper that, when the blend components have very different physical state (as, for example, a rubber dispersed in a rigid thermoplastic) the stresses exerted by the knife during smoothing applies differently on the two materials [11]. Hence, in this and similar favourable situations, the smoothing process by itself gives morphological information. In our case, PHBV dispersed particles are considerably more rigid than PCL matrix and they become quite evident after smoothing process. SEM micrographs of smoothed surfaces of PHBV and PCL treated and non-treated with peroxide are reported in Fig. 1. All the surfaces are featureless. PHBVPCL 91 M blend before and after solvent extraction are reported in Fig. 2. The already apparent PCL-dispersed phase (upon the action of knife) become more clear after removal with THF. The dispersed phase forms irregularly shaped domains of dimensions ranging from less than 1 μm to 3–4 μm. The state of dispersion seems to be rather fine. Upon the solidification of PHBV, PCL is confined in relatively small domains.

SEM micrographs of PHBVPCL 91 P blend before and after THF treatment are reported in Fig. 3. The PCL phase is dispersed in sub-micronic spherical domains. They are almost unextractable by THF and this is, in our opinion, one of the clearest proofs of the presence of intermolecular links between PHBV and PCL polymers, which in turn determine the size reduction of PCL phase.

In the case of PHBVPCL 73 M blend, smoothing process already develops a blend morphology characterized by large PCL domains (Fig. 4a). Upon etching, the morphology is revealed in full details (Fig. 4b). PCL phase is distributed in domains of irregular shape whose dimension ranges from about 1 μm (few) to 10 μm or more. The SEM surface of PHBVPCL 73 P blend, (see Fig. 5), shows a much more complicated morphology. After etching, a regular distribution of PCL domains is found, with dimensions of about 1 μm or less. The PHBV phase, which should represent the matrix of the blend, is divided into two fractions: one is the effective matrix into which the PCL phase is embedded, the other is in the shape of large (10 ÷ 30 μm) spherical domains dispersed in the two component interconnected matrix. Inside this domains there is no evidence of PCL dispersed phase. Moreover, they show phase continuity with the

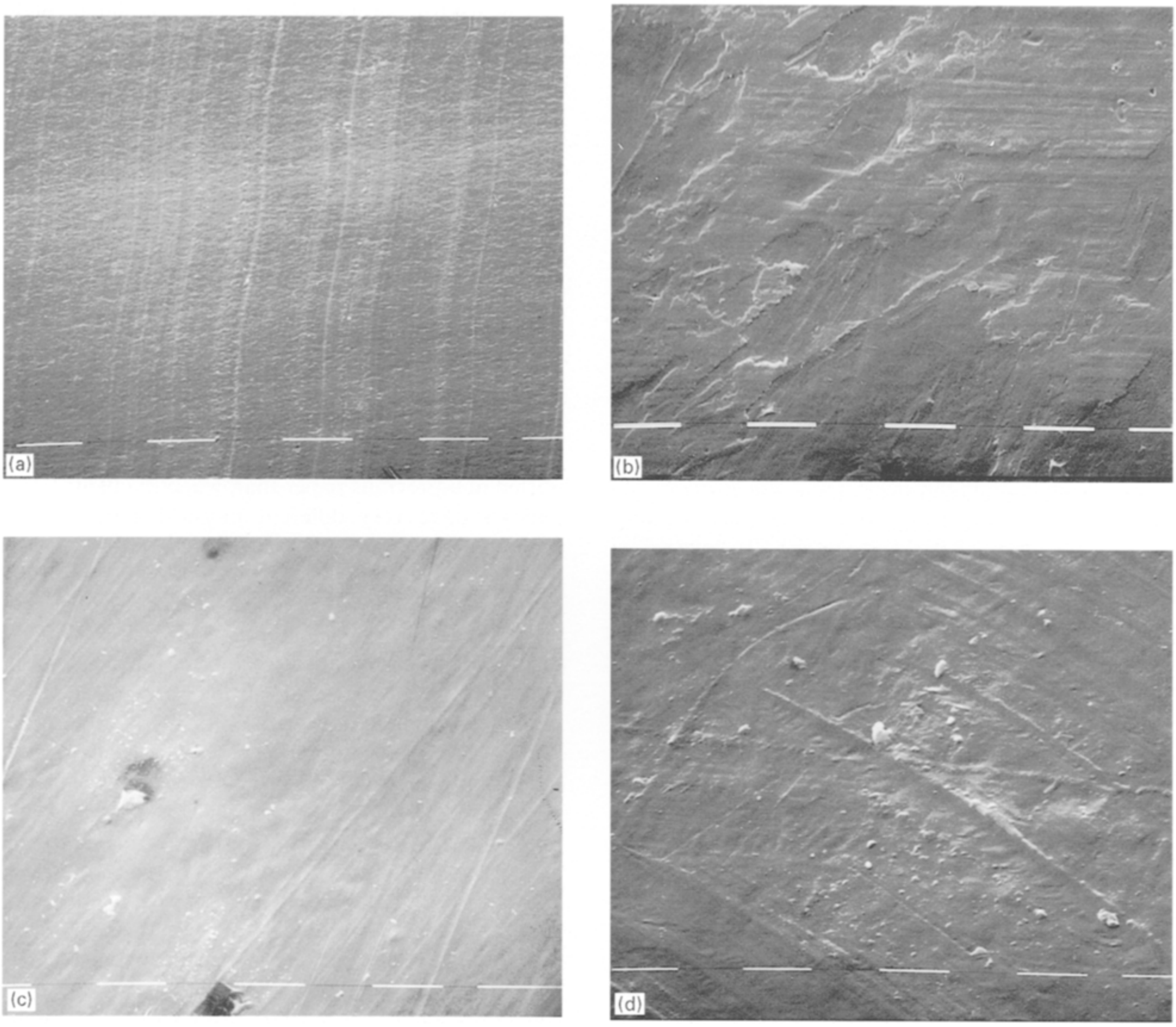

Figure 1 (a) SEM micrograph of PHBV M smoothed surface (1250 ×), marker size = 10 μm; (b) SEM micrograph of PHBV P smoothed surface (1250 ×), marker size = 10 μm; (c) SEM micrograph of PCL M smoothed surface (1250 ×), marker size = 10 μm; (d) SEM micrograph of PCL P smoothed surface (1250 ×), marker size = 10 μm.

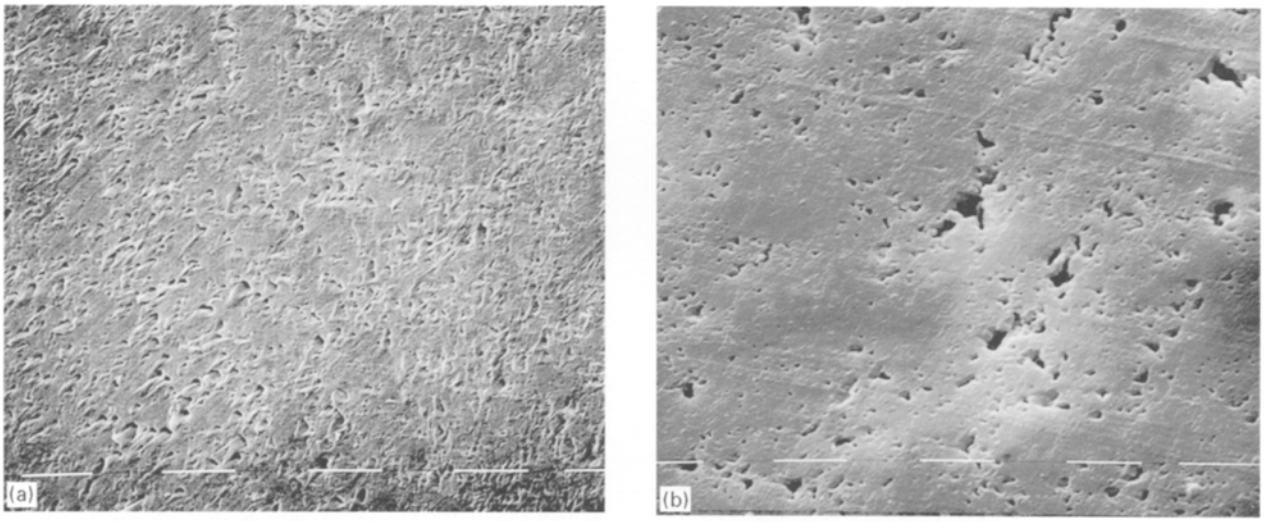

Figure 2 (a) SEM micrograph of PHBVPCL 91 M smoothed surface before etching (1250 ×), marker size = 10 μm; (b) SEM micrograph of PHBVPCL 91 M smoothed surface after 5 min THF etching (1250 ×), marker size = 10 μm.

matrix, as revealed by the number of ties surrounding their contours.

This morphology was not found in our previous work [4], in which peroxide decomposition and blending occurred at once. A possible explanation of the above finding is the following: in the present case, during blend preparation, the peroxide dissolves preferentially into molten PCL as PHBV is solid at

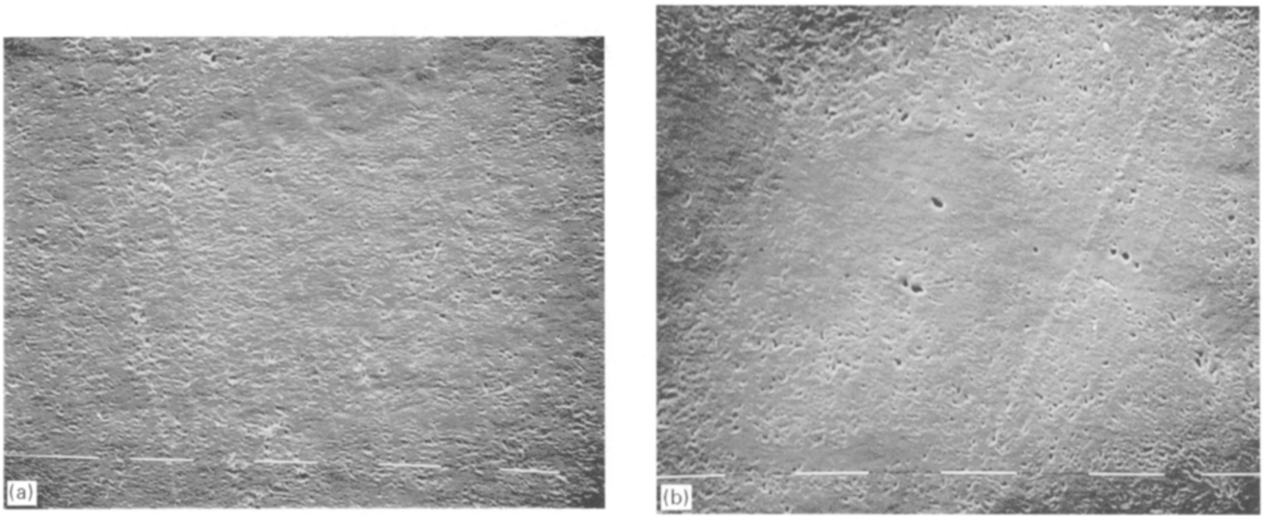

Figure 3 (a) SEM micrograph of PHBVPCL 91 P smoothed surface before etching (1250 ×), marker size = 10 μm; (b) SEM micrograph of PHBVPCL 91 P smoothed surface after 5 min THF etching (1250 ×), marker size = 10 μm.

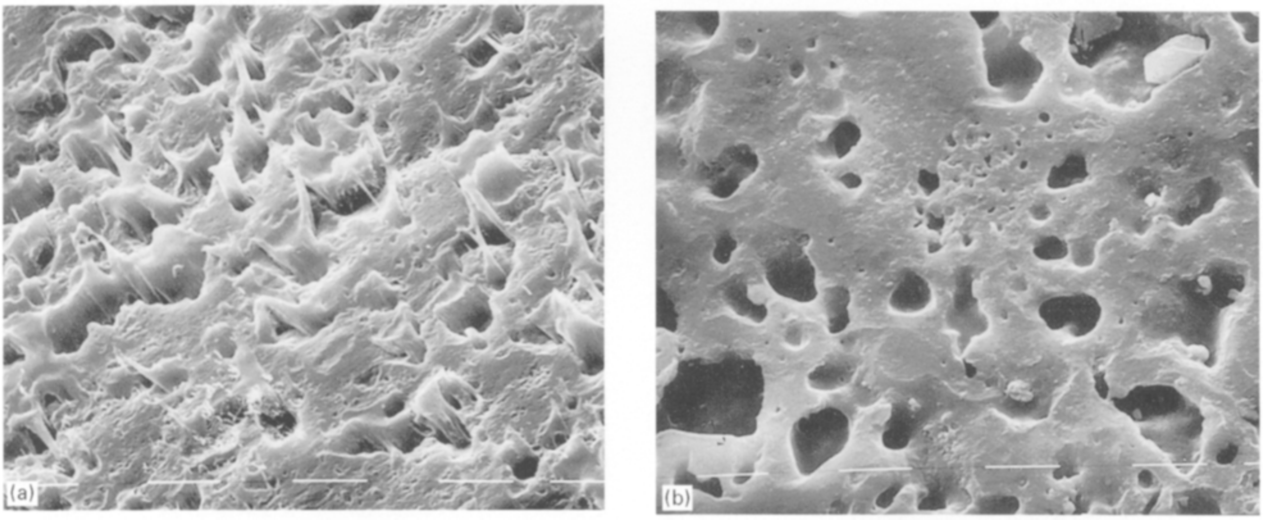

Figure 4 (a) SEM micrograph of PHBVPCL 73 M smoothed surface before etching (1250 ×), marker size = 10 μm; (b) SEM micrograph of PHBVPCL 73 M smoothed surface after 5 min THF etching (1250 ×), marker size = 10 μm.

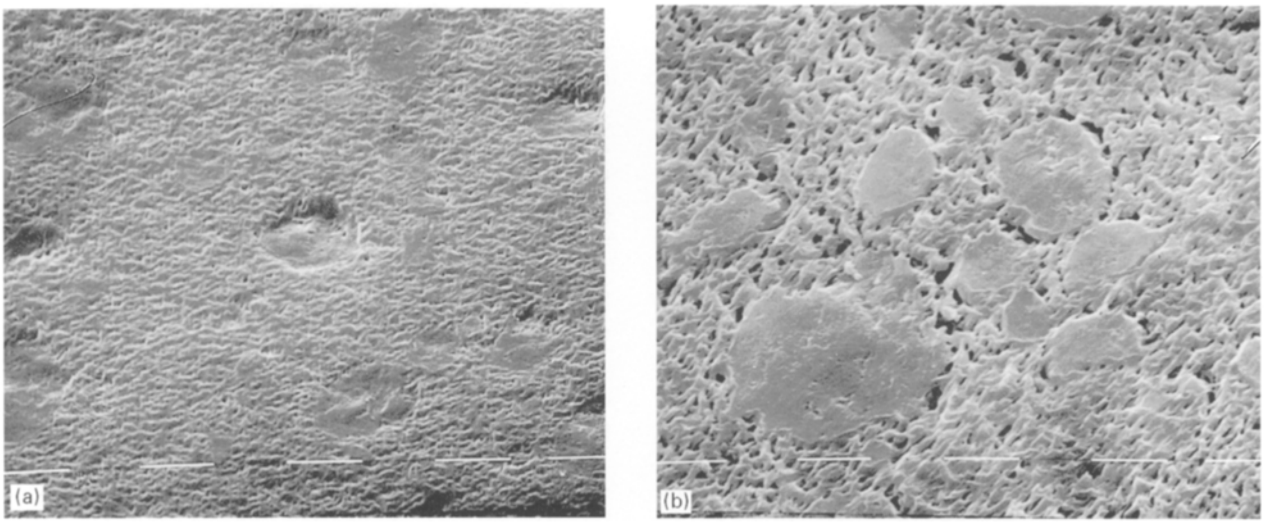

Figure 5 (a) SEM micrograph of PHBVPCL 73 P smoothed surface before etching (1250 ×), marker size = 10 μm; (b) SEM micrograph of PHBVPCL 73 P smoothed surface after 5 min THF etching (1250 ×), marker size = 10 μm.

chosen temperature. When the blend is melted and injected into the mould, the absence of shear prevents future blend homogenization. As a consequence, the chemical grafting across phase boundaries will be limited, and some regions of PHBV will not be compatibilized with PCL. This was not the case of the previous work, where the shear into the mixing chamber of the Rheocord was sufficient to assure the

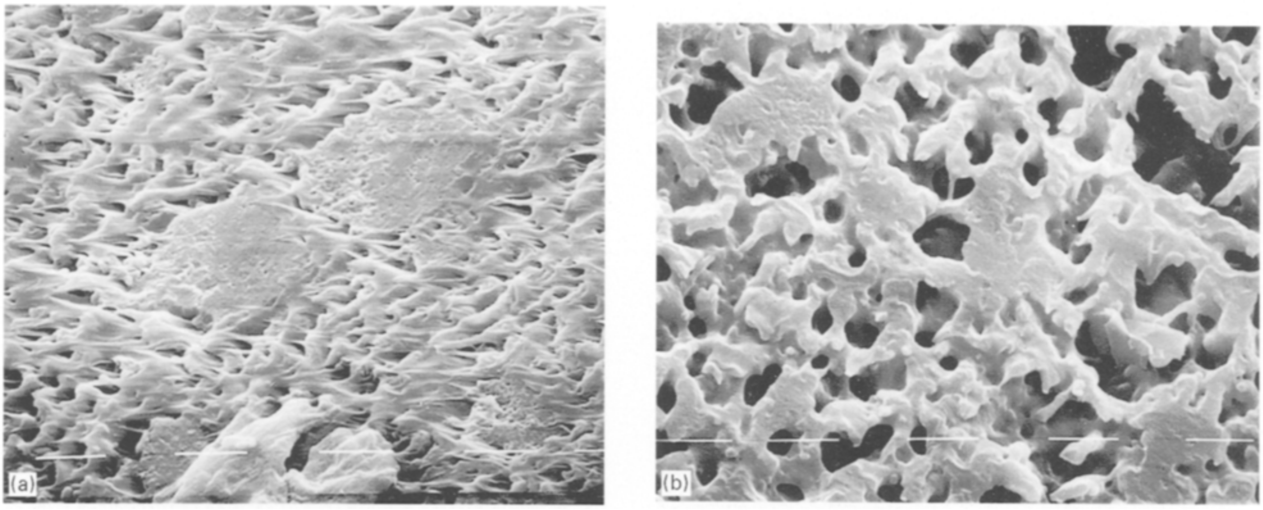

Figure 6 (a) SEM micrograph of PHBVPCL 55 M smoothed surface before etching (1250 ×), marker size = 10 μm; (b) SEM micrograph of PHBVPCL 55 M smoothed surface after 5 min THF etching (1250 ×), marker size = 10 μm.

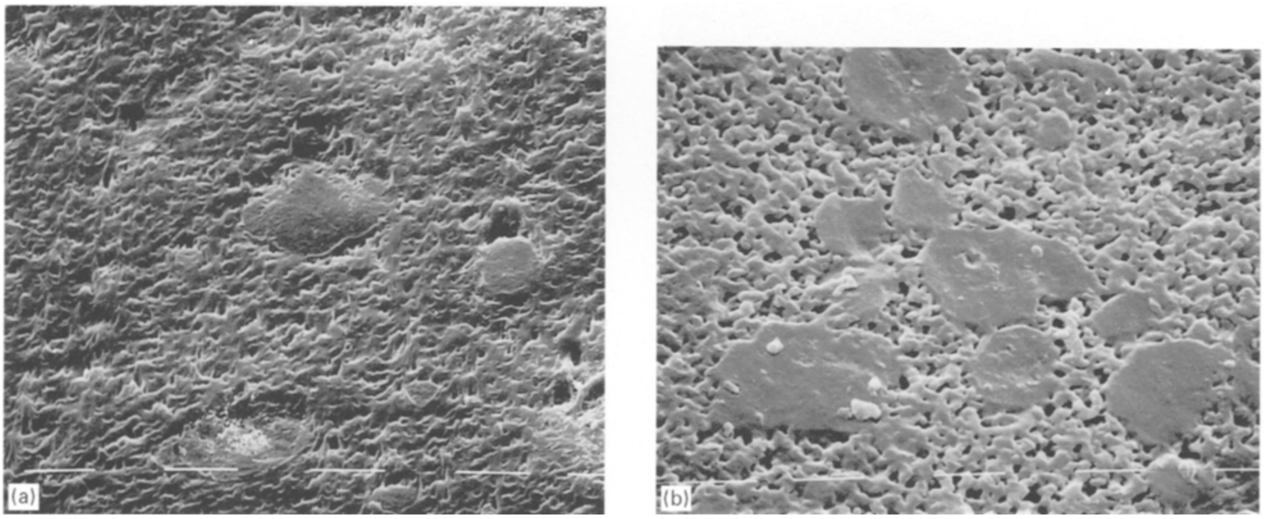

Figure 7 (a) SEM micrograph of PHBVPCL 55 P smoothed surface before etching (1250 ×), marker size = 10 μm; (b) SEM micrograph of PHBVPCL 55 P smoothed surface after 5 min THF etching (1250 ×), marker size = 10 μm.

renewal of surfacial contacts between the two phases and, hence, blend homogenization.

Similar considerations also apply to PHBVPCL 55 M blend (Fig. 6) and to PHBVPCL 55 P blend (Fig. 7). Upon etching, the mechanical blend shows the existence of co-continuous morphology, which is consistent with the blend composition. The peroxide treated blend shows again large PHBV domains with no evidence of PCL inside them, together with a very fine morphology of PHBV and PCL domains highly entangled.

Within PCL–matrix blends, as anticipated, we failed to find a selective solvent for PHBV, so some considerations will be done on the appearance of smoothed surface.

SEM surface micrographs of PHBVPCL 37 M blend are shown in Fig. 8a. Even though the morphology is disturbed by the plastic deformation of PCL matrix during the smoothing process, domains of PHBV, a few micrometres in size, are evident on the surface. The reduced dimensions of PHBV (compared to the corresponding blend on the other side of phase composition) may be due to a more efficient pre-homogenization step in view of the fact that PCL matrix is molten at processing temperature.

In PHBVPCL 37 P blend, (Fig. 8b), the chemical interactions between PCL matrix and PHBV across the phase boundary reduces the extent of plastic deformation of PCL, leading to a more clear smoothed surface. As already evidenced in the complementary PHBVPCL 73 P blend, PHBV seems to be divided in two fractions, one which is finely dispersed into PCL matrix (domains size 1 μm or less), another which concentrates in large domains (about 30 μm): once again, this effect should be attributed to the chosen processing conditions.

Similar considerations hold for extreme compositions, PHBVPCL 19 M and P blends, whose morphology of surfaces is shown by SEM micrographs in Fig. 9a and 9b, respectively.

3.3. Mechanical analysis

Flexural tests have been performed directly on cylindrical rods as obtained by the injection moulding of blends. In Table IV we report the values of σ_r and E;

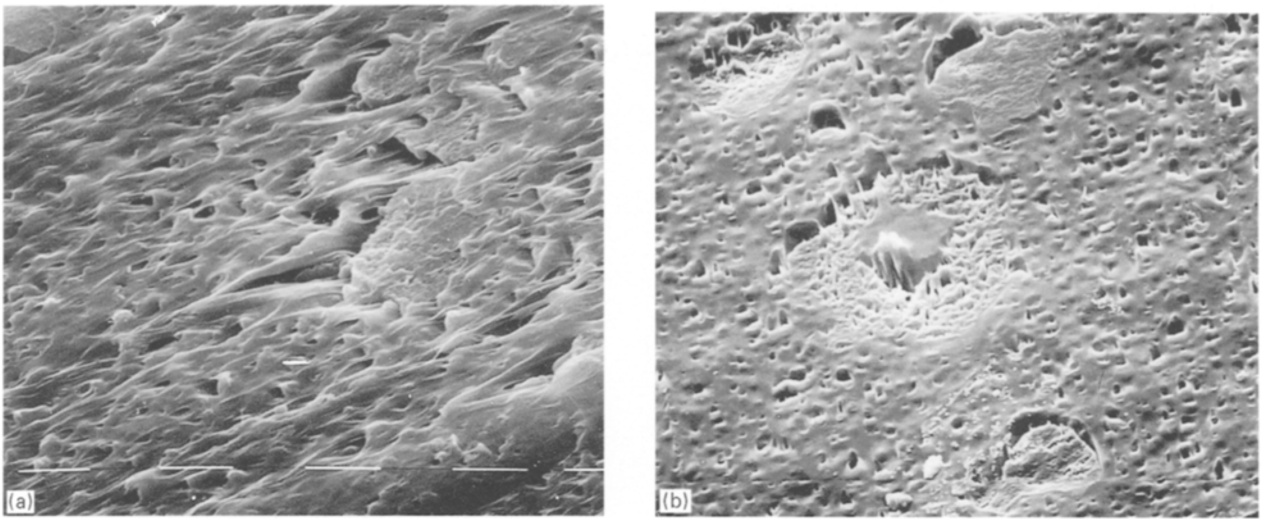

Figure 8 (a) SEM micrograph of PHBVPCL 37 M smoothed surface (1250 ×), marker size = 10 μm; (b) SEM micrograph of PHBVPCL 37 P smoothed surface (1250 ×), marker size = 10 μm.

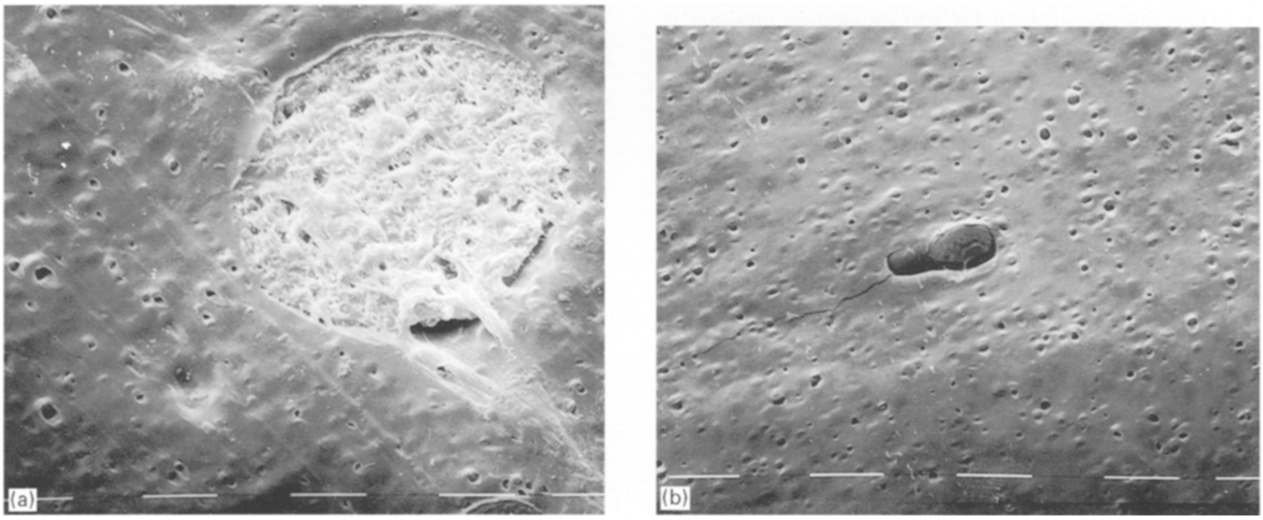

Figure 9 (a) SEM micrograph of PHBVPCL 19 M smoothed surface (1250 ×), marker size = 10 μm; (b) SEM micrograph of PHBVPCL 19 P smoothed surface (1250 ×), marker size = 10 μm.

TABLE IV Three-point flexural tests in PHBV/PCL blends and homopolymers

Sample	E (N mm^{-2})	σ_r (N mm^{-2})
PHBV M	1943.56	47.48
PHBV/PCL 91 M	1881.22	44.65
PHBVPCL 73 M	1220.95	–
PHBVPCL 55 M	797.55	–
PHBVPCL 37 M	511.77	–
PHBVPCL 19 M	344.92	–
PCL M	243.47	–
PHBV P	1732.40	42.27
PHBVPCL 91 P	1306.28	–
PHBVPCL 73 P	911.74	–
PHBVPCL 55 P	793.18	–
PHBVPCL 37 P	436.8	–
PHBVPCL 19 P	291.01	–
PCL P	292.86	–

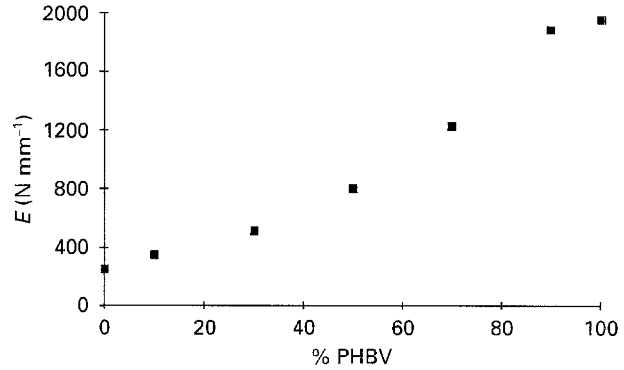

Figure 10 Elastic modulus (E) as function of composition for PHBVPCL M blends.

moreover, the values of E are plotted versus the blend composition in Fig. 10 and Fig. 11.

Prior to analysis of the behaviour of blends, we must point out the influence of the addition of peroxide onto PHBV homopolymer. The addition of peroxide to homo-PHBV causes a 10% reduction in the values of strength to rupture (σ_r), as well as in the values of Young's modulus (E). These phenomena might be ascribed to two different effects of peroxide: we have already reported [5] that the addition of

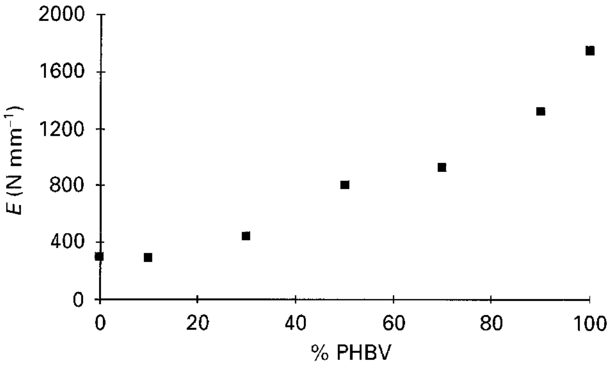

Figure 11 Elastic modulus (E) as function of composition for PHBVPCL P blends.

peroxide to PHBV causes the formation of cross-linked material. This should have a negative influence on the ability of the polymer chains to deform under stress, causing premature rupture and, hence, the reduction of the σ_r values. Moreover, we also reported [5] that the addition of DCPO causes an increase in the crystallization rate of PHBV. It is conceivable that smaller spherulites are obtained and, consequently a reduction in modulus results.

Several considerations can be drawn by the data obtained on blends: the most relevant aspect is the regular reinforcement of PCL upon the addition of PHBV. This trend is observed for compatibilized, as well as for mechanical blends. It is important to note that the increase in modulus of the mechanical blends is of more than 100% going from 10 to 30 wt % of PHBV, while is only of 50% for the peroxide treated blends. This might be related to a good state of dispersion of PHBV in PCL in the mechanical blends, as evidenced by the SEM analysis. In similar situation, the addition of a peroxide seems to play a negative role on the mechanical properties of blends.

On the other side of the blend composition, we observe that the moduli of the reactive blends show a drastic decrease compared to homo-PHBV, already upon the addition of 10% of PCL. This decrease becomes less steep for PCL contents greater than 30%. A comparison of reactive to mechanical blends shows a behaviour significantly different for addition of small amounts of PCL; the addition of 10% PCL decreases the modulus of the mechanical blend, compared to homo-PHBV, of only about 5%. Only for greater amounts of PCL do the trends of mechanical and reactive blends become similar. This different behaviour must be related to the large difference in the state of dispersion of PCL in PHBV in the mechanical and peroxide treated blends.

The different influence of the addition of small amounts of PCL to PHBV in mechanical and reactive mode is also observed when analysing the σ_r values; while PHBV breaks under flexural stress, the PHBV-based reactive blends do not break already upon the addition of only 10% of PCL. On the contrary, among mechanical blends, PHBV/PCL 90/10 blend still reaches the rupture point. For this material, σ_r value shows a reduction of 7% with respect to the homopolymer PHBV.

4. Conclusions

The present paper represents an important step toward the technological development of an innovative materials based on PHBV/PCL blends, suitable for applications *in vivo*. It is possible to prepare precursors of the final blends by incorporation of a peroxide at a temperature less than the decomposition temperature of the peroxide. Subsequently, through a kind of reaction injection moulding process, the final blend is obtained in a shape already suitable for application. The properties of the blends vary from very flexible to tough materials. Even through some improvements will be necessary in the design of the injection machine in order to assure that the desired morphology can be fully realized, we have already shown that PCL based blends are stiffer than plain PCL, while PHBV based blends are more ductile and tough than plain PHBV. It is worth stressing that preliminary attempts to carry out sterilization in an autoclave of mechanical blends in the shape of cylinders failed, due to the melting of PCL, while peroxide-treated blends maintain their shape upon sterilization, probably as a consequence of the reacted interface between the two polymers, which prevents the coalescence of PCL domains during thermal treatment.

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