JOURNAL OF MATERIALS SCIENCE **35** (2000) 523 – 545

Review
Properties of blends and composites based on poly(3-hydroxy)butyrate (PHB) and poly(3-hydroxybutyrate-hydroxyvalerate) (PHBV) copolymers

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Poly(3-hydroxy)butyrate (PHB) and poly(3-hydroxybutyrate-hydroxyvalerate) (PHBV) copolymers are microbial polyesters presenting the advantages of biodegradability and biocompatibility over other thermoplastics with useful mechanical properties. However, their costs and performances must be adjusted by blending with suitable polymers. In this article the miscibility, morphology, mechanical behaviour and other prominent characteristics of a representative number of blends and composites of PHB and PHBV are summarized. In particular, blends with a few polyethers, polyesters, polyvinylacrylates and polysaccharides are illustrated. Furthermore, a brief paragraph deals with PHB/vegetal fiber composites. A wide range of properties emerges by blending with polymers having very different molecular structures and characteristics, such as crystallinity, glass transition and melting temperatures. The microstructure of the blends, resulting from thermodynamic and kinetic factors, is regarded as an important factor in controlling the mechanical and the biodegradation behaviours. Moreover, some considerations upon the nature of the "driving force" of the miscibility have been made in order to explain miscibility behaviour differences.

1. Introduction
1.1. Background and terminology
Polymer blending quite often is a very convenient industrial process since it provides tailoredmade materials excluding any synthetic stage [1]. For instance, by blending two homopolymers, an easily processable material may be obtained preserving the major properties of the moieties. At the present time, many blends have been studied and produced showing a field of properties able to cover a large spectrum of specific needs. Clearly the main reason for blending is economy. If a material can be generated at a lower cost with properties meeting specifications, it remains competitive [2]. In general the following economy-related reasons can sustain the blending procedures:

- extending engineering polymer performance, by diluting it with a low cost polymeric material;
- achievement of materials with tailored end-properties;
- forming a high performance blend from synergistically interacting polymers;
- recycling industrial and or municipal plastic scrap.

According to thermodynamic and kinetic of mixing and crystallization process, blends can be arranged into a variety of morphologies, some of which will be described later here. Morphology is a very important factor affecting the mechanical behaviour of the blends, because even if no cohesive forces between the components are present, a strong mechanical resistance may arise from an interlocked array of the phases.

In order to understand the main characteristics of polymer blends, it is needed to know the basic terminology concerning blends.

A *miscible* blend is a homogeneous system resulting from a mixing process verifying the inequation:

$$\Delta G_M = \Delta H_M - T\Delta S_M < 0 \quad T, p = \text{cons.} \qquad (1)$$

where T is the absolute temperature, p is the pressure, ΔG_M, ΔH_M and ΔS_M are the changes in free energy, enthalpy and entropy.

Mixing is always a process entropically favoured, since it increases the number of distinguishable arrangements of the system and hence the disorder ($\Delta S_M > 0$). However, this increase of entropy is small compared to that of the mixing of low molecular weight substances. Thus endothermic mixing are not thermodynamically permitted unless the positive ΔH_M is so small to be overcome by the product $T\Delta S_M$. Instead, exothermic mixing is anywise allowed implying a negative change of free energy.

The inequation (1) is a necessary condition, but not sufficient for miscibility. As matter of fact, thermodynamic stability of a single-phase mixture may exist only when:

$$\left(\partial^2 \Delta G_M / \partial \Phi^2\right)_{T,p} > 0$$

where Φ is the composition. If this condition is not satisfied in the whole range of composition, then the blend is partially miscible, that is stable one-phase mixtures may only exist at the ends of the composition range.

The main factors affecting the miscibility are the chemical nature of the polymers and their molecular weight. The chemical nature accounts for the existence of strong interactions ($\Delta H_M < 0$) between the macromolecules, while the molecular weight influences the values of ΔG_M in two different ways. If the mixing is endothermic, then the higher the molecular weight the lower is the entropy change and less probable is the miscibility. The opposite happens if ΔH_M is negative, since the number of interactions between the macromolecules increases with increasing the molecular weight, even if these intermolecular interactions imply a reduction of ΔS_M. Miscible blends exhibit properties intermediate or even superior to that of the pure components, offering a means to improve the poor performances of polymers without sacrifice any excellent characteristic.

A *compatible* blend is a heterogeneous material having useful, not combined in a unique polymer, chemico-physical properties, even if the constituents are immiscible from a thermodynamic point of view. The good mechanical properties of compatible blends are the consequence of good adhesion between the components as much. In order to improve the properties of immiscible blends in processing and/or in performance, it has been often resorted to “compatibilization” methods. Compatibilization means to induce chemical or physical interactions or add a so-called “compatibilizer”. This latter is an agent that modifies the interfacial properties in the polymer blends.

Compatibilization may be mainly achieved by:

- addition of block or graft copolymers;
- crosslinking the blend components;
- chemical modification of one or both the homopolymers.

When the compatibilizing agent is generated *in situ* or the chemico-physical interactions are induced during the blending process, this latter is called “reactive polymer blending”.

A characteristic feature of interpenetrating network, where both polymers have mechanical continuity, may be obtained by simultaneous polymerization of two different kind of monomers in the same batch by using two non-interfering reactions [3]. A modification of this method consists of stepwise reactions [4]. First a monomer is polymerized and crosslinked, then a second monomer is added and subjected to the same treatment in presence of the preformed network.

Unlike blends, which may be monophase, a *composite* is a multiphase system constituted by a matrix including the reinforcing material. Since the stress is transferred from the matrix to the reinforce through the interface, the efficiency of the reinforcement is again controlled by the degree of the adhesion between the components.

1.2. Flory-Huggins theory of polymer solutions

This theory is based on the “fluid lattice” model [5], which considers molecules of liquids as residing in cells of a dynamic lattice. The combinatorial entropy of a liquid solution is thus related to the number of the permutations of the liquid molecules amongst the sites of the lattice. In the case of macromolecules, each site of the lattice is occupied by a segment of the polymer chain rather than a whole small molecule. Since the segments are linked, consecutive segments have to occupy next sites of the lattice. Thus the number of microstates of a macromolecular solution is reduced with respect to a solution of a low molecular weight substance. Quantitative predictions, obtained independently from Flory and Huggins [6–9] by using equations of statistical thermodynamics, are expressed by the well known relation:

$$\Delta S_M / R = -[\mathrm{N}_1 \ln \varphi_1 + \mathrm{N}_2 \ln \varphi_2] \qquad (2)$$

where N_1, N_2, φ_1, and φ_2 are the number of moles and the volume fractions of the components 1 and 2 respectively, R is the Gas Constant. Since φ_1 and φ_2 are less than one, ΔS_M is always positive and thus mixing is an entropically favoured process.

The Equation 2 may be rearranged in the following:

$$\Delta S_M / RV = -[\varphi_1 \ln \varphi_1 / V_1 + \varphi_2 \ln \varphi_2 / V_2] \qquad (3)$$

where V_1, V_2 and V are the molar volume of the pure components and the solution, respectively.

For a polymer-solvent solution, V_2 increases and the second terms on the right hand of the Equation 3 decreases up to disappears when the molecular weight of the polymer tend to infinite. Thus the entropic stabilization of a polymer solution is reduced with increasing the molecular weight. For a polymer-polymer solution, also the first term of the Equation 3 is reduced, therefore the entropic stabilization is very low. The Flory-Huggins theory also allows to calculate the enthalpy of mixing by introducing the interaction energy w for the contacts present in solution: w_{12} for contacts between different polymers, w_{11} for contacts between the polymer 1 and w_{22} for contacts between the polymer 2.

Defining the interaction energy change Δ_{w12} associated with creating a new contact type 1–2 in the mixed state, the enthalpy of mixing may be written as follows:

$$\Delta H_M / RTV = z \Delta w_{12} \varphi_1 \varphi_2 / kTV_s \qquad (4)$$

Here z is the coordination number of the lattice, k is the Boltzmann Constant, V_s the volume molar of a polymer segment, while the remaining symbols have the usual meaning. This expression may be put into a different form by defining a new parameter χ_{12}, the polymer-polymer interaction:

$$\chi_{12} = z\Delta w_{12} r_1 / kT \tag{5}$$

which is a dimensionless quantity representing the energy interaction between macromolecules of r_1 segments divided by kT. Combining Equations 4 and 5 gives:

$$\Delta H_M / RTV = \chi_{12}\varphi_1\varphi_2 / V_1 \tag{6}$$

It is worth to stress that χ_{12} depends on the number of segments r_1 of the polymer 1, that is on the molecular weight. Thus a measure of the energy interaction is better represented by the quantity χ_{12}/r_1, which is independent on the molecular weight and on the way the segment is defined. Having the expression of both ΔH_M and ΔS_M, it is possible to calculate the free energy of mixing by combining the Equation 1 with 3 and 6:

$$\Delta G_M / RTV = \varphi_1 \ln \varphi_1 / V_1 + \varphi_2 \ln \varphi_2 / V_2 + \chi_{12}\varphi_1\varphi_2 / V_1 \tag{7}$$

Thus a negative value of χ_{12} (specific interactions) cooperates with the entropic term for the stability of a polymer blend. Instead, positive values of χ_{12} (dispersive interactions) make conflict between the entropic and the enthalpic term in the Equation 7. If χ_{12} has the sufficient magnitude, the combinatorial term is overcome and phase separation occurs.

1.3. Miscibility prediction

The limitation of the Flory-Huggins theory resides in the fact that in the calculation of ΔS_M the occupational of the lattice sites is considered purely statistical, ignoring the possible specific interactions between the polymers. The specific interactions have been only considered as contributing to ΔH_M, but they will contribute to the true entropy of mixing too. Thus miscibility predictions made using the Flory-Huggins theory lead to discrepancies with experimental observations. A semi-empirical approach for such predictions was suggested by Hildebrand [10] and is based on the calculation of the solubility parameter δ. The estimation of such a parameter for a polymer can be obtained adding the molar attraction constant F for each molecular group in the structural formula and dividing the sum by the volume V_r of a repeating unit:

$$\delta = \frac{\Sigma F_i}{V_r}$$

For an endothermic process of mixing between two components, the square of the solubility parameters difference $(\delta_1 - \delta_2)^2$ is proportional to the heat of mixing ΔH_M so that the more such a difference is small, the more the mixing is favoured. In deriving the solubility parameter the assumption was made that specific forces are not present. When there are strong polar interactions or hydrogen bonds between the polymers, the ΔH_M results negative and solution may occur even if $\delta_1 - \delta_2$ is rather large. Therefore the Hildebrand scheme has severe restrictions and can be use as a rough guide to predict miscibility.

1.4. Microphase structure of blends

The type of microphase in a blend, that is its microscopic appearance, is mainly determined by the miscibility of the components.

Since most polymers are thermodynamically immiscible and the kinetics of mixing macromolecules are unfavourable to the achievement of the thermodynamic equilibrium state, most polymer blends are heterogeneous. Microheterogeneity may vary in size and arrangements. The size of microphases normally is not far from 10 μm or less, being the most characteristic range between 0.01 μm and 1 μm. Concerning the microphases morphology, two structures may arise from mechanical blending:

- co-continuous phases of different composition, due to the formation of a network extending throughout the matrix.
- a continuous matrix of the major component inglobing dispersed particles of the minor component; the simplest domains shape is spherical in order to minimize the tension surface, having the sphere the lowest ratio between surface area and volume.

These two morphology are generated by different mechanisms of decomposition [11], named spinodal and binodal respectively. The former phase transformation occurs in a continuous way, without the formation of any interface. From a thermodynamic point of view, the system which is subjected to a spinodal decomposition is an unstable system evolving to a stable system without overcome a thermodynamic barrier. Instead, a metastable system, in order to evolve, needs the occurrence of wide random fluctuations causing the formation of nuclei. Thus, in this case, from the beginning of the transformation a new phase appears very well separated form the initial phase by an interface. Once nuclei of a stable composition are formed, they subsequently grow leading to the described microphase.

1.5. Experimental assessment of miscibility

The most accepted criterion for polymer miscibility is the detection in the blend of a single glass transition temperature, whose value is an average between those of the two components. The glass transition temperature (Tg) is a fundamental characteristic of polymers. It represents the temperature below which the thermal energy is too low to overcome the rotational barrier around single bonds and thus the segmental motion are stopped. According to the temperature, amorphous portion of polymers may be in a glassy or rubbery state, while the crystalline phase is not interested in the glass-rubbery transition.

Most miscible blends exhibit a Tg dependent on the composition according to the Fox equation:

$$\frac{1}{\mathrm{Tg}} = \frac{w_1}{\mathrm{Tg}_1} + \frac{w_2}{\mathrm{Tg}_2} \tag{8}$$

where the indices 1 and 2 indicate the two components, w_1, w_2, Tg_1, Tg_2 their respective mass fractions and glass transition temperatures.

The glass transition temperature of polymers can be detected by means of several techniques, e.g. differential scanning calorimetry (DSC), dynamic-mechanical measurements, dilatometry etc. Among them, DSC is the most employed because of its versatility and rapidity.

Notwithstanding the existence of a unique glass transition temperature is an unambiguous criterion for miscibility, some discrepancies may arise for many reasons.

First of all, according to the preparation method, blends may be obtained in metastable states. This is frequently the case of blends obtained by solution casting, where the evaporation of the solvent may lead to a homogeneous system kinetically hindered to evolve in a phase separated, thermodynamically stable, system.

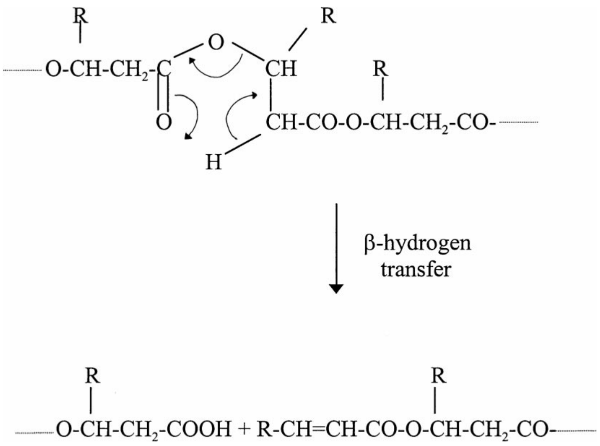
Secondly, the small size of the phases of immiscible blends may cause a false response on the Tg due to the poor sensitivity of the experimental techniques. Generally, when the components are finely dispersed, dynamic-mechanical measurements allow to discriminate between two Tg better than DSC technique(1).

There are other complications in the use of the Tg criterion. This is inappropriate when the two polymers have very close Tg and also when they are highly crystalline. Indeed, in the former case only one Tg will be detected whether or not the polymers are miscible, whereas in the latter case no glass transition due to the amorphous regions may be revealed. Microscopy observations and determination of relaxation's time by means of low resolution nuclear magnetic resonance, aids in these cases the univoque assessment of blend homogeneity. A further useful indication of miscibility is the melting point depression of a crystalline polymer in presence of an amorphous diluent. However, this effect has to be correlate to other miscibility evidences, since it has also been found for immiscible blends when some morphological changes of the crystalline component occur.

1.6. Beneficial results of PHB blending

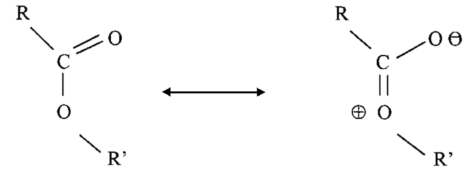
Poly(3-hydroxybutyrate) is a linear saturated polyester behaving as conventional thermoplastic materials. In Table I are reported some chemico-physical and mechanical properties of PHBV copolymers, for the comparison with the same properties of the polypropylene. Over the conventional commodities, PHB and its copolymers have the advantage of biodegradability and biocompatibility. Unfortunately, they present the drawbacks of a poor thermostability and a relatively low impact resistance.

Indeed, above 170 °C these polyesters undergo a decrease of molecular weight proportional to the time. The mechanism of the thermal degradation follows a random scission at the ester groups according to a β-hydrogen elimination [12]:



Blending of PHB may results in a decrease of the melting temperature that imply the possibility to process the materials at lower temperature, avoiding or limiting the degradation. The scarce impact resistance of the PHB is due both to its relatively high glass transition temperature and its characteristic to form very large spherulities. Poly(3-hydroxybutyrate-hydroxyvalerate) copolymers partly fill the gap of toughness, however, they exhibit, with respect to PHB, lower melting points narrowing the utilization temperature range.

PHB is unsoluble in water and soluble in almost apolar solvent such as chloroform. The hydrofobic character of the PHB has been explained in terms of a strong contribute of the charge-separated formula (II) to the actual electronic structure of the macromolecule:



(I) (II)

TABLE I Thermal and mechanical parameters of PHBV copolymers at 25 °C [13, 14] compared with isotactic polypropylene

Composition Mol % HV	Melting temperature (°C)	Glass transition temperature (°C)	Tensile strength (MPa)	Elongation (%)	Elastic modulus (GPa)
0	175	9	45	4	3.8
11	157	2	38	5	3.7
20	114	−5	26	27	1.9
28	102	−8	21	700	1.5
34	97	−9	18	970	1.2
i-polypropylene	174	−17	30	10	1.5

Indeed, the resonance hybrid results in oxygen atoms of the chain less available to the solvatation.

A not negligible property that influences the success of a plastic material on the trade, for example as commodity for wide low performance applications, is the cost. For this reason the Biopol (commercial name of poly(hydroxyalkanoates)) products have not been extensively used up to now even in applications where biodegradability is needed. Thus blending of PHB with suitable polymers may offer the chance to obtain cheaper products together with improved mechanical properties. However, a wise choice of the PHB partners should be taken into account if true biodegradability is desired to be retained in the blend. A blend truly biodegradable is obviously composed of two components able to be recognised and metabolised to small organic molecules by microbial enzymes. Nevertheless, in the case of PHB based blends containing a non-biodegradable petrol-polymer, a kind of “biodeterioration” may occur according to the morphology and surface properties of the samples. As matter of fact, the microbial attack to the PHB part of the blends causes a disintegration of the whole samples by subtracting cementing material between separate synthetic regions.

2. Blends PHB and PHBV and other polymers

2.1. Summary of the blend discussed

PHB and its copolymers have been mixed with a variety of polymers, having very different characteristics, biodegradable and non-biodegradable, amorphous or crystalline with different values of the melting point and glass transition temperature. In this article some features of blends of PHB with a few polyethers, polyesters and polyvinylacrylates will be illustrated. Furthermore, a brief paragraph will be dealing with blends of PHB and polysaccharides.

Miscible blends have been formed with polyoxyethylene (PEO), poly(epichlorohydrin) (PECH) and poly(vinylacetate) (PVAc). Partly miscible blends are formed with poly(methylmethacrylate) (PMMA), while compatible blends have been obtained with polycaprolactone (PCL), ethylene-propylene rubber (EPR), polybutylacrylate (PBA), and polysaccharides.

2.2. Poly(3-hydroxybutyrate)/polyethers blends

Miscibility data concerning PHB/polyethers blends have been here reviewed with the aim to identify the driving force for the mixing or demixing of such systems.

Aliphatic polyethers are constituted by blocks of methylenic units linked by oxygen bridges:

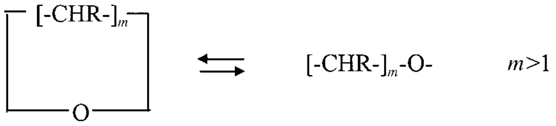
$$[-(CH_2)_x-O-]_n \quad n = 1, 2, 3..... \quad x = 1, 2, 3.....$$

The oxygen atoms and the aliphatic units which alternate along the chain of polyethers, respectively show hydrophilic and hydrophobic nature.

The main characteristic of polyethers is the presence of paired oxygen electrons giving them electron-donor properties and making these polymers potentially able to form hydrogen bonds.

The real possibility for a polyether to be involved in hydrogen bonds depends on the chance to reach the right molecular orientation requested for solvating the hydrophilic oxygen groups. This is in turn influenced by the length of the hydrophobic segments of the chain and by the presence of groups causing sterical encumbrance effects.

Polyethers are mainly synthetized by cyclic oxygenated monomers according to the reaction scheme:



The ability of the cyclic ethers to polymerize depends, from the thermodynamic point of view, on the amount of strain existing within the ring. Such strain constitutes the driving force to the polymerization and is present in the ring at different amount when $n = 2$, $n = 3$, $n = 4$, meanwhile is zero when $n = 5$ and the ring assumes the well known chair conformation. For higher values of n, nevertheless the non-planarity of the structure makes the bonding tension negligible, the polymerization reaction is again favoured because of the low probability of the two ends of the growing chain meeting each other during a reaction.

According to the kinetic mechanism (step or chain-growth) of the reaction, the polyethers are obtained as low molecular weight (maximum 20,000) or high molecular weight products (up to few million). Thus polyethers, depending on the molecular weight and degree of crystallinity, present a physical appearance varying from a viscous oil to a waxy up to a real thermoplastic material, with melting and glass transition temperatures.

There is a certain resemblance between the two homologous series of polyesters and polyethers, which may behave in a similar way.

The properties of polymers are determined by the polarity, the geometry, the stereochemistry and segmental mobility of their chains. Highly polar hydrogen bonded polymers, such as polyamides or polyurethanes, are characterized by strong intermolecular interactions which account for the little variation of properties within the respective homologous series of polymers. On the contrary, polyesters and polyethers are slightly polar polymers, thus their chains are submitted to the weak van der Waals forces. Therefore little changes in chemical structure can influence the symmetry, polarity or flexure of the chain molecules and consequently determine a strong variation of chemico-physical properties. As an example, at room temperature polyoxyethylene is miscible with water in all proportions, while polyoxymethylene, polyoxypropylene and tetraoxymethylene are water-insoluble polymers. On the other hand, melting points and crystallinity of polyesters are markedly sensitive to small structural changes, either of constitutional or configurational types.

In particular, a singular alternating trend in the values of some properties has been observed passing from a polyester whose repeating unit contains odd number of tetrahedral carbon atoms to an other having even number of carbon atoms in its constitutional unit [13].

This so-called "alternating behaviour" concerns melting and glass transition temperatures besides density, crystallization and mechanical properties.

Nevertheless the nature of this phenomenon is not yet well known, no doubt it is related to the configurational and chain packing differences between odd and even members in homologous series.

Because of the large range of properties of polyethers, their use as blending materials offers the potential advantage to obtain less expensive biodegradable products with a wide spectrum of useful properties. Miscibility studies also concern derivatives of polyethers in which one or more hydrogen atoms in the repeating units are replaced by chlorine atoms.

2.2.1. Poly(hydroxy butyrate)/ poly(methyleneoxide) (PHB/PMO) blends

Poly(methyleneoxide) (PMO), whose repeating unit is -CH_2-O-, is a crystalline polymer having melting point of about 180°C and glass transition temperature, depending on the measurement method, between -40°C and -60°C. Crystallographic data [14] indicate that the PMO crystallizes according to a trigonal ($a = b = 4.471$ Å, $c = 17.39$ Å) or orthorhombic system ($a = 4.767$ Å, $b = 7.660$ Å, $c = 3.563$ Å) assuming a conformation of a $2^*9/5$ and $2^*2/1$ helix respectively.

Blends of poly(3-hydroxybutyrate) (PHB)/poly-(methylene oxide) (POM) have been prepared by melt mixing and subsequent compression moulding [15]. Crystallization, thermal behaviour, morphology and mechanical properties of the blends were studied by using differential scanning calorimetry, optical and scanning electron microscopy, dynamic-mechanical analysis.

Dynamic mechanical properties of such blends have demonstrated the immiscibility of the two polymers in the amorphous phase. Indeed, relaxation spectra show two peaks in correspondence of the glass transition regions of the two components. Moreover, two distinct spherulitic phases have been evidenced in the solid state and changes of the texture structure with the composition also were observed. By cooling PHB/POM blends, it is possible to isothermally crystallize first the POM, meanwhile the PHB remains in the liquid state. The crystallization of PHB starts only by cooling the samples to much more lower temperatures.

Indeed, it is known that kinetic factors make a polymer able to crystallize only at temperature well below the melting point [16]. In other words, it is needed a certain minimum "supercooling" to crystallize a polymer and the crystallization from melt does not take place until the requested supercooling is achieved.

In the case of PHB/POM blends, the isothermal two-step crystallization is possible because POM and PHB need very different supercoolings to crystallize.

Thus, low supercoolings (corresponding at temperatures ≥ 150°C) allow to crystallize only the POM meanwhile the crystallization of the PHB is still kinetically hindered. The subsequent isothermal crystallization of the PHB may be obtained by further cooling at temperatures below 120°C. The selected crystallization temperature of PHB for optical observations was 90°C, a value corresponding to a rather fast, but still isothermal, crystallization. The observation of films of the blends in the molten state showed two separated phases for almost all the prepared compositions. For the blends richest in POM, droplets of PHB, whose size ranges from tens to hundreds microns, are dispersed in the liquid matrix Isothermally crystallized samples of PHB/PMO blends shows spherulitic regions of both the phases, whose morphology depends on the composition. In particular, almost spherical particles of the minor phase are dispersed in the major phase and the size-distribution of the particles depends on the crystallization conditions. As an example, Fig. 1 shows the PMO spherulites growing isothermally at 151 °C from their own molten phase in a PHB/PMO blend containing 40% by weight of PHB. The spherulites of POM may grow undisturbed until they impinge one another or on the edge of the liquid domains of PHB. In this case the further growth of the spherulites of POM is not allowed in the direction of the impingement and the circular shape of spherulites is compromised.

Morphological analysis of blends more rich in PHB than PHB 40 has shown a fine dispersion of separated POM droplets (up to 5 microns in diameter) in a PHB matrix. Nevertheless the immiscibility, the presence of PHB causes a slow down of the linear growth rate of POM spherulites. Being PHB and POM immiscible, the observed depression of the growth rates of POM spherulites in the blends may be explained by the lower thermal conductivity of the molten heterogeneous phase from which they arise [17]. Thermal conductivity is a measure of the velocity to which the heat is removed from a material. Comparing the values of this thermal parameter for PHB (0.156 W/m/°C) and POM (0.292 W/m/°C), it emerges that the former exhibits less tendency to propagate heat. Thus the presence of PHB droplets obstructs the getting rid of crystallization heat from solid-liquid interface of POM phase causing a slow down of the linear growth rate of spherulites. A strong depression of the melting point (about 16 degrees centigrade) of the PHB phase is also found in the blends, whereas the melting point of the POM remains practically unchanged. This remarkable decrease of the melting temperature has been attributed to the change of lamellar morphology of PHB in the blends because of the previous crystallization of the POM.

In fact, during the crystallization of POM, the growing spherulites shove against the surrounding liquid medium causing space restrictions that influence the subsequent crystallization of PHB. This constriction forces the PHB to adopt a greater lamellar thickness, which accounts for the lower melting point found in the blends. Moreover, the crystallinity of each component is preserved in the blends, since no decrease of the total crystallinity, with respect to the contributions of the

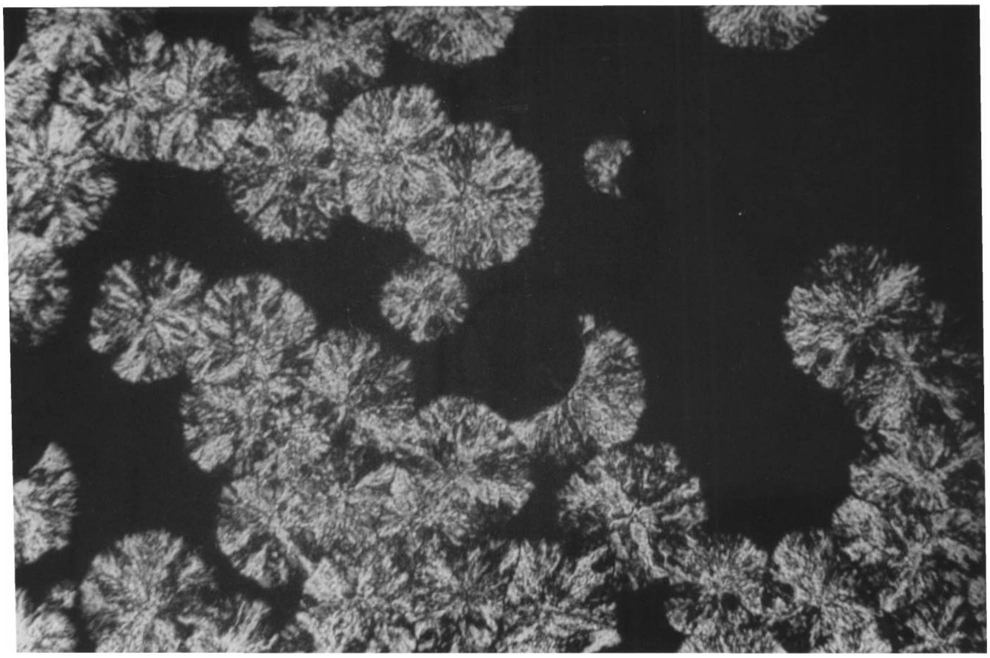


Figure 1 Optical micrograph of PMO spherulites growing from PHB/PMO (40/60 wt %) at a crystallization temperature of 151 °C. Magnification 125X.

isolated components, has been observed. Finally, the mechanical resistance of the blends is not drastically reduced with respect to the components.

2.2.2. Poly(hydroxy butyrate)/poly(ethylene oxide) (PHB/PEO) blends

Blends of PHB and PEO have been obtained by slowly solution casting from chloroform [18, 19]. Such blends, at least those obtained with low molecular weight PEO (up to 50,000), exhibit a single glass transition temperature Tg in the whole composition range, indicating a complete miscibility of the two components in the amorphous phase. The dependence of the Tg on the composition follows the Fox equation, reported previously.

The DSC curves of PHB/PEO samples, heated from room temperature up to 200 °C, show two distinct endothermic peaks. The higher temperature peak (about 175°C) represents the fusion of the PHB phase while the lower temperature peak (about 60°C) represents the melting fusion of the PEO phase. In presence of PEO, the melting temperature of PHB results strongly depressed. As an example, the melting temperature of the blend containing the 20% of PEO has been found equal to 163°C, while the neat PHB crystallized under the same conditions, showed a melting point of 194°C. This fact allows to process the blends at lower temperature with respect to the neat PHB, avoiding the PHB degradation occurring at only few degrees above its melting point.

In agreement with the miscible nature of the blend, isothermal crystallization has shown that the PEO, acting as a diluent, reduces the linear growth rate of PHB spherulites. According to the Flory-Huggins theory, the interaction parameter χ_{12} between PHB and PEO is proportional to the enthalpy of mixing ΔH_M and so a negative value of χ_{12} is indicative of miscibility. The analysis of the melting point depression allows to determine the value of the interaction parameter χ_{12}, by means of the Hoffmann-Weeks method, based on the equation:

$$\mathrm{Tm}' = \mathrm{Tc}/\gamma + (1 - 1/\gamma)\mathrm{Tm} \tag{9}$$

where γ is a constant, generally ranging between 1 and 5, Tm′ is the apparent melting point and Tm the equilibrium melting point of a crystalline phase defined as the fusion temperature of a perfect crystal having infinite thickness. Tm may be derived, for each blend composition, by plotting the experimental melting points Tm’ of the PHB phase against the isothermal temperature Tc at which the crystallization took place. As illustrated in Fig. 2, the intersection of the experimental line with

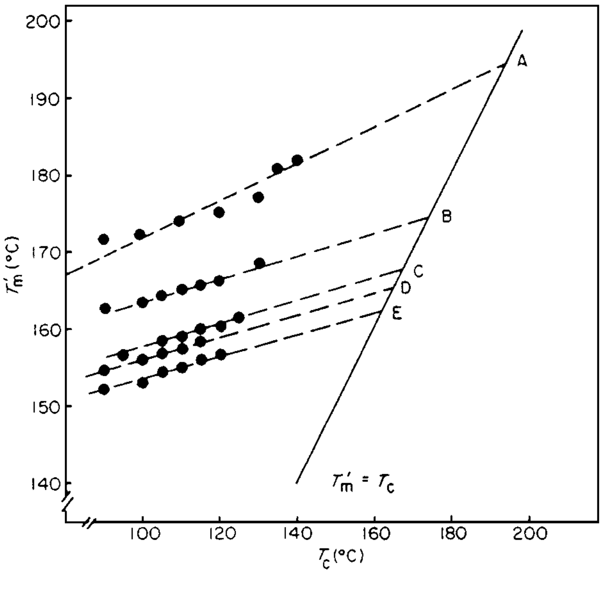


Figure 2 Plots of Tm′ vs. Tc for different PHB/PEO blend compositions: A)neat PHB; B),C),D),E) blends containing 20, 40, 60, 80% of PEO respectively.

the line Tm = Tc gives the equilibrium melting temperature Tm of the crystalline PHB in the blend. Then, the interaction parameter can be derived from the equation:

$$\frac{1}{\mathrm{Tm}}-\frac{1}{\mathrm{Tm}^\circ} = -\frac{RV_2}{\Delta H^\circ V_1}\left[\frac{\ln\Phi_2}{m_2}+\left(\frac{1}{m_2}-\frac{1}{m_1}\right)\Phi_1+\chi_{12}\Phi_1^2\right] \qquad (10)$$

where Tm and Tm° are the equilibrium melting points of the blends and homopolymer respectively, ΔH° is the theoretical heat of fusion of PHB 100% crystalline, V_1, m_1, Φ_1 and V_2, m_2, Φ_2 are the molar volume of the repeat unit, the degree of polymerization and the volume fraction of the PEO and PHB respectively. Rearranging the terms, the Equation 10 may be rewritten as follows:

$$\frac{\Delta H^\circ V_1}{RV_2}\left(\frac{1}{\mathrm{Tm}}-\frac{1}{\mathrm{Tm}^\circ}\right)+\frac{\ln\Phi_2}{m_2}+\left(\frac{1}{m_2}-\frac{1}{m_1}\right)\Phi_1 = -\chi_{12}\Phi_1^2 \qquad (11)$$

Replacing in the expression (11) the values of Tm and Tm° derived by the Hoffmann-Weeks method, the experimental known values of Φ_1 and Φ_2, and using the literature values [19] of $\Delta H^\circ = 3001$ cal/mol, $V_1 = 44$ cm^3/mol, $V_2 = 75$ cm^3/mol, $m_1 = 454$ and $m_2 = 3245$, the plot of the left side of the Equation 11 versus Φ_1^2 gives a straight line having as slope the opposite of the interaction parameter χ_{12} (see Fig. 3). Notwithstanding a negative value, equal to -0.075, of the interaction parameter has been found, it is so close to zero that does not constitute a reliable proof of an exothermic process of mixing. It is, anyway, a strong evidence of miscibility.

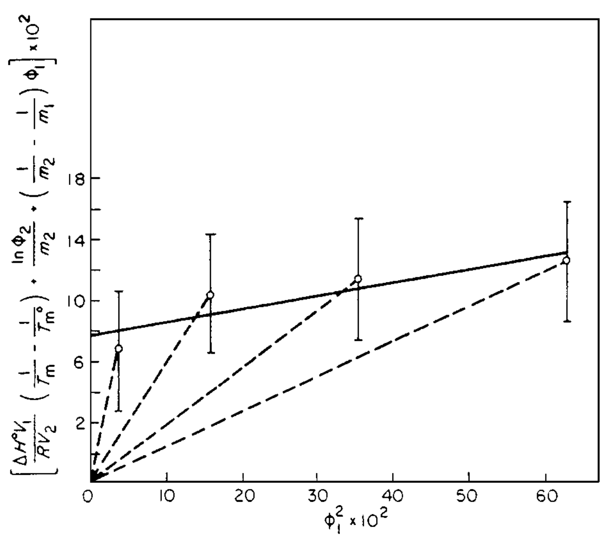


Figure 3 Plot of the left hand side of the Equation 11 against Φ_1^2.

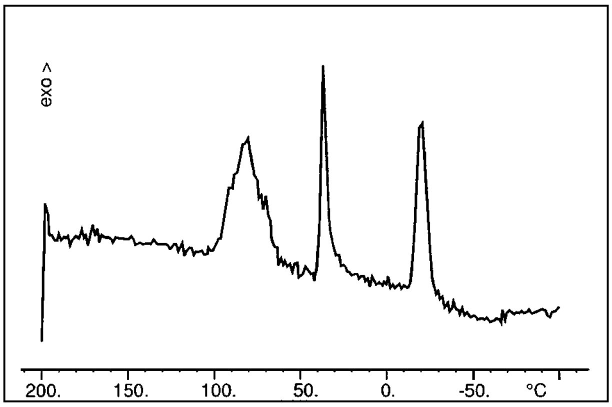
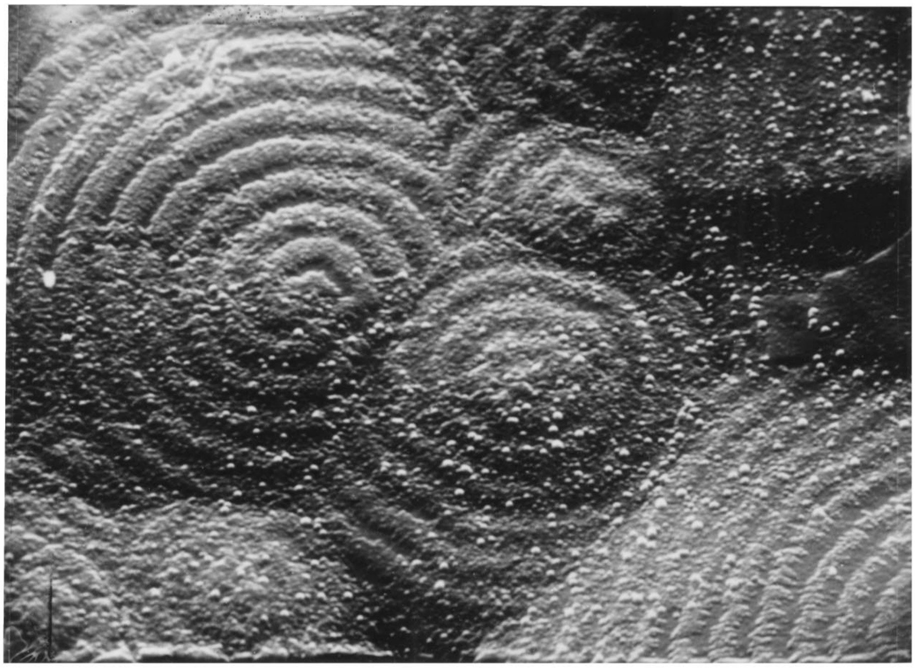
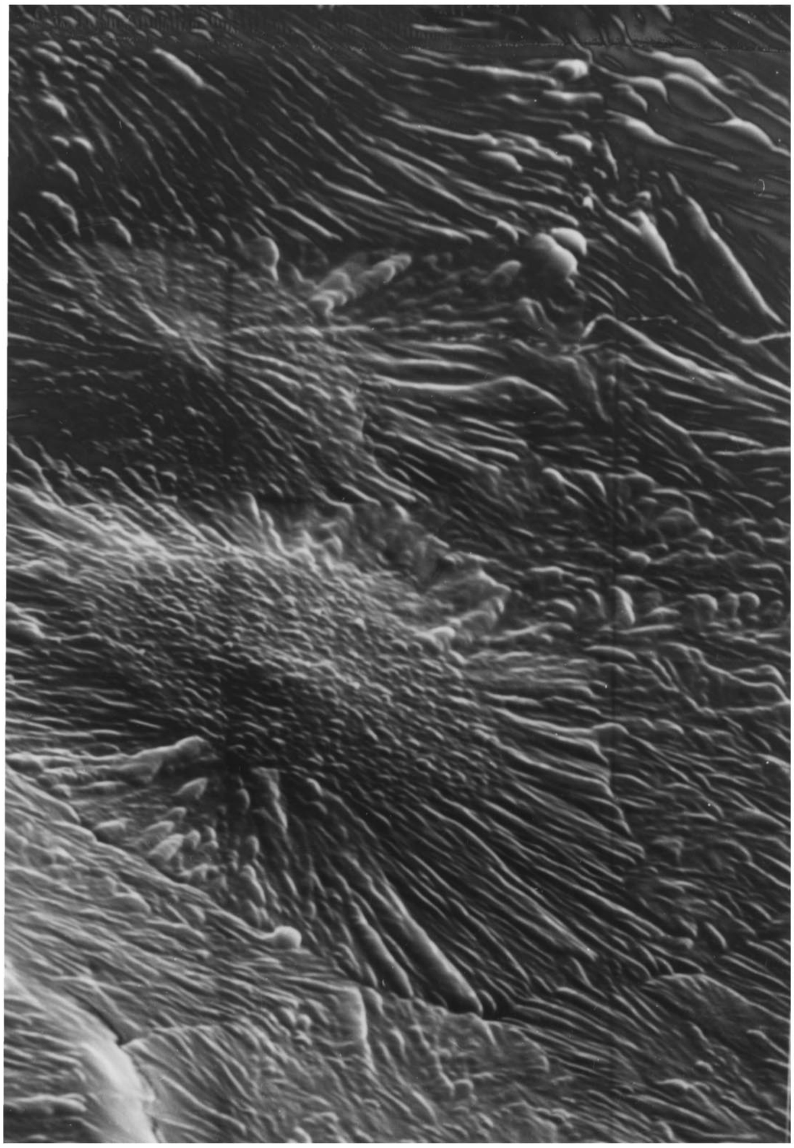


Figure 4 DSC crystallization curve of a PHB/PEO sample containing 40% of PEO. The sample was cooled from 200°C to −100°C at a cooling rate equal to 6 °C/min.

Even if two semicrystalline polymers of a blend are miscible in the amorphous phase, the crystallization of the two components in the same crystalline lattice, that is the so-called co-crystallization, is a very rare phenomenon being only one example reported in the literature for poly(4-methyl pentano) and poly(3-methyl butene-1) [20]. Thus, when the thermodynamic conditions are changed and the field of stability of the solid state is reached, a complex phase separation takes place. In particular, owing to the high purity of the biosynthetic polyester and to its ability to crystallize at temperature higher than PEO crystallization temperature, PHB/PEO blend exhibits the fractionated crystallization phenomenon [21]. This latter consists in the crystallization of a substance in more than one step. As matter of fact, the crystallization of the PEO phase after the PHB crystallization, occurs in two different steps at different supercoolings $\Delta T = \mathrm{Tm} - \mathrm{Tc}$ (about 20°C and 80°C respectively), as shown in Fig. 4. The two different exothermic peaks relative to the PEO crystallization in the DSC curve have been attributed to a homogeneous (high supercooling) and a heterogeneous (low supercooling) nucleation mode respectively. The crystallization mode of PEO is influenced by the crystallization conditions, the thermal history and the crystallization rate previously used to crystallize the PHB phase. The morphology of the blend is, in turn, affected by the crystallization conditions. Observations by means of an optical microscope, have shown that, once the crystallization of the PHB has taken place, the PEO subsequently crystallized is unable to form spherulites. Spherulites are polycrystalline entities, consisting in a radiating array of lamellar fibrils [22]. Each fibril contains both lamellar crystals, e.i. crystals having a dimension much more developed than the other two, and amorphous regions. Thus a diluent may be trapped in interfibrillar (larger scale of distribution) or interlamellar (finer distribution) regions within the spherulites or rejected during the crystallization in interspherulitic domains. The position and the grade of dispersion of a diluent may be predicted by means of the Keith and Padden [23] parameter $\delta = D/G$, being δ the dimensional order of segregation, D the diffusion coefficient of the uncrystallized component and G the linear growth rate of the spherulites. Depending on the comparison of the values of D and G, the amorphous diluent may reside between lamellae, fibrils or even in larger domains within the spherulites. Electronic microscopy has demonstrated that PEO crystallizes in intraspherulitic regions, as shown in Fig. 5, likely because



(a)



(b)

Figure 5 SEM micrographs of PHB/PEO blends, containing 20% of PEO, cooled from melt up to $-100\,^{\circ}$C with a scan rate of $20\,^{\circ}$C/min: (a) Weight average molecular weight of PEO equal to 300,000, magnification 640X; (b) weight average molecular weigh of PEO equal to 20,000, magnification 320X.

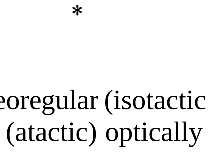
of the high mobility of PEO chains and the slow growth rate of the PHB spherulites. Moreover, by settling the crystallization rate of the PHB, it is possible to control the dispersion grade of the PEO in the blend. Thus, at slower cooling rate implying lower crystallization temperature, the effect of the reduced PEO mobility must prevails on the increase of the radial crystallization rate of PHB.

Choi *et al.* [24] have studied the rheological properties of PHB/PEO blends by means of low shear rate and dynamic flow experiments. The measurements have demonstrated that the rheology of the PHB/PEO blend containing 20% of PHB is superior to that of the pure PHB. For instance, this blend composition has higher values of shear viscosity, first normal stress difference and storage viscosity (modulus) than PHB. For the remaining compositions, the modulus strongly depends on the variation of frequency and it is lower than that of the pure PHB. Moreover, the loss modulus is higher than the storage modulus, implying that the energy dissipation caused by the viscosity is larger than the elastic energy storage. The rheological behavior has been correlated to the morphological feature of PHB/PEO blends. Analysis of the fractured surface of specimens, performed by using scanning electron microscopy (SEM), showed that pure PHB had many vacancies throughout the fracture surface and 20% of PEO exactly fill the vacancies of the PHB matrix. This morphological reason seems to be responsible for the superior rheology performance of the PHB containing 20% of PEO.

The enzymatic degradation of the PHB/PEO blends [18] has been performed in a 0.1 M phosphate buffer solution by adding an extracellular PHB depolymerase. The weight loss of the blend has been monitored as a function of the time. The process involves first the dissolution of PEO in the buffer solution and then the enzymatic and/or hydrolytic degradation of the PHB. The rate of the PHB degradation increases in the blends as a result of the enhanced permeability due to the PEO dissolution.

2.2.3. Poly(hydroxy butyrate/ poly(propyleneoxide) (PHB/PPO) blends

Poly(propyleneoxide) (PPO) is commercial available as low molecular weight polymers. Having an asymmetric atom:



$$[-\mathrm{O}-\underset{*}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}}-\mathrm{CH_2}-]_n$$

it can exist as stereoregular (isotactic or sindiotactic) or non-stereoregular (atactic) optically inactive. Isotactic PPO has a crystalline structure with a planar zig-zag conformation. Atactic PPO is the polymer commercially important and constitutes the subject of this paragraph.

PHB/PPO blends were prepared by solution casting from chloroform using as starting materials PHB (Mw = 400,000) and PPO (Mw = 4,000) supplied by Aldrich and Polysciences respectively [25]. Miscibility studies were performed by observing under an optical microscope the crystallization process of PHB from the blends. Films prepared by squeezing were melted at 200 °C and kept under this temperature for 2 minutes in order to destroy any traces of previous crystallinity. The molten materials is clearly heterophasic, as shown in Fig. 6a where circular domains of PPO are present in the PHB matrix, some of which coalesce after a short time. By falling the temperature, crystallization of the PHB begins. During this process, the spherulites of PHB segregate the amorphous domains of PPO, as shown in Fig. 6b. Moreover, the blends of PHB/PPO examined at the differential scanning calorimeter exhibit two glass transition temperatures at about −62°C and 5°C, in agreement with the values of the neat components.

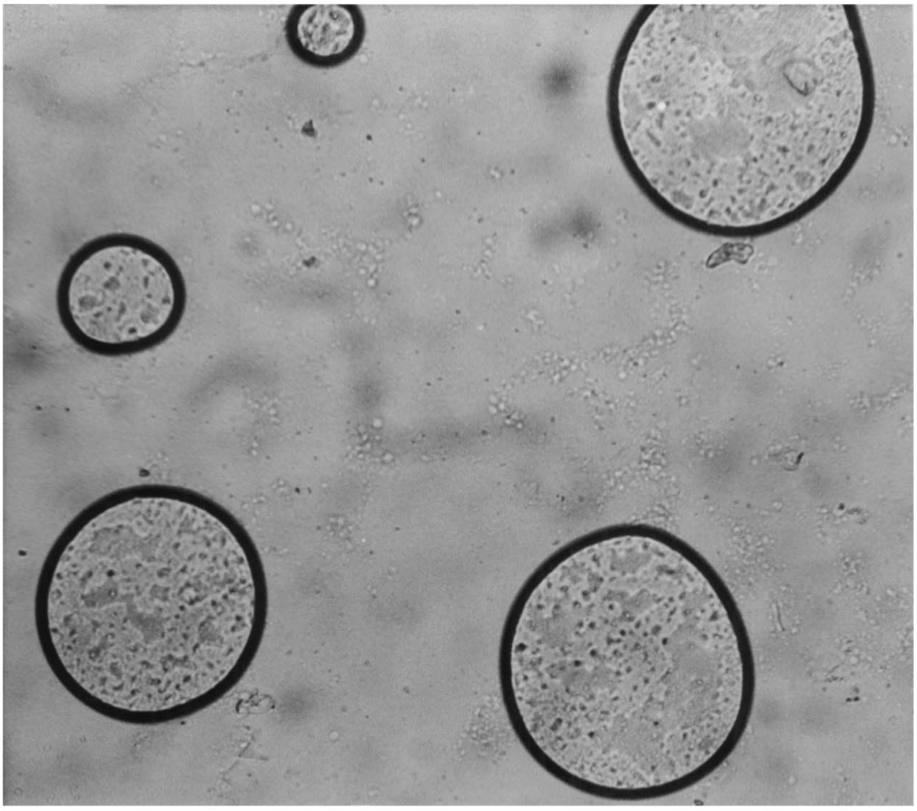
Differently from PPO, atactic PECH, formally derived from PPO by replacing a hydrogen atom with a chlorine atom, has been reported to be miscible with PHB [26].

The different behaviour of the PECH must be attributed to electronic factors, favouring the intermolecular interaction between the two components of the blend, and/or to sterical encumbrance effects. Indeed, the presence of a strongly electron-attractor atom such as Cl, makes likely possible the formation of hydrogen bonds between carboxylic oxygen of PHB and "acid" hydrogen of the lateral group of the PECH. Moreover, sterical effects are correlated to the flexibility of a polymer chain and hence with the free volume, that is the space in a polymer sample which is not occupied by molecules. If two polymer chains are of different flexibility, their mixing will occur with a difference of free volume. The free volume effect causes contributions in both ΔH_M and ΔS_M, which could not cancel in ΔG_M and so fall in the χ_{12} parameter. For instance, a volume contraction brings the molecules of the system closer together causing a positive free volume contribution in χ_{12}, which is thus unfavourable to mixing. The same results may arise for a volume expanding ($\Delta V_M > 0$) mixing of polymers having different free volume and same cohesive energy density. At the same manner of the couple PECH-PPO, polyvinylchloride results miscible with PHB [27], while polyethylene does not.

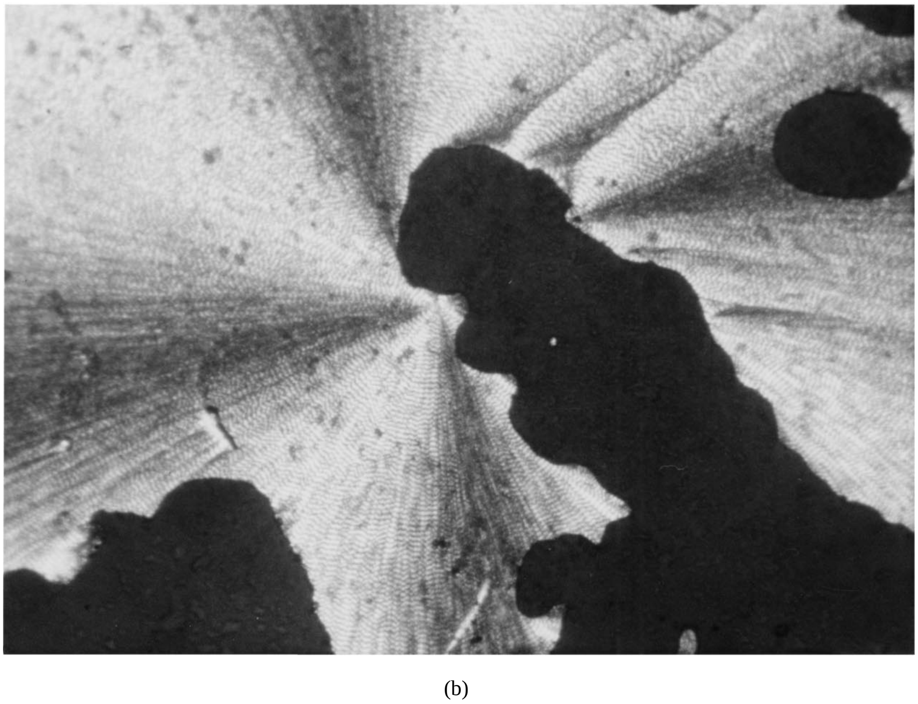
2.2.4. Poly(hydroxy butyrate)/ poly(tetramethyleneoxide) (PHB/PTMO) blends

Poly(tetramethylene oxide)(PTMO) obtained by step-condensation reactions is a waxy solid with low melting point (about 50°C) and glass transition temperature (close to −70°C). The crystalline structure of the PTMO is zigzag planar.

Dave *et al.* [27] have reported that blends of poly (3-hydroxybutyrate-co-16%-3-hydroxyvalerate) and PTMO are immiscible. Work performed in our laboratory on PHB/PTMO (PTMO having weight average molecular weight equal to 2,900) blends, obtained by



(a)



(b)

Figure 6 Optical micrographs of PHB/PPO 90/10: (a) Molten sample at 200 °C (magnification 200X); (b) PHB phase after complete crystallization at 90 °C (magnification 90X).

solution casting from chloroform, has confirmed the presence of two Tg in the differential scanning calorimetric curves. Fig. 7 shows the biphasic appearance of a blend of PHB/PTMO containing 40% by weight of PHB.

2.2.5. Comparison of the miscibility behaviour of PHB with polyethers

Table II reports the solubility parameters of Hildebrand of PHB and polyethers, calculated according to Hoy.

TABLE II Solubility parameters calculated according to Hoy

	δ [(cal/cm^3)$^{1/2}$]	$\delta - \delta_{\mathrm{PHB}}$ [(cal/cm^3)$^{1/2}$]
PHB	9.4	0
PMO	9.9	0.5
PEO	9.1	−0.3
PPO	8.3	−1.1
PTMO	8.6	−0.8
PECH	9.6	0.2
PVC	9.5	0.1
PVAc	9.8	0.4
PMMA	9.0	−0.4

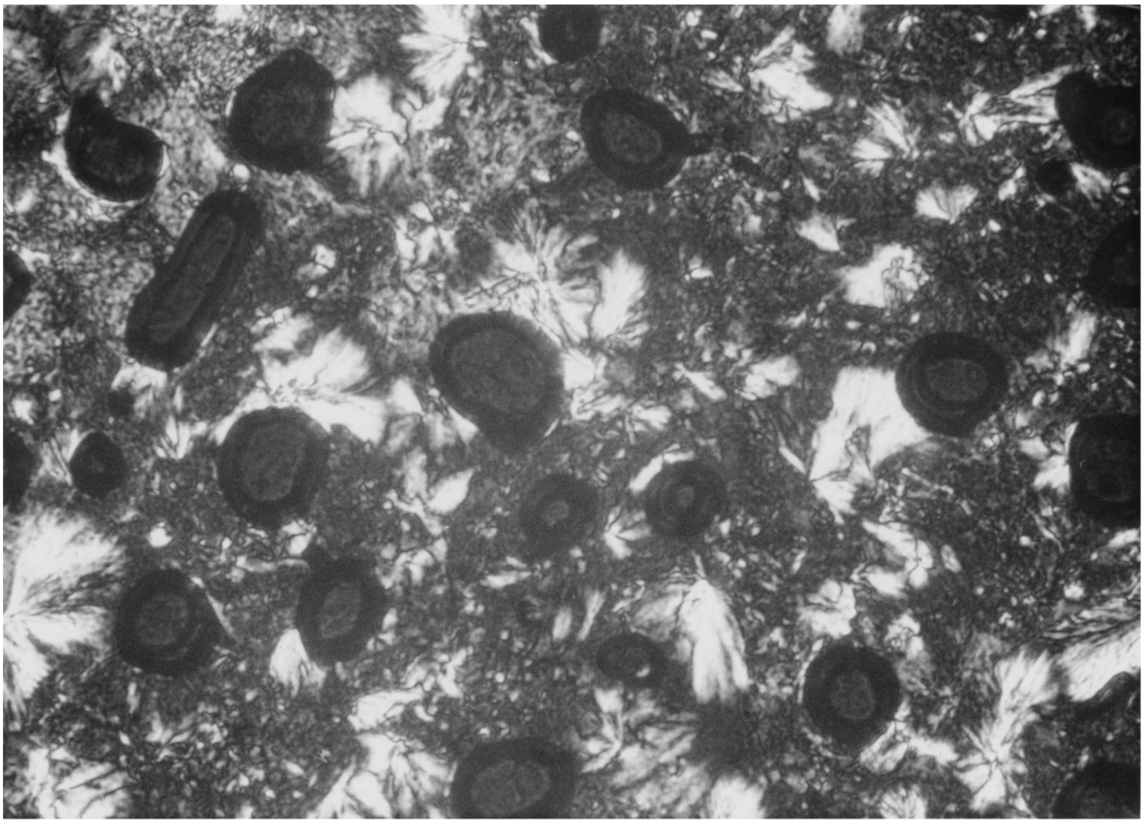


Figure 7 Optical micrograph of PHB/PTMO 40/60 taken at 90 °C after the crystallization of the PHB matrix. Magnification 250X.

TABLE III Attraction molar constants F and molar volume V_r according to Hoy

Group	$F[(\text{cal cm}^3)^{1/2}/\text{mol}]$	$V_r[\text{cm}^3/\text{mol}]$
CH_3	148.3	22.8
CH_2	131.5	16.45
CH	86.0	9.85
C	32.0	4.75
O	115.0	8.5
Cl	207	18.4
COO	362.6	24.6

In such table, also the solubility parameters of PECH, PVC, PVAc and PMMA are reported. The group contributions used for the calculations of the solubility parameters are also reported in Table III. The values of the solubility parameters seem to agree with the experimental miscibility findings. Indeed, among the polyethers, only PEO exhibits a solubility parameter close to that of PHB. Slightly different chemical formulae or tacticity may change the miscibility behaviour because of influence on the values of both enthalpy and entropy of mixing. The equilibrium between these two terms seems to be altered by little structural changes. The miscibility of two polymers is often attribute to the formation of specific strong interactions (such as dipole-dipole, hydrogen bond etc.) between the macromolecules.

PHB can form hydrogen bonds as proton acceptor through the carbonylic oxygen, while, because of the low acidity of the hydrogen atoms in α-position with respect to the carbonyl group, interactions as proton donor are much less likely to occur. However, miscibility may be caused by entropic reasons even if enthalpically unfavoured process of mixing, that is endothermic, are involved. It is not easy, in absence of clear experimental evidences, to decide if a mixing is due to enthalpic or entropic reasons. For example, in PHB/PECH and PHB/PVC, PHB could form hydrogen bonds through the carbonyl group with the hydrogen atoms having low electronic charge density and linked to the carbon atom involved in the C-Cl bound of PVC and PECH. This strong interaction could be responsible for their miscibility. Instead, polyethers have not hydrogen atoms able to form hydrogen bonds and so they can only act as proton acceptor. Thus no strong hydrogen bond are expected between PHB and polyethers. Moreover, PVAc is a weak proton-donor substance and thus the different miscibility behaviour of PVAc and PMMA is unlikely due to the absence of hydrogen atoms in α to the carbonyl group in PMMA. In other words, the thesis that PHB is miscible with those polymers able to act as proton donor (PVC, PECH, PVAc) and immiscible with polyethers and other polymers (such us PMMA) that cannot behave like that, is not completely satisfactory. Pouchly and Biros [28] have provided evidence that the miscibility of PVC with many other polymers involves the chlorine atoms of the PVC and the oxygen of the counterpart. Indeed, they have shown that small-molecules of chlorinated hydrocarbon enthalpically mix with ethers, independently if they have or not a hydrogen attached to the carbon bearing chlorine. Therefore, the miscibility of PVC with polyethers and polyester has been explained by the formation of charge-transfer (CT) interactions where the oxygen is the electron donor and C1 the acceptor. The CT interactions have also been brought up by Cruz *et al.* [29] for polyester-polycarbonate blends. In agreement with the mentioned authors, the miscibility of PVAc and chlorinated polyethers with PHB may be attributed to CT interactions.

Concerning PHB and non-chlorinated polyethers, it is possible to assume that the mixing is endothermic and so miscibility is unlikely to occur, except for PHB and PEO pair. The miscibility of PEO with PHB should be discussed in terms of the contribution of weak dipolar interactions on the entropic term of mixing. Indeed, mixing could be aided by a conformational change of PEO in presence of PHB. This phenomenon has been observed in PEO/PMMA blends [30], where PMMA forces PEO molecules to adopt a zig-zag planar conformation. An other evidence of the entropic nature of the PHB/PEO miscibility is the influence of the molecular weight on the mixing process. As matter of fact, two glass transition temperatures are obtained for intermediate compositions (from 40 to 60% of PEO) of PHB/PEO blend having higher molecular weight (Mw(PEO) = 300,000)). The partial miscibility caused by an enhancement of the molecular weight is a theoretically predicted consequence(1) of the endothermic process of mixing, while opposite influence have on esothermic processes the molecular weight increasing.

The variety of miscibility behaviours allows to realize that a competition between enthalpic and entropic terms exists and just a little structural change may affect their match, influencing not only the miscibility but also the reasons of the miscibility themselves.

2.3. Poly(hydroxy butyrate)/poly(epichlorohydrin) (PHB/PECH) blends

Atactic PECH, i.e. poly(oxy-2-chloromethyl-ethylene), is an uncrystallizable polymer whose blend with PHB has been prepared by solution casting from dichloromethane [26] in a wide range of composition. The thermal and microscopic analysis of the blends has shown a single glass transition temperature, which values fit the Fox equation. Moreover, the melting point of the PHB decrease with blending and the interaction parameters coming out from the Equation 11 is equal to −0.068. The used values of the variables were the following: $\Delta H = 12.6$ KJ/mol, $V_1 = 80$ cm^3/mol, $V_2 = 76$ cm^3/mol, $m_1 = 1742$, $m_2 = 7565$. These findings suggest that PHB and PECH form a miscible blend in the amorphous phase.

Microscopy observations have not shown phase separation even in the solid state. As matter of fact, after the crystallization of the PHB nor segregation of the PECH component in interspherulitic contact zones, neither separate intraspherulitic regions of PECH have been revealed, suggesting that the uncrystallized component is incorporated in the interlamellar or interfibrillar regions of PHB spherulites. Moreover, the growth rate of spherulites, at constant crystallization temperature, decrease with the increasing of PECH percentage. The addition of the PECH to PHB also causes a reduction of the overall crystallization rate calculated by applying the Avrami equation [31]:

$$X_t = 1 - \exp(-kt^n) \qquad (12)$$

where X_t is the crystallinity developed at the time t, k is the kinetic constant of the growth and n is a parameter depending on the geometry of the growing crystals and on the nucleation process. The global crystallization rate is the inverse of the semitransformation time, $t_{1/2}$ defined as the time at which 50% of the final crystallinity has been developed, i.e. $t = t_{1/2}$ for $X_t = 0.5$.

Small angle X-Ray scattering (SAXS) studies on PHB/PECH blends [32] provided information about the localization of the amorphous component in the spherulitic structure of the crystalline polymer. The scattering observed for the blends resulted from the superposition of the scattering due to the crystalline regions (made up by alternate stacking of lamellae and thin amorphous layers) and from the amorphous PECH inhomogeneity placed outside them. Glatter and Debye-Bueche approaches were applied to obtain structural information. The result evidenced that the PECH molecules are dispersed at the molecular level in interfibrillar zones, where they can assume a random-coil conformation. Moreover, the blends were annealed (i.e. kept for long time at a temperature between the crystallization and the melting temperatures) in order to investigate the influence of this thermal treatment on the crystalline structure. It has been assessed that the annealing treatment promotes a general perfectioning and rearrangement of the sample morphology, enhancing the crystallinity and the crystal dimensions of PHB in the pure state and in the blends, likely favouring the trend of the PECH molecules to assume a globular conformation.

Enzymatic and bacterial degradation of the blends were also investigated [33, 34] leading, according to the experimental conditions, to opposite results. Kumagai and Doi [33] found that the biodegradability and the tensile properties of PHB are markedly improved by blending with atactic PECH. Indeed, the presence of PECH promotes the enzymatic degradation of PHB in buffer solutions, likely because of a easier permeation of the PHB depolymerase into the films.

Sadocco *et al.* [34] utilized the *Aureobacterium saperdae* to degrade PHB/PECH blends of different composition. The culture growth was followed by spectrophotometric measurements of the optical density at 540 nm. The polymer degradation was determined by measuring the weight loss of the films after bacterial growth. The experimental procedure requested periodic remotion of samples, washing with distilled water several times and drying up to reach constant weight. The growth rate of *Aureobacterium saperdae* were found to decrease with increasing the PECH content in the blend, up to drop to zero when the percentage of PECH is 60(wt.%). The compromised degradation of PHB by using *Aureobacterium saperdae* in the blends have been attributed to the reduced accessibility of the PHB to the bacteria.

2.4. Poly(hydroxy butyrate)/poly(vinyl acetate)-poly(vinyl alcohol) (PHB/PVAc and PHB/PVAl) blends

Like PEO and PECH, the PVAc and its derivatives by hydrolysis, such as the poly(vinyl alcohol), are also miscible with PHB and its copolymers PHBV in the melt. As matter of fact, PHB/PVAc blends prepared by film casting are characterised by only one Tg, composition dependent and intermediate between that of the PHB and PVAc [35]. Moreover, at a given temperature, the growth rate *G* of PHB spherulites decreases with increasing PVAc content and a drastic depression of the equilibrium melting temperature of PHB is found. This indicates that PHB spherulites grow in equilibrium with a one-phase melt. The phase structure in the solid state, illustrated in Fig. 8, is characterized by the presence of a homogenous amorphous phase situated mainly in interlamellar regions of crystalline PHB and consisting of PVAc molecules and uncrystallized PHB chains. The secondary nucleation process is influenced by the presence in the PHB melt of PVAc molecules acting as diluent. According to the latest theory of polymer crystallization [36], the growth process of plain PHB crystals, conforms to regime III, whereas that of crystals growing from a melt blend, at the same Tc, conform to regime II. This last finding is certainly related to the lower melting point of PHB crystallized from blends compared with that of plain PHB.

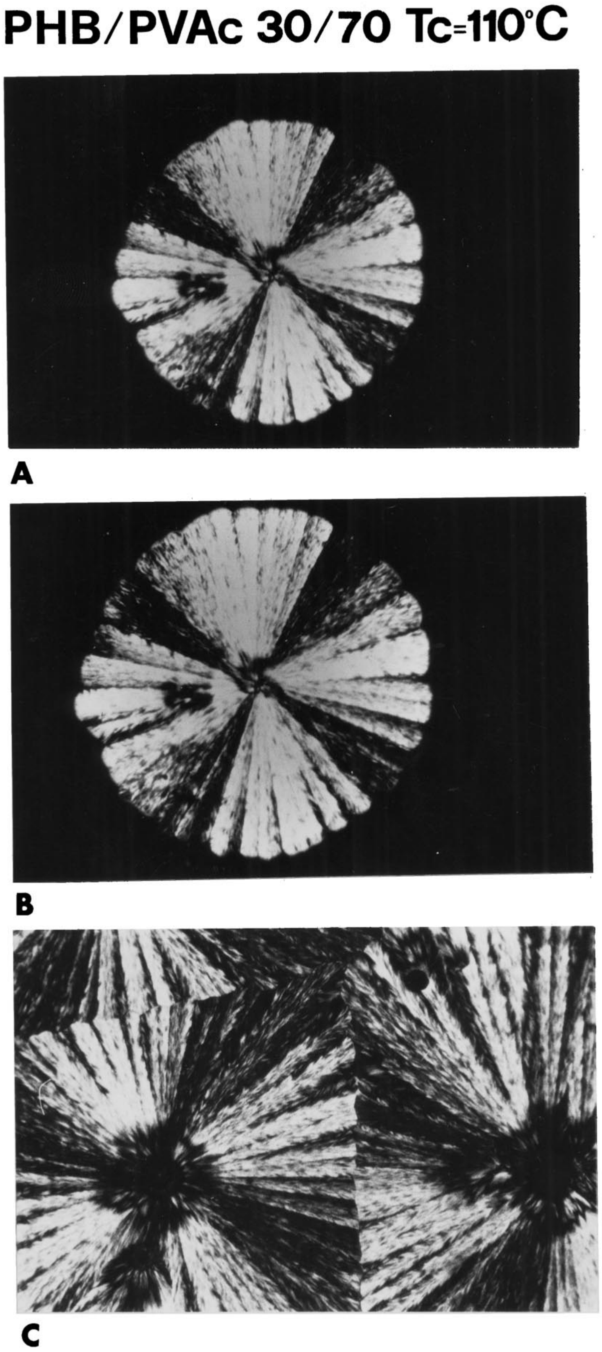


Figure 8 Optical micrographs (crossed polars) of growing PHB spherulites at Tc = 110°C (A and B) after completation of crystallization (C) for PHB/PVAc 30/70 (w/w) blend.

Naoko Yoshie *et al.* [37] have examined the thermal behaviour and miscibility of PHB/PVA1 blends films by means of DSC, NMR and density measurements. They observed that the melting temperature Tm of the PHB phase decreased as PVA1 content increased, whereas Tm of the PVA1 phase remained almost unchanged. The crystallinity of the PHB in the blends also decreased with increasing PVA1 percentage indicating that the thermal behavior of the PHB was influenced by the presence of PVA1. Miscibility in the amorphous phase of the blend has been analysed by density measurement and solid-state ^{13}C NMR technique. Experimental data indicated that miscibility between PHB and PVA1 enhances with increasing PVA1 content.

2.5. Poly(hydroxy butyrate)/poly(methyl methacrylate) (PHB/PMMA) blends

Blends of PHB/PMMA have been prepared by melt mixing and the miscibility of the two components has been deeply investigated [38, 39]. Yoon *et al.* [39] have utilized chloroform vapour sorption to measure the polymer-polymer interaction parameter by means of the following Flory-Huggins equation:

$$\ln(P/P_0) = \ln\Phi_1 + (1+\Phi_1) + (\chi_{12}\Phi_2 + \chi_{13}\Phi_3)(1-\Phi_1) - \chi_{23}\Phi_2\Phi_3 \quad (7)$$

where P_0 is the vapour pressure of chloroform at the sorption temperature; Φ_1, Φ_2 and Φ_3 are the volume fractions of the chloroform, PMMA and PHB respectively; χ_{12}, χ_{13} and χ_{23} are the interaction parameters of PMMA/chloroform, PHB/chloroform and PMMA/PHB respectively.

By using sorption data, the interaction parameters have been calculated by the Equation 7:

$$\ln(P/P_0) = \ln\Phi_1 + (1-\Phi_1) + \chi_{1i}\Phi_i^2 \quad (i = 2, 3)$$

An average parameter interaction for PHB/PMMA blend of 0.195 has been found and it seems to be almost independent on the activity of the chloroform.

A further evidence of the immiscibility of the PHB/PMMA system is the presence of two distict Tg. As matter of fact, both DSC thermograms and viscoelastic spectra of PHB/PMMA blends with a PHB content less than 20% show only a glass transition temperature lower than that of the pure PMMA and composition dependent; a second transition, corresponding to the glass transition temperature of pure PHB, appears when the PHB content is greater than 20%, together with a composition independent glass transition corresponding to a mixture 20/80 of PHB/PMMA. Moreover, the Tg of the PHB phase increases while that of the PMMA slightly decreases with increasing the second component, implying slight and partial mixing between the two phases.

M. Scandola *et al.* [38] have assessed that blends containing up to 20 wt% of PHB are single-phase in the amorphous state, with a composition dependent glass transition temperature. Blends richer in PHB undergo a demixing in pure PHB coexisting with a constant composition PHB/PMMA (80/20) mixture. As consequence of this partial miscibility, the nucleation of the PHB spherulites in the blend is retarded and their growth rate becomes lower as the PMMA content increases.

2.6. Poly(hydroxy butyrate)/ poly-ε-caprolactone (PHB/PCL) blends

Blends of poly-ε-caprolactone and PHB or PHBV are very interesting due to their technological properties and their inherent biocompatibility and biodegradability. Kumagai and Doi [40] have investigated the miscibility, morphology and biodegradability of such blends. These authors, in agreement with subsequent studies performed by Owen and Gassner [41], found that PHB and PCL are immiscible in the amorphous state. On the contrary, miscibility have been reported by McCarthy *et al.* [42], likely because of the very low molecular weight of the utilized PCL.

Although PHB and PCL are immiscible on the molecular scale, a small amount of solubilization of one component into the other has been suggested to explain the depression of the melting point in the blends [41].

In general, PCL acts as a polymeric plasticizer (i.e. it lowers the Tg and hence the elastic modulus making a material more flexible). From dynamic-mechanical measurements, it has been inferred that for a PCL content of 60% and above, the PCL phase forms a continuous matrix, with PHB spherulites embedded in it. The mechanical behaviour of the blends then dominated by the ductile PCL matrix. Instead, for composition with less than 60% of PCL, the PHB phase becomes continuous. However the inclusion of soft PCL does not catastrophically lower the rigidity of the sample.

Notwithstanding PCL and PHB physically blended are compatible, no synergetic effects have been found that could be exploited to obtain a material with better performances than those of the individual components. To induce compatibilization the approach of reactive blending of PCL and PHBV has been undertaken [43]. The two polymers have been melt mixed by adding peroxide (i.e. dibenzoylperoxide (DBPO) and dicumylperoxide (DCPO)). According to the type of peroxide, two different temperatures were employed in the blend preparation. The same blend compositions have been prepared in absence of peroxide for comparative purpose. Changes of the thermal properties of the PHBV (in particular the apparent melting point Tm) suggested that DCPO induces some structural change in PHBV. As matter of fact, PHBV is longer soluble in chlorinated solvents after DCPO treatment, indicating the formation of crosslinks by radicalic reactions. The same phenomenon is present in PHBV-matrix blends, while it is absent in PCL-matrix blends, since the peroxide seems to have no influence on the PCL melting point as well as on its solubility characteristics.

Beyond calorimetric analysis, spectroscopic and morphological investigations of the reactive PHBV/PCL blends have evidenced the existence of a graft copolymeric phase in the interfacial regions between the polymers. Furthermore, the decrease of the elastic modulus of the blends obtained with DCPO has been correlated to the larger plastic deformation of PCL particles in such blends.

Biodegradation study on injection moulded PHBV/PCL samples were performed under municipal solid waste composting conditions according to the Laboratory Scale Composting Test Method [44]. All samples completely disappeared after composting for 21 days. Moreover, it has been observed that the biodegradation increases rapidly with increasing PCL content in the blends. This acceleration may be caused by the decreasing of crystallinity of the whole samples and/or by the modification of the surface.

2.7. Poly(hydroxy butyrate)/ ethylene-propylene rubber (PHB/EPR) blends

In the case of blends constituted by PHB and EPR, a complete immiscibility in the melt was observed [35]. Particularly, the glass transition temperature values (Tg) for both PHB and EPR components do not vary in the blend. Moreover, no change in the radial growth rate G of spherulites occurs with increasing EPR content, whereas the crystallinity of the PHB phase is only slightly influenced by blend composition. As shown in Fig. 9, the spherulites of PHB in the blend grow in presence of a two-phase melt consisting of PHB molten containing EPR domains as dispersed phase. During their growth the EPR particles are first ejected and then occluded in intraspherulitic region according to a mechanism described by Martuscelli [45] in the case of isotactic polypropylene/polyisobutylene and isotactic polypropylene/low density polyethylene blends. The resulting morphology consists in PHB spherulites occluding particles of EPR in intraspherulitic regions.

The tensile properties of PHB/EPR and PHB/modified-EPR blends have been examined by Abbate *et al.* [46]. EPR was modified by inserting i)succinic anhydride (EPR-g-SA) and dibutylmaleate (EPR-g-DBM) groups, ii) ethylene vinylacetate copolymer (EVA) modified by a partial transformation of acetate groups in alcoholic groups. Better mechanical properties (elongation and tensile strength) have been found in the case of blends containing modified rubber with respect to PHB/unmodified EPR blends.

2.8. PHBV/poly(butyl acrylate) blends

An attractive route to impact modification of PHBV by a reactive blending method involves the use of acrylate rubber, such as poly(butyl acrylate)(PBA). A method in which the PHB (or PHBV) powders, as they came out from the bacterial polymerization and subsequent

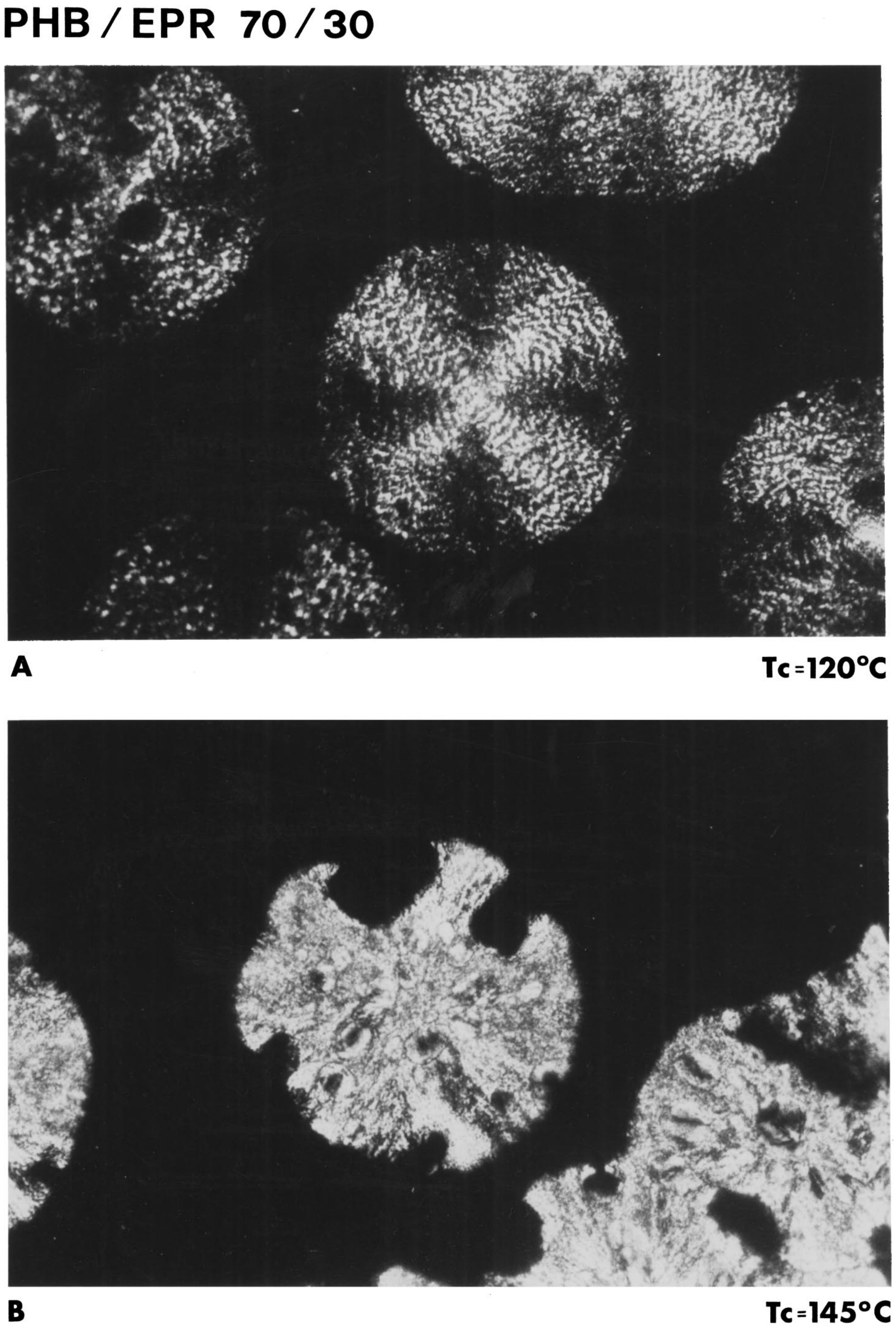


Figure 9 Optical micrographs (crossed polars) of growing PHB spherulites of PHB/EPR 70/30 blend at different Tc : (A) Tc = 120 °C; (B) Tc = 145 °C.

purification, are thoroughly mixed with proper amounts of acrylate monomers and free-radical initiator has been developed by Martuscelli [47], resulting in a minor elastomeric phase intimately dispersed in the polyester matrix. Blends were prepared by mixing 70 g of polyester powder with 30 g of acrylic monomer, into which 60 mg of benzoyl peroxide (0.2 wt. % of acrylic monomer) are dissolved. The mixture is gently stirred for 24 hours at room temperature. Subsequently, this homogeneous mixture is warmed to 90–100 °C and allowed to remains at this temperature under stirring, for more than 24 hours, to permit acrylate polymerization.

The impact properties obtained by Charpy impact tests on sharply notched samples of PHB and PHBV containing 4% of valerate (PHBV4) and on their blends with PBA, demonstrated that a positive influence is exerted by the rubber on the fractured toughness of microbial polyesters. The effect is particularly marked at temperatures close and above room temperature. In fact, while PHB and PHBV4 are brittle at room temperature, their blends are much more ductile. The enhancement of properties is less pronounced on PHBV4, because the addition of valerate comonomer is already effective in the induction of ductility [48].

Swelling experiments have been carried out on several blends in order to investigate the possible formation of crosslinks between PHBV and PBA. It is, in fact, well known that the addition of peroxides to aliphatic polyesters, like polycaprolactone, can induce the formation of macroradicals by extraction of labile hydrogen from the polymeric backbone [49]. It is conceivable that PHBV can undergo similar reactions leading to graft copolymers in presence of BA monomer and/or growing PBA macroradicals. The microbial degradation of plain PHBV and PHBV/PBA blends with normalized has been studied by Avella *et al.* [50].

Aureobacterium saperdae cultures, where the only carbon source was the polymeric sample, were used to degrade pure PHBV4 and PHBV4/PBA blends (80/20 and 70/30 weight ratios). The micro-organism was precultured overnight on 0.1% LB broth, about 3.5 mL aliquots of this culture were used to inoculate 500 mL flasks containing 100 mL of mineral medium (mineral medium compsoition: 1mg/mL NH_4Cl, 0.5 mg/mL $MgSO_4{\cdot}7H_2O$ and 0.005 mg/mL $CaCl_2 \cdot 2H_2O$ in 66 nM KH_2PO_4 (pH = 6.8). The flasks were added with polymeric samples and incubated at 30°C, under shaking, for 15 days. In addition, control experiments were run to verify chemical hydrolysis of polymeric samples immersed in mineral medium and no weight loss was found after 15 days. Cultures at different species of polymer degradation percentages were stopped and the samples were used to perform various morphological analysis. The percentage of polymer degradation was determined by measuring the weight loss of the sample during bacterial attack. Having preliminary checked the non-biodegradability of PBA phase, the weight loss was normalized on the PHBV content, thus obtaining the percent of degradation in blends. Polymer samples were removed from the culture medium at different time lengths, washed several times with distilled water and dried under vacuum up to constant weight. The thickness of the polymeric samples was measured before and after the bacterial attack. Since decrease of the thickness during the biodegradation corresponds to the percentage of weight loss, the polymer erosion must take place via surface dissolution. SEM analysis of the surface of pure PHBV4 after bacterial attack evidenced the homogeneous superficial erosion caused by the degradative enzymes, while no change took place inside the sample. During bacterial degradation of the PHBV4/PBA blend 80/20, pieces of PBA component released in the culture were macroscopically visible. As a consequence of the bacterial attack, the PHBV4 present on the surface was eroded and pieces of the dispersed PBA component were released, allowing new PHBV4 zones to be accessible to the degradative enzymes (see Fig. 10).

2.9. PHBV/polysaccharide blends

Poly(hydroxybutyrate-co-valerate) has been blended with cellulose and starch derivatives [51, 52]. In particular, thermoplastic cellulose esters such as cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP), have been found to form miscible blends with PHBV in the amorphous phase. These blends offer the opportunity to show as the miscibility criterion of a single Tg should be applied to be on the safe side. As matter of fact, PHBV/CAB up to 50% of CAB exhibit only one low temperature glass transition both in DSC measurements and dynamic-mechanical analysis. At intermediate compositions, ranging between 50 and 70% of CAB, a broad glass transition ideally separable in two next steps by a flexural point, has been found. Finally, for blend compositions with CAB percentage larger than 70%, a single glass transition at higher temperature is detectable. The higher glass transition temperature values follow the Fox equation in the range 0–50% of PHBV. This situation apparently fit the case of partial miscibility of PHB and CAB, with a separation of pure PHBV at CAB contents less than 30%. However, a more careful analysis leads to a different explanation. Indeed, the heights (ΔC_p, being C_p the heat capacity) of the glass transitions permit the calculation of the composition of unknown multiphase by means of the relationships:

$$\Delta C_1 = x_\mathrm{A}^1 \Delta C_\mathrm{A} + \left(1 - x_\mathrm{A}^1\right) \Delta C_\mathrm{B}$$

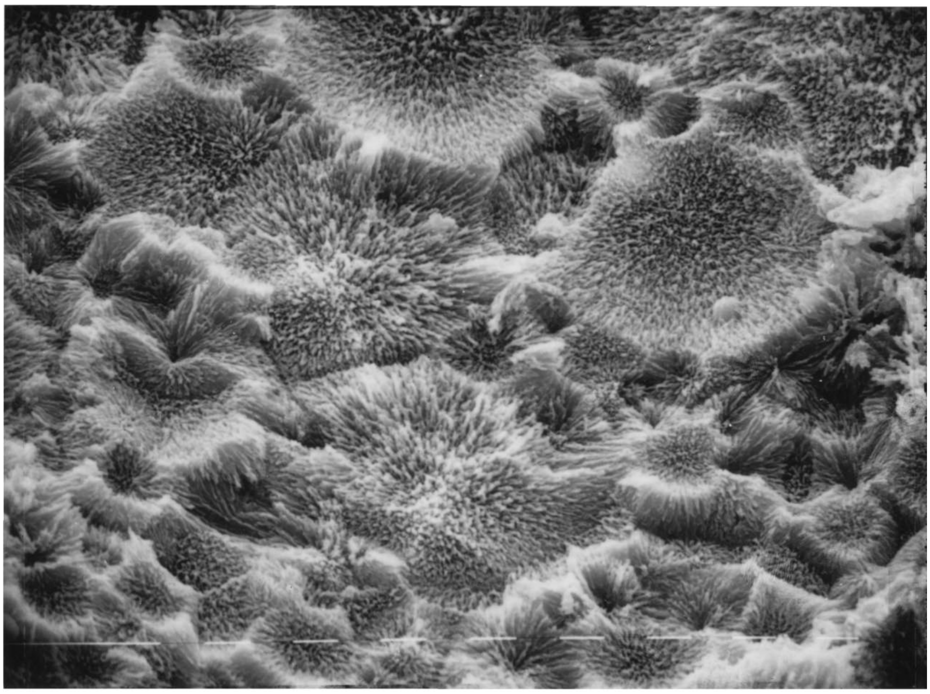
$$\Delta C_2 = x_\mathrm{A}^2 \Delta C_\mathrm{A} + \left(1 - x_\mathrm{A}^2\right) \Delta C_\mathrm{B}$$

where ΔC_1 and ΔC_2 are the heights of the glass transition steps related to phase 1 and 2, ΔC_A and ΔC_B are the specific heat capacity changes corresponding to the glass transition of the pure components A and B, and x_A^1 and x_A^2 are the molar fraction of the component A in the phases 1 and 2 respectively.

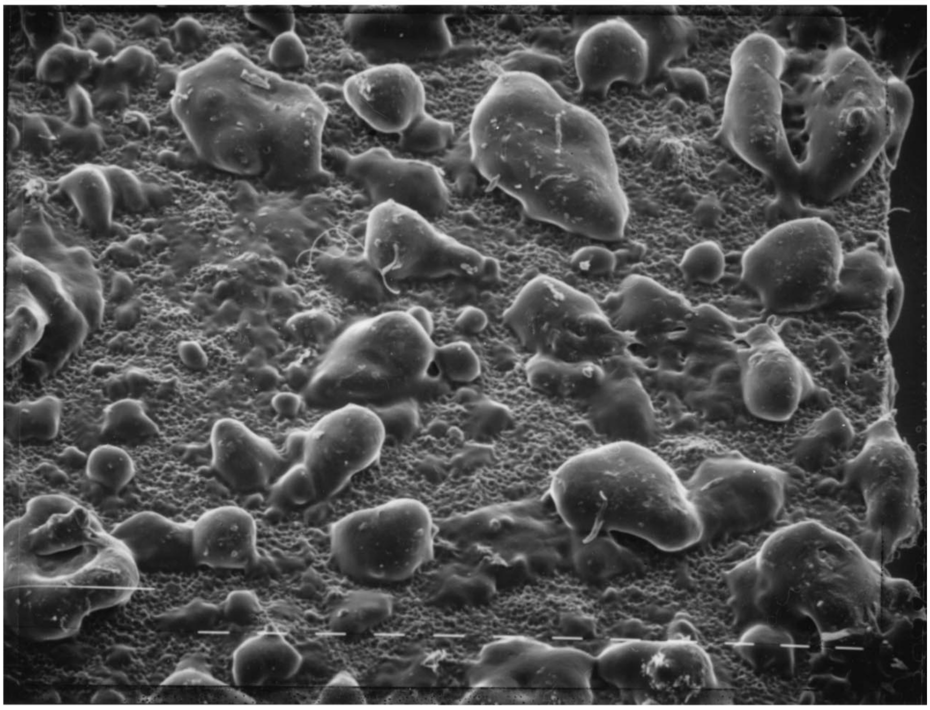
Being the ΔC_p value associated to the low temperature transition much larger than that expected on the basis of the PHBV content, it comes out that both the components should contribute to the low temperature glass transition of the blends. Thus the hypothesis of partial miscibility of PHBV and CAB with separation a pure phase of PHBV must be excluded.

The behaviour of PHBV/CAB blends has been delucidated by carbon ^{13}C-NMR studies [52]. These studies demonstrated that PHBV and CAB are miscible in the amorphous phase and two glass transitions are revealed owing to the existence of dynamic heterogeneity. These heterogeneity reflect different molecular mobilities of the blend components, even if these latter experience equivalent or average free volumes [53]. As matter of fact, the equivalence of free volumes does not necessarily imply a single glass transitions temperature, as demonstrated by Miller *et al.* [54].

When CAB is the major component, the PHBV crystallization is completely inhibited and no trace of crystallinity is revealed even after months of blend storage at room temperature. Blends richer in PHBV crystallize by storing at ambient temperature, becoming opaque. The mechanical properties of blends containing 20–50% of PHBV reflect, of course, the amorphous character of such blends. Indeed, in the range 20–50% of PHBV the elastic modulus and the tensile strength decrease with increasing PHBV percentage.



(a)



(b)

Figure 10 SEM micrographs of samples after microbial attack: (a) PHBV4 50% deg. (scale bar 10 μm, magnification 640X); (b) PHBV/PBA 80/20, 50% deg. (scale bar 100 μm, magnification 40X).

The tear strength is almost constant, while the elongation at break remarkably increases. Above 50% of PHBV the elastic modulus, the tensile strength and the tear strength increase while the elongation at break drops significantly. In particular, a synergetic effect is found for PHBV/CAB compositions above 70% of PHBV.

PHB and PHBV copolymer have also been combined with starch [55, 56], an inexpensive biodegradable filler produced in surplus for food needs.

Owen and Koller [55] have investigated the structure and the mechanical properties of meltpressed sheet of PHB and PHBV filled with various amounts of maize starch granules. No further component such as a bonding agent was used. The addition of starch to the PHB and PHBV causes a decrease in breaking strain and stress and an increase of the elastic modulus. Thus the PHB becomes even more brittle by addition of starch. This latter increases the crystallinity content of the matrices without changes the nucleation density of the spherulites. Shogren [56] has shown that poly(ethyleneoxide)(PEO)-coated granular starch causes a large improvement in tensile properties of PHBV/starch composites over uncoated starch. PEO interfacial layer seems to enhance the degree of adhesion between the starch and the PHBV and/or increase the toughness and resistance to crack propagation around starch granules.

Biodegradation studies on PHBV blended with native cornstarch and with cornstarch precoated with PEO have been carried out by Imaman *et al.* [57]. The weight loss of the samples were measured and the deterioration in tensile strength tested. The extend and rate of weight loss were similar in PHBV pure and in PHBV containing starch, while the weight loss was slowest in PHBV blends prepared with PEO-coated starch. The rate of deterioration of mechanical properties was highest for pure PHBV and less for PHBV/PEO-coated starch. By means of FTIR spectroscopy, it has been assessed that a more extensive starch degradation occurs as the starch content increases, while the PHBV in the blends becomes less susceptible to the enzymatic attack.

2.10. PHBV/natural fibers

In the last year natural fibers have emerged as renewable and cheap reinforcement for composite materials [58]. The earliest natural fiber/polymer composites were obtained by reinforcing thermosetting matrices such as epoxy, phenol-formaldehyde and polyester resins [59–62]. These studies showed the feasibility of utilizing abundantly vegetal fibers in composites not designed for particular applications. Not long after, attemps were done to incorporate natural fibers in thermoplastic polymers, such as polypropylene, and several fiber or matrix treatments [63, 64] were proposed in order to improve dispersion, adhesion and compatibility. For instance, Felix and Gatenholm [63] investigated the influence of a modifying agent (polypropylene-maleic anhydride copolymer) on cellulose fiber/polypropylene composites, demostrating the improvement of mechanical properties as consequence of better adhesion between the two phases. Lignocellulosic-based natural fibers possess high specific properties, good mechanical properties and are abundantly available [65]. In the light of the previous investigations, biodegradable thermoplastic composites reinforced with wheat straw and hemp fibers were studied [66]. The aim of this work was to reinforce PHB by replacing more expensive and non-biodegradable conventional reinforcements (glass, asbestos, carbon etc.).

In order to obtain natural fibers richer in cellulose content and more reactive, they were submitted to a pretreatment by using an innovative process called Steam Explosion Process (SEP) [67]. This procedure allows:

1. Fractionation of lignocellulosics into their components to obtain either neat cellulose, or cellulose associated with a small quantity (5–10%) of hemicelluloses and lignin;
2. Changes in the morphology and structure of the lignocellulosic components to enhance their faculty to form interfacial bonds with thermoplastic polymers.

The morphology and structure of wheat straw and hemp undergo marked changes after SEP. In fact, the release of pressure induces an extensive fractionation of the solid matrix, and an autohydrolysis reaction induces a large reduction of the lignin and hemicellulose content, without markedly depolymerizing the cellulose chains [60–69]. It was observed that at low pressure and short reaction times a gradual defibration of material took place, the vessels and epidermal tissues of the straw being almost competely destroyed (see Fig. 11a,b,c). After SEP the X-ray diffractograms (Fig. 12) show an increase in the crystallinity degree of the straw celullose as well as an increase in the crystal dimension, as evidenced by the sharpening of the reflection related to the (002) crystallographic plane.

In summary SEP destroys the morphology of natural fibers, eliminates most lignin and hemicellulose components, and increases the anisotropy of cellulose fibers, permitting the use of these fibers as reinforcing fibers with a high capacity to interact with thermoplastic polymers. In this study, PHB, molecular weight, MW = 400,000, was supplied by ICI and used as received. The wheat straw (Italian and EC sources), 100 g per sample, was steam exploded in laboratory apparatus (Deltalab EC 300) as follows. The straw or hemp was put into the vessel and heated with saturated vapor at 230°C (28 kgf/ cm^2) for a residence time of 120 s. At the end of this time the sudden release of pressure leads to an adiabatic expansion of the water present in the wood tissues. The straw fibers were discharged into the cyclon receiver, collected and placed in an oven (80°C) for a period of time sufficient to release the water adsorbed during the steam explosion process, after which the straw was packed in polyethylene bags and frozen for storage. When the time came to prepare the composites, the straw fibers were blended with the PHB for 5 min in a Brabender-like apparatus, operating at 180°C with a roller speed of 32 rotations per minute.

Table IV reports, for all examined samples, the critical strain release rate, Gc and the critical stress intensity factor, Kc, calculated according to Linear Elastic Fracture Mechanics (LEFM) as a function of fibers content.

The Kc and Gc values of composite materials containing 10% or 20% straw or hemp fibers are higher than those of neat PHB while composite materials containing 30 or 50% straw fibers present about the same values of neat PHB. This indicates that the fiber plays an important role towards the reinforcement of PHB,

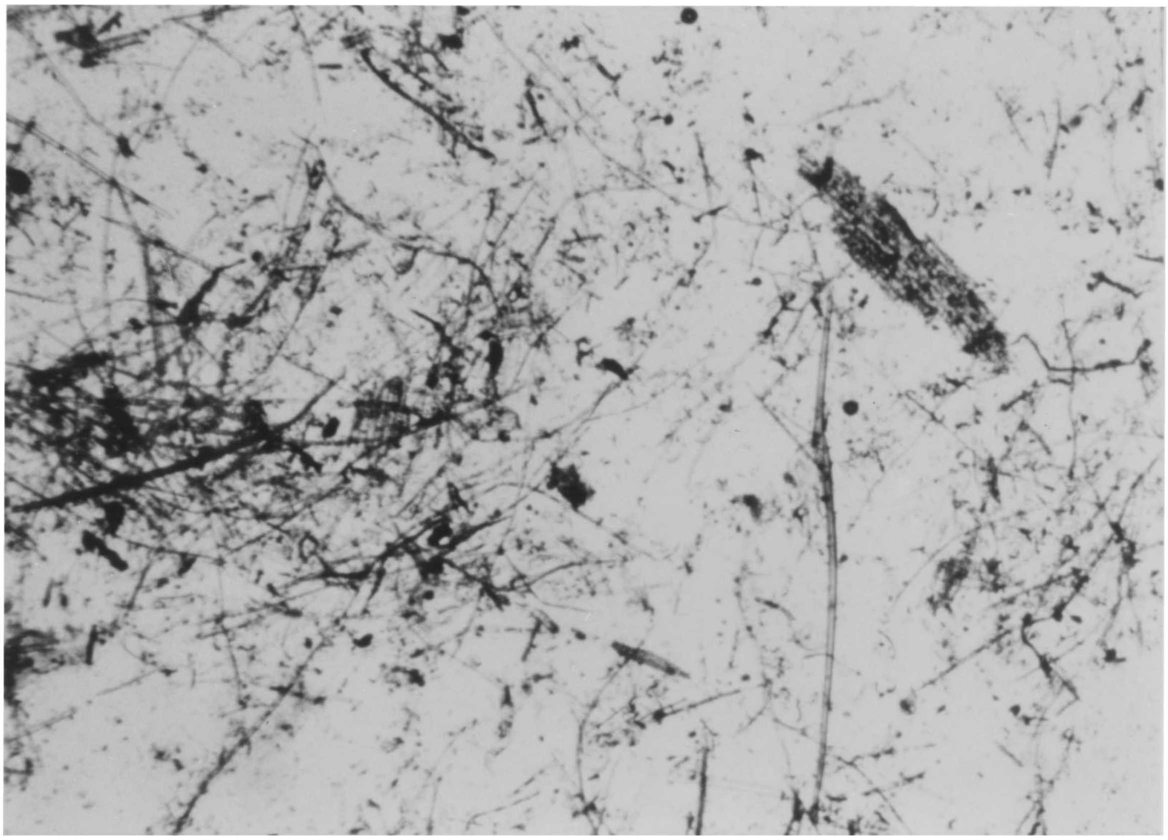
TABLE IV Fracture parameters of PHB/straw and hemp composites

	PHB	PHB/straw	PHB/straw	PHB/straw	PHB/straw	PHB/hemp
		90/10	80/20	70/30	50/50	90/10
Kc (MNm-$^{3/2}$)	1.8	2.2	2.2	1.8	1.6	2.7
Gc (KJm^{-2})	1.1	1.4	1.3	1.1	1.1	1.9

(a)

(b)

Figure 11 Optical micrographs of straw fibers after SEP: (a) $T = 205^\circ\text{C}$, $t = 2$ min; (b) $T = 220^\circ\text{C}$, $t = 2$ min; (c) $T = 235^\circ\text{C}$, $t = 2$ min. (*Continued*)



(c)

Figure 11 (*Continued*).

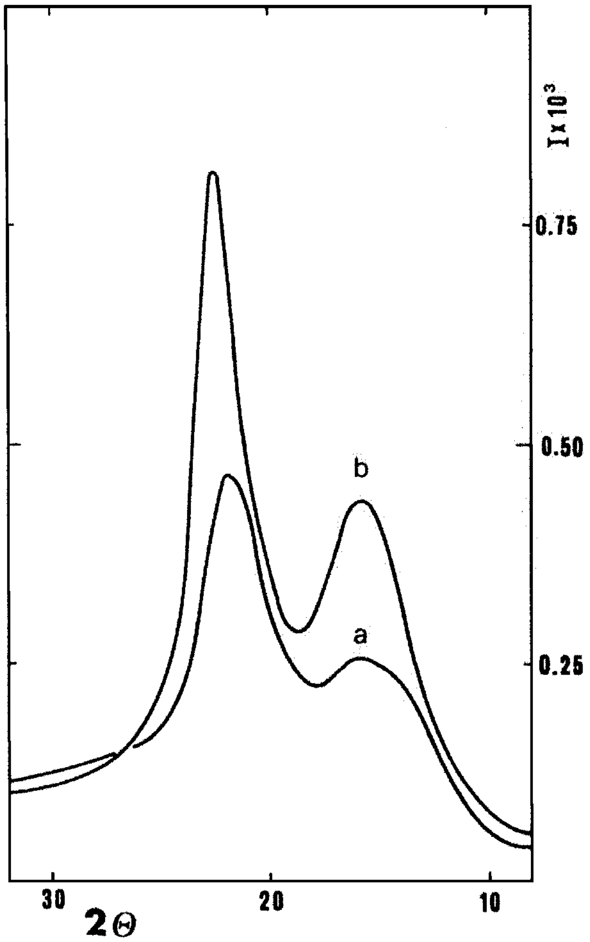


Figure 12 X-ray diffraction pattern of wheat staw: (a) Untreated (b) treated at 230 °C for 2 min.

probably due to the high adhesion between fiber and matrix (see Fig. 13). In fact, if the adhesion is good a high load is necessary to cause separation of the matrix at the interface, where the stress concentration is maximum.

Comparison of Gc and Kc values makes evident that 10% and 20% straw seem to be an optimum content for toughening PHB. In fact any further increase in the straw content result in a decrease in the Gc and Kc values to those of PHB homopolymer. This improvement of physico-mechanical properties in the composites is attributable to the formation of hydrogen bonding between the C=O groups of PHB and the hydroxyl groups of the straw, more widely available by steam explosion treatment.

In conclusion, PHB/straw composites represent a new class of biodegradable materials that, considering their performance and the reduction of PHB costs, have great industrial potential. The addition of 10–20% steam exploded straw to PHB markedly increases the physico-mechanical characteristics of the PHB as a consequence of intermolecular interactions that occur mainly in the amorphous regions of the two polymers. The interactions result in the formation of hydrogen bonding between the C=O groups of PHB and the hydroxyl groups of the straw, made widely available by the SEP.

Thus, PHB/straw and hemp fiber composites can represent a potential new class of materials that can find application in sectors such as agriculture mulching, transplanation etc., where biodegradable properties are needed.

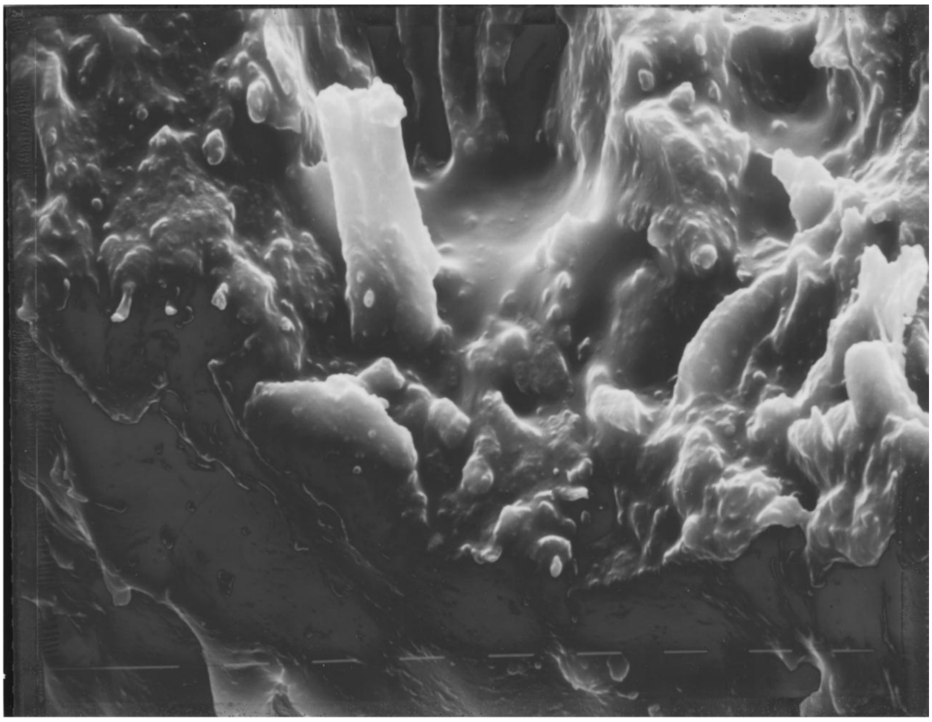


Figure 13 SEM micrograph of fracture surface of PHB/straw 80/20 (w/w) composite. Magnification 640X.

References

1. D. R. PAUL and S. NEWMAN, "Polymer Blends" Vol. 1 (Academic Press, 1978).
2. L. A. UTRACKI, "Polymer Alloy and Blends," Vol. 1 (Hanser Publishers, 1989).
3. L. H. SPERLING and R. R. ARNTS, *J. Appl. Polym. Sci.* **15** (1971) 2317.
4. A. A. DONATELLI, D. A. THOMAS and L. H. SPERLING, in "Recent Advances in Polymer Blends, Grafts and Blocks," edited by L. H. Sperling (Plenum Press, New York, 1974) p. 375.
5. R. L. LACOMBE and I. C. SANCHEZ, *J. Phy. Chem.* **80** (1976) 2568.
6. P. J. FLORY, *ibid.* **9** (1941) 660.
7. *Idem.*, *ibid.* **10** (1942) 51.
8. M. L. HUGGINS, *ibid.* **9** (1941) 440.
9. *Idem.*, *Ann. N. Y. Acad. Sci.* **43** (1942) 1.
10. J. H. HILDEBRAND and R. L. SCOTT, "The Solubility of Nonelectrolytes," 3rd ed (Van Nostrand-Reinhold, Princeton, New Jersy, 1950) Reprinted, Dover, New York, 1964.
11. J. W. CAHN, *Trans. Met. Soc. AIME* **242** (1968) 166.
12. M. KUNIOKA and Y. DOI, *Macromolecules* **23** (1990) 1933.
13. H. F. MARK, N. G. GAYLORD and N. M. BIKALES (eds), "Encyclopedia of Polymer Science and Technology," Interscience Publishers (Wiley & Sons, New York, London, Sydney 1964).
14. J. BRANDUP and E. H. IMMERGUT, "Polymer Handbook," 2nd Ed. (New York, 1975).
15. M. AVELLA, E. MARTUSCELLI, G. ORSELLO, B. PASCUCCI and M. RAIMO, *Polymer* **38** (1997) 6135.
16. B. WUNDERLICH, in "Macromolecular Physics," Vol. 2 (Academic Press, 1973).
17. *Introduzione ai Materiali* (Biblioteca della Est. Edizioni Scientifiche e Techniche-Mondadori, 1976).
18. Y. KUMAGAI and Y. DOI, *Pol. Deg and Stab.* **35** (1992) 87.
19. M. AVELLA and E. MARTUSCELLI, *Polymer* **29** (1988) 1731.
20. F. P. REDING and E. R. WALTER, *J. Polym. Sci* **37** (1959) 555.
21. M. AVELLA, E. MARTUSCELLI and M. RAIMO, *Polymer.* **34** (1993) 3234.
22. A. SHARPLES, in "Polymer Science," Vol. I, edited by A. D. Jenkins (North Holland Publishing Company-Amsterdam-London) chapter 4.
23. H. D. KEITH and F. J. JR. PADDEN, *J. Appl. Phys.* **34** (1963) 2409. *ibid.* **35** (1964) 1270.
24. H. J. CHOI, S. H. PARK, J. S. YOON, H. S. LEE and S. J. CHOI, *Polym. Eng. Sci.* **35** (1995) 1636.
25. M. AVELLA, E. MARTUSCELLI and M. RAIMO, submitted manuscript.
26. E. DUBINI PAGLIA, P. L. BELTRAME, M. CANETTI, A. SEVES, B. MERCANDALLI and E. MARTUSCELLI, *Polymer* **34** (1993) 996.
27. P. B. DAVE, N. J. ASHAR, R. A. GROSS and S. P. McCARTHY, *Polymer preprints.*
28. J. POUCHLY and J. BIROS, *J. Polym. Sci., Pt. B.* **7** (1969) 463.
29. C. A. CRUZ, J. W. BORLOW and D. R. PAUL, *Macromolecules* **12** (1979) 726.
30. G. RAMANA RAO, C. CASTIGLIONI, M. GUSSONI, G. ZERBI and E. MARTUSCELLI, *Polymer* **26** (1985) 811.
31. M. AVRAMI, *J. Chem. Phys.* **7** (1939) 1103.
32. P. SADOCCO, M. CANETTI, A. SEVES and E. MARTUSCELLI, *Polymer* **34** (1993) 3368.
33. Y. KUMAGAI and Y. DOI, *Makromol. Chem., Rapid Commun.* **13** (1992) 179.
34. P. SADOCCO, C. BULLI, G. ELEGIR, A. SEVES and E. MARTUSCELLI, *Makromol. Chem.* **194** (1993) 2675.
35. P. GRECO and E. MARTUSCELLI, *Polymer* **30** (1989) 1475.
36. J. D. HOFFMANN, *ibid.* **24** (1983) 36.
37. Y. AZUMA, N. YOSHIE, M. SAKURAI, Y. INOUE and R. CHUJO, *ibid.* **33** (1992) 4763.
38. N. LOTTI, M. PIZZOLI, G. CECCORULLI and M. SCANDOLA, *ibid.* **34** (1993) 4935.
39. J. S. YOON, C. S. CHOI, S. J. MAING, H. J.CHOI, H. LEE and S. J. CHOI, *Eu. Polym. J.* **29** (1993) 1359.
40. Y. KUMAGAI and Y. DOI, *Polymer Degrad. Stab.* **36** (1992) 241.
41. F. GASSNER and A. J. OWEN, *Polymer* **35** (1994) 2233.
42. M. GADA, R. A. GROSS and S. P. McCARTHY, in "Biodegradable Plastics and Polymers," edited by Y. Doi and K. Fukuda (Elsevier Science B.V. 1994).
43. M. AVELLA, B. IMMIRZI, M. MALINCONICO, E. MARTUSCELLI and M. G. VOLPE, *Polymer International* **39** (1996) 191.
44. J. GU, D. T. EBERIEL, S. P. McCARTHY and R. A. GROSS, *Journal of Environmental Polymer degradation* **1** (1993) 143.
45. E. MARTUSCELLI, *Polym Eng. Sci.* **24** (1984) 563.
46. M. ABBATE, E. MARTUSCELLI, G. RAGOSTA and G. SCARINZI, *J. of Mater Sci.* **26** (1991) 1119.

47. M. AVELLA, B. IMMIRZI, M. MALINCONICO, E. MARTUSCELLI, G. ORSELLO, A. PUDIA and G. RAGOSTA, *Die Angew. Makromolek. Che*. **205** (1993) 151.
48. ICI Bullettin MBL 8710, Technical Bullettin on MBL Biopol.
49. M. NARKIS, in European Regional Meeting, PPS, September 1991, Palermo (Italy).
50. M. AVELLA, L. CALANDRELLI, B. IMMIRZI, M. MALINCONICO, E. MARTUSCELLI, B. PASCUCCI and PATRIZIA SADOCCO, *J. Envir. Polym. Deg*. **3** (1995) 49.
51. N. LOTTI and M. SCANDOLA, *Polymer Bullettin* **29** (1992) 407.
52. C. M. BUCHANAN, S. C. GEDON, A. W. WHITE and M. D. WOOD, *Macromolecules* **25** (1992) 7373.
53. B. WUNDERLICH, in "The Basis of the Thermal Analysis," edited by Turi, E. A (Academic Press, New York, 1981) pp. 92–234.
54. J. B. MILLER, K. J. MCGRATH, C. M. ROLAND, C. A TRASK and A. N. GARROWAY, *Macromolecules*, **23** (1990) 4543.
55. I. KOLLER and A. J. OWEN, *Polymer International* **39** (1996) 175.
56. R. L. SHOGREN, *J. Envir. Polym. Deg*. **3** (1995) 75.
57. S. H. IMAM, S. H. GORDON, R. L. SHOGREN and R. V. GREENE, *ibid*. **3** (1995) 205.
58. P. ZADORECKI and A. J. MICHELL, *Polym. Compos*. **29** (1989) 69.
59. D. N. BHATTACHARYA, I. B. CHAKRABORTI and S. R. SENGUPTA, *J. Scient. Ind. Res*. **200** (1961) 193.
60. T. PARAMASIVAN and A. P.J. ABDUL KALAM, *Fibre Sci. and Tech*. **7** (1974) 85.
61. J. M. SINGH and S. K. JAIN, *Plastics and Rubber Materials Application* **65** (1980).
62. A. N. SHAH and S. L. LAKKED, *Fibre Sci. and Tech*. **41** (1981) 15.
63. J. M. FELIX and PAUL GATENHOLM, *J. App. Pol. Sci*. **42** (1991) 609.
64. A. K. BLEDZKI, S. REIHMANE and J. GASSAN, *ibid*. **59** (1996) 1329.
65. J. F. KENNEDY, G. O. PHILLIPS and P. A. WILLIAMS, "Wood Processing and Utilization" (Ellis Horwood UN. England 1989).
66. M. AVELLA, B. FOCHER, E. MARTUSCELLI, A. MARZETTI, B. PASCUCCI and M. RAIMO, *J. Appl. Polym. Sci*. **49** (1993) 2091.
67. B. FOCHER, A. MARZETTI and V. CRESCENZI (eds.), "Steam Explosion Techniques: Fundamental and Applications" (Gordon and Breach Science Publs., Philadelphia, 1991).
68. R. H. MARCHESSAULT, S. COULOMBA, H. MORIKAWA and D. ROBERT, *Can. J. Chem*. **60** (1982) 2372.
69. M. TANAHASHI, *J. Wood Res*. **77** (1991) 49.
70. Y. DOI, "Microbial Polyesters" (VCH Publishers, 1990).
71. H. MITORNO, P. J. BARHAM and A. KELLER, *Polym. Commun*. **29** (1988) 112.

Received 15 October 1998
and accepted 23 April 1999