polymer review

Polymer blends containing poly(3-hydroxyalkanoate)s

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The remarkable properties of poly(3-hydroxyalkanoate)s (PHAs) have resulted in a growing interest in these polymers. They offer a wide variety of useful mechanical properties and show excellent biodegradability. However, they are still expensive and poly(3-hydroxybutyrate) (PHB) in particular is quite brittle. Polymer blending offers interesting possibilities to prepare less expensive biodegradable materials with useful mechanical properties. In this review the literature concerning PHA-containing blends has been summarized. Blends incorporating either PHB or copolymers of 3-hydroxybutyrate and 3-hydroxyvalerate (P(HB-HV)) were discussed. The thermal and crystallization behaviour of the blends, their mechanical properties, morphology and biodegradability have been reviewed. Among the conclusions drawn from the literature, it is evident that PHAs can form miscible blends with polymers containing the appropriate functional groups via hydrogen bonding and/or donor–acceptor interactions. The crystallization behaviour of the PHAs is influenced by both the miscible and immiscible components. Immiscible PHA-containing blends show improved apparent biodegradability when compared to miscible blends. Their apparent biodegradability (weight loss) is mostly controlled by the blend morphology. Blends of PHA with other biodegradable polymers also usually show improved biodegradability when compared with pure PHAs.

(Keywords: polyhydroxyalkanoates; blend miscibility; biodegradability)

INTRODUCTION

The success of polymeric materials lies in their strength, low cost and resistance to chemical and biological attack. These properties have led to useful applications of polymers but have also created a disposal problem. Concern is rising that plastic waste will accumulate in the environment, leading to long-term environmental and waste management problems. These problems may be reduced by increased incineration, by recycling and by using biodegradable polymers[1–3]. Each option has its strong and weak points, with no one choice likely to predominate.

Recently, there has been considerable discussion over the options of polymer recycling and the use of biodegradable polymers. Recycling is mainly focused on poly(vinyl chloride) (PVC), polystyrene (PS), polyolefins and polyesters (like polycarbonate (PC) and poly(ethylene terephthalate) (PET)), since these can be found in large quantities in municipal waste[4]. Current research in this area includes the study of the effects of multiple processing cycles on mechanical properties[5] as well as the assessment of the properties of blends prepared from waste polymers[6] or from virgin (homo)polymers with a recycled one[7]. Especially in the case of the blends, the incorporation of compatibilizers can be used to simplify mixed plastic waste recycling operations[6].

Biodegradable plastics offer an attractive route to environmental waste management when used in specific applications. These polymers can replace conventional ones when recovery for recycling or incineration is difficult and/or not cost-effective. Research has focused on the addition of a biodegradable component to common thermoplastics[8] and on purely biodegradable natural and synthetic polymers.

There is great confusion concerning both the definition of biodegradability and the choice of appropriate test protocols. This led the ASTM committee D-20 (the Committee on Plastics) to form a subcommittee 'Environmentally Degradable Plastics'[3,9]. They had a mandate to define the terms 'degradable' and 'biodegradable' plastics[10] and have elaborated standard aerobic and anaerobic test procedures[11].

Authors interested in biomedical devices often use the term 'biodegradable' only in reference to those polymers which degrade in the human body. For our purposes we will use the term 'biodegradable' in the sense of being environmentally biodegradable. More specifically, this term will be applied to any polymer that is readily degraded to CO_2, H_2O and microbial biomass by consortia of common soil micro-organisms. 'Readily' and 'common' are subjective terms, but for practical purposes the aforementioned definition is synonymous with 'compostable'.

Biodegradable plastics can be divided into two categories based on whether they were polymerized synthetically or biologically[2,3,12]. The first type consists of synthetic polymers with vulnerable groups susceptible to enzymatic attack. The most easily biodegradable synthetic polymers are aliphatic polyesters, like poly-

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(glycolic acid) (PGA), poly(lactic acid) (PLA) and poly(ε-caprolactone) (PCL). Two water-soluble polymers of this type are poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO).

The second class of biodegradable plastics are naturally occurring processable polymers, the most prominent examples of which are poly(3-hydroxyalkanoate)s (PHAs). The PHA copolymer of 3-hydroxybutyrate and 3-hydroxyvalerate (P(HB-HV)) has been commercialized under the name of Biopol[13]. P(HB-HV) is less susceptible to aqueous hydrolysis than PLA[14] or PCL[15]. It is not water-soluble and is generally more readily biodegradable than even some of the water-soluble biodegradable plastics such as PVA[16].

There is little doubt that P(HB-HV) in particular and PHAs in general would be in widespread use if it were not for their high price. P(HB-HV) currently sells for US $8.50 per pound. This price is artificially high owing to the low supply/demand ratio. Nevertheless, using the present production technology it is doubtful that P(HB-HV) could be sold at a profit for less than US $2 per pound, which is still much more expensive than non-biodegradable thermoplastics with comparable physical properties (i.e. polypropylene (PP), US $0.35 per pound[17]). One method of reducing this price spread is by blending PHA with another, less expensive, material while retaining or improving its desirable properties, such as stiffness and biodegradability. In a recent review the properties of PHAs and their blends were examined[18] with less emphasis on blends. The present review concentrates solely on PHA-containing blends.

CHARACTERISTICS OF POLYMER BLENDS

Polymer blends by definition are physical mixtures of structurally different homopolymers and/or copolymers. At equilibrium, a mixture of two polymers in the amorphous phase may exist as a single phase of intimately mixed segments of the two components. Such a blend is *homogeneous* on a microscopic scale and is considered to be *miscible* in the thermodynamic sense[19–21]. When a mixture of two polymers separates into two distinct phases consisting primarily of the individual components, the blend is *heterogeneous* on the microscopic scale and is considered to be *immiscible* in the thermodynamic sense. Most polymers are immiscible from the thermodynamic standpoint since the entropic contribution to the free energy of mixing is negligible[19–21].

The terms 'compatible' and 'incompatible' refer to the degree of intimacy in blends that are heterogeneous on a microscopic scale (immiscible two-phase blends). Immiscible polymers may be described as 'compatible' when their blend does not exhibit gross symptoms of polymer segregation, i.e. there is good adhesion between the constituents. The mechanical properties of such blends are an average of those of the two components. An immiscible polymer blend is 'incompatible' when it is heterogeneous, both on a microscopic and on a macroscopic scale[19–21].

Thermal characterization of polymer blends is a well known method to determine their miscibility. Miscibility between any two polymers in the amorphous state is detected by the presence of a single glass transition temperature (T_g) intermediate between those of the two component polymers. For ideal systems, which are miscible and amorphous over the entire composition range, the relationship between the T_g and the composition of the blend can be predicted by simple equations, for instance by the Fox equation[22]:

$$\frac{1}{T_g(\text{blend})} = \frac{W(1)}{T_g(1)} + \frac{W(2)}{T_g(2)} \qquad (1)$$

where T_g(blend), $T_g(1)$ and $T_g(2)$ are the T_g values of the blend, component 1 and component 2, and $W(1)$ and $W(2)$ are the weight fractions of polymer 1 and 2, respectively.

Immiscibility of two polymers is demonstrated by the retention of the T_g values of both individual components. It is not uncommon to find the T_g values of immiscible blends to be broader than that of the pure components, owing to composition fluctuations in the mixture. For an immiscible blend showing partial miscibility, there are still two T_g values but they fall between those of the individual polymers, i.e. the T_g values are shifted towards each other. Such behaviour is due to some degree of molecular mixing at the interface between the two polymeric phases.

A miscible blend containing a semicrystalline polymer possesses two important characteristics in addition to the single T_g of the mixed amorphous phase. The first characteristic is that a change is observed in the crystallization behaviour of the semicrystalline polymer. A change is observed in the growth rate of spherulites when a miscible polymer constituent is added. The crystallization rate will be lowered if the T_g of the blend is higher than that of the crystallizable polymer. Conversely, a higher crystallization rate will be expected if the resultant blend T_g is lower. Addition of an amorphous polymer to a semicrystalline polymer results in a decrease in the overall crystallinity of the blend. The crystallinity of the semicrystalline polymer, however, remains mainly unchanged. When the blend consists of two semicrystalline polymers, a change in the overall crystallinity is not necessarily observed.

The other characteristic demonstrating miscibility of blends containing a semicrystalline polymer is the depression of the equilibrium melting point of that polymer when an amorphous polymer is present. According to the Flory–Huggins theory[23,24] an appropriate analysis of this depression can give information about the interaction parameter χ_{12} between the two polymers, as can be expressed by the Nishi–Wang expression[24]:

$$\frac{1}{T^0_{\text{mb}}} - \frac{1}{T^0_{\text{m}}} = -\frac{RV_2}{\Delta H^0 V_1}\chi_{12}\phi_1^2 \qquad (2)$$

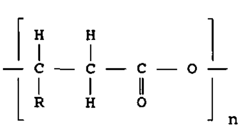
where T^0_{mb} and T^0_{m} are the equilibrium melting points of the semicrystalline polymer in the blend and in the pure state, respectively, ΔH^0 is the heat of fusion of the semicrystalline polymer, V_1 and V_2 are the molar volumes of the repeat units in the amorphous and semicrystalline polymer, respectively, ϕ_1 is the volume fraction of the amorphous polymer and R is the gas constant. With this equation the interaction parameter χ_{12} can be determined for miscible polymer blends when the equilibrium melting temperatures are known.

The equilibrium melting points for crystalline phases in blends, T^0_{mb}, and for semicrystalline polymers in the pure state, T^0_{m}, are usually derived through the use of the Hoffman–Weeks method[25]. In this method a plot of the experimental melting points of the crystalline phases in the blend, T_{mb} (or of the semicrystalline polymer in the pure state, T'_m), against the temperature where isothermal crystallization occurred, T_c, allows determination of the equilibrium melting point via extrapolation. However, the propensity for crystalline lamellae to reorganize during the thermal analysis experiment, resulting in crystal thickening and perfection, greatly influences the determination of the 'true' experimental T'_{mb} (or T'_m)[26]. A depression of the experimental melting point can therefore also reflect a morphological effect and need not necessarily indicate any miscibility in the amorphous state.

The properties of immiscible, heterogeneous blends are controlled by the morphology and the degree of compatibility. The morphology of immiscible blends depends to varying degrees on the viscosity ratio, composition, interfacial modification, shear stress and various other processing conditions (among others[27–33]). The degree of compatibility is usually controlled by the polymeric interfacial interactions, which can be modified by the addition of compatibilizers or by reactive processing (among others[27,34,35]). The choices of polymers, blending equipment, operating conditions and additives all influence the properties of the final product and its applications.

POLY(3-HYDROXYALKANOATE)S (PHAs)

PHAs serve as intracellular carbon and energy storage materials for many bacteria and algae. Their synthesis acts as an electron sink, allowing re-use of reduced pyridine nucleotides such as NADPH (reduced nicotinamide adenine dinucleotide phosphate). They undoubtedly have other biological functions that remain to be elucidated. There are two classes of PHAs. The short-side-chain PHAs such as PHB and P(HB-HV) are produced by a wide variety of micro-organisms and have monomers with five or fewer carbon atoms (*Figure 1*). The long-side-chain PHAs are limited to certain bacteria of the genus *Pseudomonas* and related organisms. The best-studied member of this diverse group of long-side-chain copolymers is poly(3-hydroxyoctanoate) (PHO), in which the eight-carbon component predominates. PHO has a much lower melting point and very different mechanical properties than short-side-chain PHAs (*Table 1*), but lack of availability has limited its study. This review will be limited to the most readily available PHAs, which are PHB homopolymer and P(HB-HV) copolymers (i.e. short-side-chain PHAs).



$$\left[-\underset{R}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{O}{\overset{}{\underset{\|}{C}}}-O- \right]_n$$

R = CH_3 (ß-hydroxybutyrate or HB)
R = C_2H_5 (ß-hydroxyvalerate or HV)
R = C_5H_{11} (ß-hydroxyoctanoate or HO)

Figure 1 Structure of some common poly(3-hydroxyalkanoate)s (PHAs)

First isolated and characterized by Lemoigne in the 1920s[40], PHB is a thermoplastic polymer with a melting point of about 180°C. It has a high degree of crystallinity and possesses characteristics comparable to those of isotactic polypropylene (PP). However, PHB is unstable in the molten state[41]. In addition to a narrow processability window, brittleness limits the use of PHB as a plastic. Improvements can be achieved by incorporating other HA units into the polymer backbone. Different PHA copolymers can be produced depending on the bacterial strain and the cultivation conditions. The properties of these copolymers, such as melting point and crystallinity, vary considerably depending on the monomeric composition. P(HB-HV) has been studied extensively. It was found that P(HB-HV) exhibits the phenomenon of isodimorphism as the constituent composition is varied[42]. Incorporation of HV units in the PHB backbone results in a decrease of the melting temperature from 178°C for high-molecular-weight pure PHB to about 75°C at 40 mol% HV[43]. Above this molar percentage the melting temperature begins to increase again. The addition of HV constituents also results in improved toughness. (The composition of P(HB-HV) copolymers is normally reported as a molar percentage of HV units. For this review, it has been assumed that all the percentages of HV units reported in the literature are original molar percentages.)

Blends containing PHB homopolymer are discussed separately from those containing P(HB-HV) copolymer in this review. A distinction has also been made between blends containing only one biodegradable component (PHA) and blends containing PHA and another biodegradable polymer.

BLENDS CONTAINING POLY(3-HYDROXYALKANOATE) AND A NON-BIODEGRADABLE POLYMER

POLY(3-HYDROXYBUTYRATE)-CONTAINING BLENDS

Summary of blends discussed

Miscible blends containing PHB have been formed with poly(vinyl acetate) (PVAc)[44,45], poly(epichlorohydrin)

Table 1 Properties of various PHAs compared to polypropylene[36]

Properties	PP[37]	PHB[37]	P(HB-HV)[38] (4–20%)	PHO[39]
Crystalline melting point (°C)	176	175	157–102	61
Crystallinity (%)	70	80	69–39	30
Molecular weight (× 10^5)	2	5	6	5
Glass transition temperature (°C)	−10	4	2 to −8	−35
Density (g cm^{-3})	0.905	1.25[a]	1.2	1.0
Tensile strength (MPa)	38	40	36–22	6–10
Extension to break (%)	400	6	8–10	300–450

[a] This is the value for a semicrystalline polymer with a crystallinity of 80%

(PECH)[46,47], poly(vinylidene fluoride) (PVDF)[48,49], a block copolymer of atactic poly((*R*,*S*)-3-hydroxybutyrate) and poly(ethylene glycol) (PEG) (P(*R*,*S*-HB-*b*-EG))[50] and poly(methyl methacrylate) (PMMA)[51].

Immiscible blends have been prepared by mixing PHB with poly(1,4-butylene adipate) (PBA)[45], rubbers, such as ethylene–propylene rubber (EPR)[44,52], ethylene–vinyl acetate (EVA)[52], modified EPR rubbers, grafted with succinic anhydride (EPR-*g*-SA) or dibutyl maleate (EPR-*g*-DBM), or a modified EVA polymer containing OH groups (EVAL)[52], and poly(cyclohexyl methacrylate) (PCHMA)[51].

Determination of miscibility

From measurement of the glass transition temperature (T_g). A single T_g was found for blends of PHB and PVAc[44,45], PECH[46], PVDF[49] and the P(*R*,*S*-HB-*b*-EG) block copolymer[50]. The blends exhibit T_g–composition dependence. These results strongly suggest that the polymers of each blend are miscible, both in the melt and in the amorphous solid state. *Figure 2* shows the agreement between the experimental and theoretical (as calculated with equation (1) (full line)) T_g values of PHB/PECH blends as a function of the PECH concentration. In this case the PHB/PECH blends have been quenched from the melt to −60°C. For PHB/PECH blends isothermally crystallized at 100°C a single T_g appears at a temperature value close to the T_g of pure PECH (−20°C)[47]. This can be ascribed to weak interactions between the two polymers at the segmental level.

The variation of T_g with composition for solution-blended and melt-blended PHB/PVDF blends is not as large as expected on the basis of the Fox equation[49]. This is because PVDF cannot be quenched to a pure amorphous state as it readily crystallizes even during rapid quenching. Owing to the existence of a crystalline PVDF phase, the amorphous phase contains a higher PHB concentration, thereby producing a higher T_g than might be expected.

Melt-quenched PHB/PMMA blends containing up to 20 wt% PHB are single-phase amorphous materials with a composition-dependent T_g (ref. 51). At higher PHB content all of the PMMA is involved in a 20/80 PHB/PMMA miscible phase while excess PHB segregates and forms a partially crystalline phase.

Immiscibility of PHB/PBA[45] and PHB/EPR[44] blends has been demonstrated by the presence of the T_g values of the individual components in d.s.c. measurements. The melt-quenched PHB/PCHMA blends also show two T_g values with constant temperatures that correspond to those of the pure blend components (d.s.c. and d.m.t.a. measurements)[51].

From determination of a melting-point depression. A depression of the experimental melting point of PHB is found in all the miscible blends mentioned above when the amount of the second polymer is increased[44,46,48,50]. In the case of the melt-blended PHB/PVDF blends, a depression of the experimental melting point of PVDF is also observed (*Figure 3*).

A very small depression of the equilibrium melting point of the PHB phase is observed in the immiscible PHB/EPR blends[44]. This is probably caused by morphological effects.

A decrease in the equilibrium melting temperature of PHB is seen in blends containing PVAc[44] or PECH[46] when the second component is added. With equation (2), negative values of χ_{12}, indicating strong interactions and miscibility, are found for these blends. However, there is an indication of composition dependence of χ_{12} and that morphological effects influence the melting-point depression of the blends. The latter conclusion is confirmed when the interaction parameter is calculated with the Kwei–Frisch equation for non-infinite molecular-weight polymers[53]:

$$\frac{\Delta H^0(T^0_m - T^0_{mb})}{\phi_1 R T^0_m} - \frac{T^0_{mb}}{m_1} - \frac{\phi_1 T^0_{mb}}{2m_2} = \frac{C}{R} - \chi_{12} T^0_{mb}\phi_1 \quad (3)$$

where m_1 and m_2 are the degrees of polymerization of the amorphous and semicrystalline polymers, and C is the proportionality constant for the morphological contributions. With this equation, a positive value of χ_{12} is found for the PHB/PVAc blends, which can only be partly explained by a composition dependence of this parameter. For the PHB/PECH blends, a negative value of χ_{12} is found, which depends on composition but whose value is similar to that derived with equation (2). It is clear that morphological effects also influence the melting-point depression of these blends.

For the PHB/PVDF blends a similar depression of the equilibrium melting point of α-phase PVDF crystals has been determined and has also been suggested for the PHB phase[48,49].

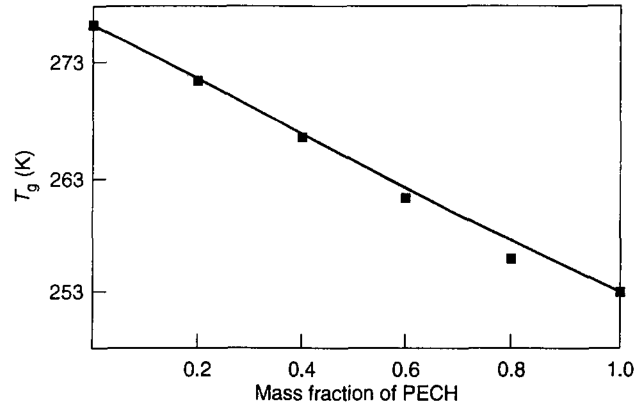


Figure 2 Glass transition temperature (T_g) *versus* composition of PHB/PECH blends: (■) experimental points; (——) calculated using the Fox equation (equation (1)). (Reprinted with permission from ref. 46)

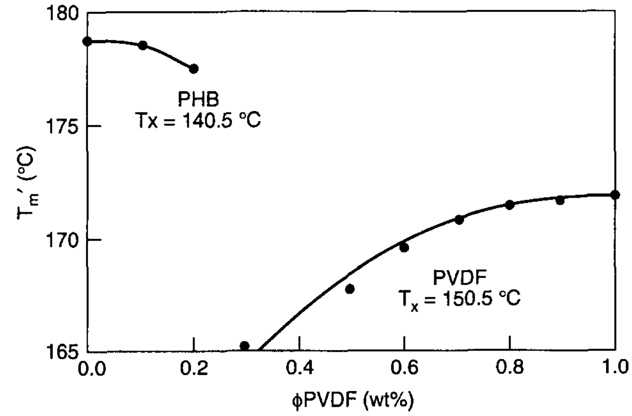


Figure 3 Experimental melting point (T'_m) of PVDF and PHB as a function of PVDF content for blends crystallized isothermally at T_x = 150.5°C and 140.5°C, respectively. (Reprinted with permission from ref. 48)

Interactions are likely to occur between polymers that contain chlorine atoms and ones that contain oxygen[54,55]. Holmes *et al.*[56] reported the partial miscibility of PHAs with polymers containing chlorine or nitrile groups. Blends of PHAs and several chlorinated or nitrile-containing polymers showed improvement in mechanical properties. It was suggested that the chlorine and nitrile groups promote hydrogen bonding with the carbonyl groups of the PHA polymers[56].

The interactions between PHB and PECH are probably also due to hydrogen bonding. Dipole–dipole interactions seem to be responsible for the interactions between PHB and PVDF or PVAc, comparable with those between PVDF and PMMA[55].

From morphological studies. Addition of 20% of any of the rubbers previously mentioned results in immiscible blends as concluded from the determination of the blend morphologies after impact failure[52]. All these blends show phase separation, indicating immiscibility. The blends containing the modified rubbers show a finer dispersion and better adhesion between the two polymers, indicating some compatibility. This is especially evident for the PHB/(EPR-*g*-SA) blend. It is reported that a graft copolymer (EPR-*g*-SA)-*g*-PHB probably forms during blending and acts as a compatibilizer. However, data on thermal transitions are needed to confirm partial miscibility.

Crystallization behaviour

The crystallization behaviour of PHB is similar whether blended with PVAc or with PECH[44,46,47]. After crystallization of PHB from a one-phase melt, the other polymer appears to be rejected into the interlamellar or interfibrillar regions of the PHB spherulites. Here it forms a homogeneous mixture with amorphous PHB molecules. The growth rate of PHB spherulites becomes slower with increasing amount of the second polymer.

Small-angle X-ray scattering (SAXS) of PHB/PECH blends[47] revealed additional information on the crystallization behaviour of these blends. The PECH molecules, rejected into the interfibrillar zones, are dispersed at the molecular level and probably assume a random-coil conformation. This can hinder close contact between PECH and PHB molecules in the continuous interfibrillar zone. Annealing of the blends promotes a general crystal perfection and rearrangement of the morphology, increasing the crystallinity and the crystal dimensions of PHB (in the pure state and in the blends), and probably favouring the trend for PECH molecules to assume a globular conformation.

PHB spherulites grow from a two-phase melt with EPR as the dispersed phase in PHB/EPR blends[44]. During spherulite growth, EPR materials are first rejected and then occluded in intraspherulite regions.

The crystallization behaviour of PHB/PVDF blends is largely influenced by competitive nucleation and spherulitic growth processes for PVDF and PHB spherulites[48]. It has been reported that PVDF α-crystal spherulites always form first. PHB spherulites have been observed to develop after an induction period that is long enough to allow for the PVDF spherulites to grow to their fullest extent. The growth front of the PHB spherulites is perturbed by the fact that it must progress past existing PVDF spherulites, and their coarseness increases with increasing PHB content. Another study[49] has concluded that, at a given crystallization temperature, the decrease in growth rate of α-phase PVDF crystals between pure PVDF and a 50/50 blend can be accounted for by a dilution effect at the growth front and by a decrease in the actual undercooling.

Even though the T_g behaviour is identical for solution- and melt-blended PHB/PVDF, the dynamic crystallization behaviour differs significantly[49]. It is observed that the PHB component crystallizes faster at a given temperature from solution-blended mixtures than from melt blends. This is caused by thermal degradation of PHB during melt blending. The low-molecular-weight PHB in the melt-blended samples should have a lower nucleation density than the solution-blended PHB and thus should crystallize more slowly.

The crystallization of PHB from blends with PMMA is delayed, both when the crystallization is carried out isothermally from the molten state and also when it occurs upon heating from the rubbery state[51]. This implies that, although pure phase-separated PHB is available for crystallization in blends with more than 20% PHB, the coexisting 20/80 mixed PHB/PMMA phase interferes with the crystallization process. This delay of crystallization only occurs when the crystallization temperature is lower than the T_g of the mixed phase. At higher crystallization temperatures, the mobile, rubbery mixture does not hinder the crystallization.

In the PHB/PCHMA blends no retardation of the crystallization process is observed[51]. PHB crystallizes from its blends with PCHMA at a constant rate, independent of blend composition.

Mechanical properties

The Young's modulus and tensile strength of PHB decrease linearly with increasing PBA content, while the influence of PBA on the elongation to break is marginal[45].

Addition of 20% rubber[52] to PHB results in a decrease of the tensile strength σ_R and the modulus of elasticity E, but in an improvement of the elongation to break ε_R (*Table 2*). The increase in elongation to break is especially evident for the EPR-*g*-SA/PHB blend, and results from better compatibility and better adhesion of the rubber to the matrix owing to the formation of an (EPR-*g*-SA)-*g*-PHB graft copolymer during blending[52].

When PHB is blended with the P(*R*,*S*-HB-*b*-EG) block copolymer, a decrease of the modulus and tensile strength is found[50]. The elongation at break increases markedly

Table 2 Modulus of elasticity E, stress σ_R and elongation ε_R at rupture for PHB homopolymer and for PHB/rubber blends (from ref. 52, reproduced by permission of the publishers, Chapman & Hall)

Sample	$E \times 10^{-3}$ (kg cm^{-2})	σ_R (kg cm^{-2})	ε_R (%)
PHB	2.1	290	1.5
PHB–EPR	1.5	170	2.0
PHB–EVA	1.6	175	2.0
PHB–EVAL	1.7	185	3.0
PHB–EPR-*g*-DBM	1.6	175	4.0
PHB–EPR-*g*-SA	1.6	180	6.5

from 5% to 90% as the block copolymer content increases from 0% to 50%.

Degradation tests

Weight-loss studies have been performed on PHB/PBA, PHB/PVAc and PHB/P(*R*,*S*-HB-*b*-EG) blends[45,50]. The tests were carried out at 37°C in a 0.1 M phosphate buffer (pH 7.4) containing extracellular PHB depolymerase, which is a stereospecific enzyme acting on both crystalline and amorphous short-side-chain PHAs. PHB/PBA and PHB/PVAc blends were tested for 19 h and the blends containing the block copolymer for 5 h.

It was found that the weight loss of PHB/PBA blends decreases linearly with increasing PBA weight fraction[45]. The rate of enzymatic degradation appears to be proportional to the PHB fraction at the surface only. This is probably due to the fact that, although these blends show micro-phase separation of components, there is none of the macro-phase separation commonly observed for immiscible blends.

Miscible PHB/PVAc blends containing 50 to 100% PVAc show no enzymatic degradation[45]. Weight loss of the blend with 25% PVAc takes place only during the early stages of the test since, after the initial removal of the PHB fraction at the surface, a layer of PVAc molecules remains that cannot be degraded by the PHB depolymerase.

Weight loss of blends containing the P(*R*,*S*-HB-*b*-EG) block copolymer is reported to be greater than that of pure PHB[50]. A 50/50 blend showed a weight loss of 50% compared to 20% for pure PHB during the same time period. There was very little degradation of the block copolymer by the PHB depolymerase. The increased rate of weight loss can be attributed to the fact that PHB depolymerase degrades amorphous PHB more quickly than the crystalline fractions[57,58], indicating that the PHB phase in the blends has a decreased crystallinity. A lowering of the overall crystallinity of the blends was measured by X-ray diffraction analysis[50] but no data have been reported specifically on the crystallinity of the PHB phase.

Table 3 D.s.c. results for component polymers and blends
(a) Component polymers

Polymer	T_g (°C)	T_m (°C)	Ref.
P(HB-*co*-16% HV)	3	135	59–61
PVC	85	–	59–61
ABS	108	–	59–61
PTMG	–	46	60
PS	107	–	59, 61
SAN	108	–	59, 61

(b) Blends (A/B)

Blend	T_g (°C) of A	T_g (°C) (Fox)	T_g (°C) of B	Ref.
P(HB-HV)/PVC				59–61
20/80	60	65	–	
50/50	18	38	–	
80/20	–	16	–	
P(HB-HV)/ABS				59–61
20/80	63	81	–	
50/50	59	47	–	
80/20	49	19	–	
P(HB-HV)/PTMG				60
20/80	0	–	–	
50/50	0	–	–	
80/20	0	–	–	
P(HB-HV)/PS				59, 61
20/80	4	80	92	
50/50	4	47	95	
80/20	4	19	89	
P(HB-HV)/SAN				59, 61
20/80	50	81	–	
50/50	47	47	–	
80/20	–	19	–	

POLY(3-HYDROXYBUTYRATE-*co*-3-HYDROXYVALERATE)-CONTAINING BLENDS

Summary of blends discussed

Miscibility has been reported for P(HB-*co*-16% HV) melt blended with poly(vinyl chloride) (PVC)[59–61]. P(HB-*co*-16% HV) polymer has also been reported to be partially miscible with acrylonitrile–butadiene–styrene (ABS) copolymer and styrene–acrylonitrile (SAN) copolymer, and immiscible with polystyrene (PS) and poly(tetramethyleneglycol) (PTMG) when prepared via solution blending from chloroform[59–62]. Immiscible blends of P(HB-*co*-16% HV) and PS or SAN (containing 35 or 64% AN) are formed by melt blending[63]. Blends of P(HB-*co*-16% HV) and PS or polyethylene (PE), with or without compatibilizer, are reported to be immiscible but no data have been shown[64]. Melt blending P(HB-*co*-15% HV) with EVA (containing 28 mol% vinyl acetate (VA)) in a single-screw extruder followed by injection moulding results in immiscible blends[65]. Blends of P(HB-*co*-19% HV) and polypropylene (PP), with and without a metal stearate, have also been reported to be immiscible, but no data on miscibility have been presented[66].

Determination of miscibility

From measurement of the glass transition temperature (T_g). Miscibility of P(HB-HV)/PVC blends has been reported based on the existence of single T_g values[59–61]. However, the T_g values do not correspond to those predicted by the Fox equation (*Table 3*), which adds considerable doubt to the conclusion that these blends are indeed miscible.

Solution-blended mixtures of P(HB-HV) and a SAN or ABS copolymer are reported to be partially miscible[59–62]. The single T_g values for the P(HB-HV)/SAN and P(HB-HV)/ABS blends (*Table 3*) were attributed to the formation of a phase that has an intermediate T_g but for which the T_g does not vary proportionally with blend composition. These blends were therefore considered to be partially miscible. However, for partial miscibility a shift of the T_g values of the polymers is usually observed[19,67]. The d.s.c. curves of the blends[59,62] do not clearly indicate partial miscibility, and further information is needed before conclusions are drawn.

The thermal characteristics of solution-blended P(HB-HV)/SAN mixtures indicate some degree of interaction between the two polymers. It is likely that this interaction is similar to that between PCL and SAN copolymers[68].

This proton donor–acceptor interaction is similar to that which occurs between PHB and PVC[56] as well as between PVC and other oxygen-containing polymers[21,54,55].

T_g values of the two individual components were determined for solution-blended mixtures of P(HB-*co*-16% HV) and PS[59–62]. For the PTMG/P(HB-*co*-16% HV) blends, only the T_g of PHB is found[59–62]. Since the T_g values are not shifted, these blends can be considered immiscible.

P(HB-*co*-15% HV)/EVA (28 mol% VA) blends are considered to be immiscible although the differential thermal analysis (d.t.a.) curves shown do not clearly show the existence of two T_g values[65]. The T_g of the P(HB-HV) polymer is hardly noticeable in the d.t.a. diagram of pure P(HB-HV). In the d.t.a. diagram of the blends, only the T_g of the EVA polymer is detectable and it is not influenced by the presence of P(HB-HV) polymer.

From determination of a melting-point depression. A depression of the experimental melting point of P(HB-HV) has been reported for the blends with PVC but no data were shown[59–61]. Although this points to miscibility, further confirmation is needed.

From measurements of the crystallinity. Wide-angle X-ray scattering (WAXS) analysis of P(HB-*co*-15% HV)/EVA blends showed a mixture of the scattering patterns of the two polymer structures, with no other reflections apparent[65]. This suggests the formation of separate crystalline phases with no co-crystallization. D.t.a. analysis showed that the crystallinity of P(HB-*co*-15% HV) was considerably lowered by the addition of EVA. The crystallinity of EVA was not significantly affected by the presence of the biopolymer.

From dynamic mechanical measurements. Measurements of the dynamic tensile modulus were performed on P(HB-*co*-15% HV)/EVA blends[65]. The curves of the imaginary part E'' of the modulus showed two relaxation transitions for the blends due to the glass transitions of the two components. Although the transitions are shifted slightly towards each other, these blends can be considered immiscible.

Mechanical properties

Injection-moulded specimens of melt-processed P(HB-*co*-16% HV) blends containing PS or SAN are relatively brittle[63]. Although no T_g data have been reported, these blends can be considered immiscible based on their mechanical properties. SAN-containing blends have poor mechanical properties, indicating that there is no compatibility between the polymers. This is in contradiction with the solution-blended mixtures of P(HB-*co*-16% HV) and SAN, which have been reported to show some degree of miscibility[59–62].

Although the authors have claimed compatibility based on values of the tensile modulus for P(HB-*co*-16% HV)/PS blends, a thorough examination of the results gives little indication of any compatibility between these polymers. The values of the tensile modulus of the blends are well below those calculated with the additivity rule, with the exception of the 20/80 PS/P(HB-HV) blend (higher than additivity). However, the existence of interactions requires confirmation by other methods. Addition of a block copolymer (low-molecular-weight blocks of PS and PHB) to a 50/50 P(HB-HV)/PS blend improves the mechanical properties by increased compatibility. The tensile modulus of a blend containing 2% block copolymer was found to be 2 times higher than that of the uncompatibilized blend and 2.5 times higher than that of pure P(HB-HV). This indicates that there is compatibility between the block copolymer and both PHA and PS.

The use of compatibilizers has also been reported for blends consisting of P(HB-HV) and PS or PE[64]. The copolymers used were SAN and poly(styrene–maleic anhydride) (SMA) for PS-containing blends and poly(ethylene-*co*-vinyl alcohol) for the PE-containing blends. The blends were reported to be compatibilized, but no supporting data were presented.

Stress–strain measurements of P(HB-*co*-15% HV)/EVA blends show that the deformation behaviour is strongly dependent on the composition[65]. Blends with a high (>75%) P(HB-*co*-15% HV) content show brittle behaviour due to the nature of the matrix. Samples with a high (>65%) EVA content show considerable plastic deformation at low stress levels. In the intermediate region the EVA matrix is deformed plastically while the P(HB-*co*-15% HV) remains virtually undeformed.

Degradation tests

Weight-loss studies have been performed on the solution-blended P(HB-HV)/PS and P(HB-HV)/SAN mixtures[59–62]. Films of these blends were exposed to a supernatant containing an extracellular PHA depolymerase for 2 or 4 days at 28°C. The partially miscible P(HB-HV)/SAN blend degrades at a slower rate when compared to the immiscible P(HB-HV)/PS blend systems.

Degradation studies of injection-moulded strips of P(HB-HV)/PS and P(HB-HV)/SAN blends have shown very low weight losses[63]. Although strips were exposed to a supernatant containing a PHA depolymerase for 4, 8 and 12 days at 28°C, there may have been very low PHA depolymerase activity.

D.s.c. measurements of samples from the degraded surfaces of P(HB-HV) strips show increased crystallinity after partial degradation[63]. This indicates that the amorphous region of the biopolymer, at the surface of the strip, degrades first, leading to an overall increase in sample crystallinity. A similar trend is found for strips of PS- or SAN-containing blends[63].

Soil degradation tests of P(HB-*co*-15% HV)/EVA blends have shown a clear correlation between weight loss and P(HB-*co*-15% HV) content[65]. Since only the biopolymer is degraded, these blends must be regarded as being biodestructible (or biodisintegrating) as opposed to biodegradable.

Blends of P(HB-*co*-19% HV) (50%), PP (50%) and a metal stearate (1%) are claimed to be both photodegradable and biodegradable[66]. Degradation tests were performed in soil slurries at 55°C for up to 8 weeks. The presence of a metal stearate enhances deterioration. Similar behaviour is suggested for blends containing P(HB-HV) with an HV content of 0–30% or a copolymer of PP and an α-olefin comonomer. The effect of the stearate is further augmented by exposure of the blends to u.v. rays. The role of the metal stearate is surprising since its effects have been previously correlated only with photodegradation and not biodegradation.

BLENDS CONTAINING TWO BIODEGRADABLE COMPONENTS

POLY(3-HYDROXYBUTYRATE) AND A (MODIFIED) NATURAL BIODEGRADABLE POLYMER

PHB–fibre composites

Addition of wood cellulose fibres to PHB improves its strength and stiffness but also increases brittleness[69]. Addition of HV units (6, 10 or 15%) to PHB results in composites with increased elongation at break and improved ductility. Cellulose fibres do not influence PHA crystallinity (determined from d.s.c.), but restrict the mobility of the chain segments in the amorphous phase (decrease of loss factor in d.m.t.a. measurements). However, the increased volume of the amorphous phase when P(HB-HV) is the matrix compensates for the reduction of the loss factor. In fact, damping is higher in a 40% cellulose composite with P(HB-*co*-15% HV) as the matrix than in pure PHB. The composites having a composition such as this show increased stiffness over the entire temperature range as compared to unfilled PHB.

Compounding in a Brabender kneader results in a finer distribution of the cellulose fibres than one-step compounding in a single- or twin-screw extruder owing to a more severe fibre attrition. SEM studies of extracted fibres show defibrillation, possibly caused by hydrolysis of cellulose by crotonic acid formed *in situ* as a result of thermal degradation of the PHA matrix.

Addition of steam-exploded wheat straw fibres to PHB improves the mechanical properties[70]. This is due to the intermolecular interactions that occur mainly in the amorphous regions of the two materials due to the formation of hydrogen bonds between the C=O groups of PHB and the hydroxyl groups of the straw. The hydroxyl groups are made available by the steam explosion process, which leads to highly fractionated lignocellulosic materials (neat cellulose or cellulose associated with a small quantity of hemicellulose and lignin) but also increases the reactivity of the materials themselves. Another advantage of the addition of the straw fibres is that production costs are dramatically reduced because wheat straw is very inexpensive.

PHB–cellulose ester blends

Miscibility was observed for blends of PHB with cellulose acetate butyrate (CAB) (containing 5–50% PHB) and cellulose acetate propionate (CAP) (containing 5–60% PHB)[71]. These transparent blends are stable homogeneous amorphous glasses, showing a single T_g, which decreases linearly with increasing PHB content, in excellent agreement with the behaviour of miscible blends (*Figure 4*). Blends with higher PHB content are partially crystalline. PHB and CAB can crystallize from the blends only at temperatures higher than the composition-dependent T_g. Pure CAB, melt-quenched and refrigerated prior to measurement to prevent crystallization, does not crystallize above its T_g, but addition of 15% PHB lowers this T_g sufficiently to allow CAB to crystallize. The crystallization of PHB is retarded by increasing amounts of CAB and is shifted to higher temperatures with increasing CAB content. The depression of the experimental melting point of the crystalline phases is a result of the mixing of the two polymers. In addition to the highly composition-dependent T_g, another relaxation, located in proximity to the T_g of PHB, was observed for totally amorphous blends (0–50% PHB) with dynamic mechanical thermal analysis (d.m.t.a.). This relaxation peak shifts slightly to higher temperatures with increasing CAB or CAP content. The very large specific-heat increment indicates that both blend components contribute to this low-temperature glass transition. It was suggested that the two relaxations represent two mobilization processes, one of segmental motions of the cellulose ester under the plasticizing effect of the low-T_g PHB while the low-temperature relaxation indicates the mobilization of PHB under the effect of the high-T_g CAB or CAP component[71].

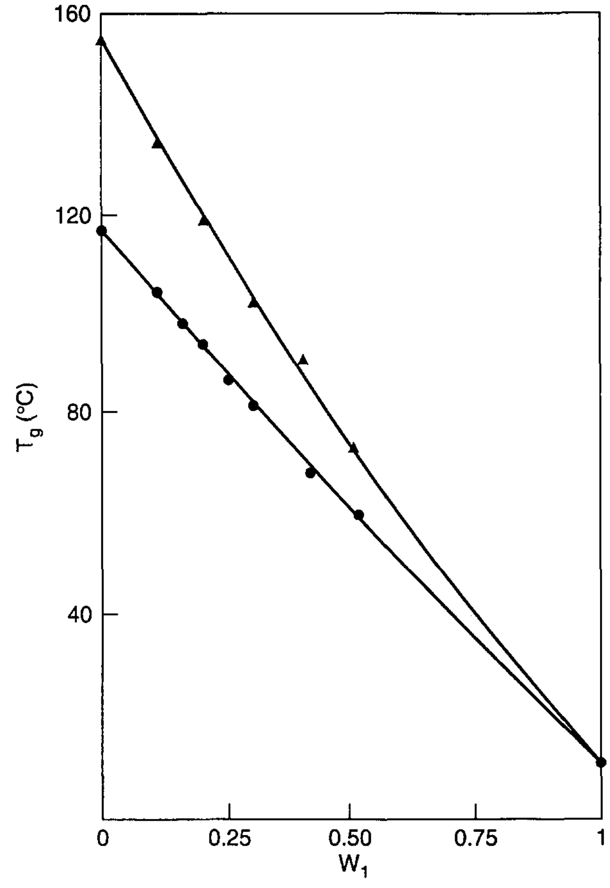


Figure 4 Dynamic mechanical T_g values of PHB/CAP blends (▲) and PHB/CAB blends (●) as a function of PHB weight fraction W_1. Full curves were calculated with Wood's equation[72]: $T_g(\text{blend}) = [W_1 T_g(1) + kW_2 T_g(2)]/(W_1 + kW_2)$ ($k = 0.70$ and 0.65 for PHB/CAB and PHB/CAP blends, respectively). (Reprinted with permission from ref. 71, © 1992 American Chemical Society)

The addition of di-n-butyl phthalate (DBP) plasticizer to miscible CAB/PHB blends influences the above-mentioned mobilization processes at all compositions[73]. The plasticizer, miscible in all proportions with both polymers, causes a significant decrease of the composition-dependent high-temperature T_g of the binary polymer blends. It also almost completely eliminates the slight dependence of the low-temperature transition on CAB content seen in the binary blends.

PHB/P(HB-HV) blends

Mixtures of PHB and P(HB-*co*-8% HV) obtained by co-dissolving the two polyesters in chloroform and precipitating the mixtures in diethyl ether show one single sharp endotherm[74]. This suggests that the two components have co-crystallized. The blends are highly crystalline and of the PHB lattice type.

Blends consisting of PHB and P(HB-*co*-76% HV) prepared by solution blending show two T_g values in d.s.c. measurements, indicating immiscibility[75]. In addition, no depression of the experimental melting point is found for either polymer. The rates of enzymatic degradation of the blends as measured by weight loss in aqueous buffer solution containing PHB depolymerase are higher than the rate of degradation of the pure polymers (*Figure 5*). This is attributed to the phase-separated morphologies of the blends.

Blends of PHB and P(HB-*co*-18.4% HV) are miscible over most of the composition range but separate into a two-phase system at higher copolymer concentration[76,77]. D.s.c. and microscopy studies have shown that a region of liquid–liquid phase separation exists in the melt. Two-phase crystallization is observed at low temperatures for compositions containing 60–70% or more of the copolymer. Two-phase crystallization at low temperatures and liquid–liquid phase separation at the higher temperatures occur over the same composition range (*Figure 6*). The results obtained are governed largely by kinetic factors.

POLY(3-HYDROXYBUTYRATE-*co*-3-HYDROXYVALERATE) AND A (MODIFIED) NATURAL BIODEGRADABLE POLYMER

Recently, results have been published on the blending of P(HB-HV) copolymers with polysaccharides[1,78–81] or a cellulose ester[82,83]. It has been reported that the addition of 25 wt% amylose or amylopectin to P(HB-*co*-11.6% HV) causes a sharp increase in brittleness and a decrease in strength, but no supporting data were presented[1].

Immiscible blends of P(HB-HV), containing 7 or 16% HV[78] or 19.1% HV[79], and up to 50% starch were prepared at temperatures of 160°C. These were not true blends but rather composites consisting of solid starch particles dispersed in the P(HB-HV) matrix. In both studies it was found that the addition of starch results in a decrease in the tensile strength and elongation at break. Flexibility diminishes as the Young's modulus increases from 1525 to 2498 MPa when the amount of starch is increased from 0 to 50%[79]. Microscopic studies have shown no apparent interaction between the two components. An increased rate of degradation is found as the starch content increases when the blends are exposed to microbial attack under aerobic conditions. It has been shown that a 150 μm thick film of a 50/50 starch/P(HB-*co*-19.1% HV) blend could be completely degraded in 8 days, while it took a month for complete degradation of pure P(HB-HV) (*Figure 7*). The starch particles disappear first during the degradation tests, owing to solubilization in water and/or enzymatic hydrolysis[79].

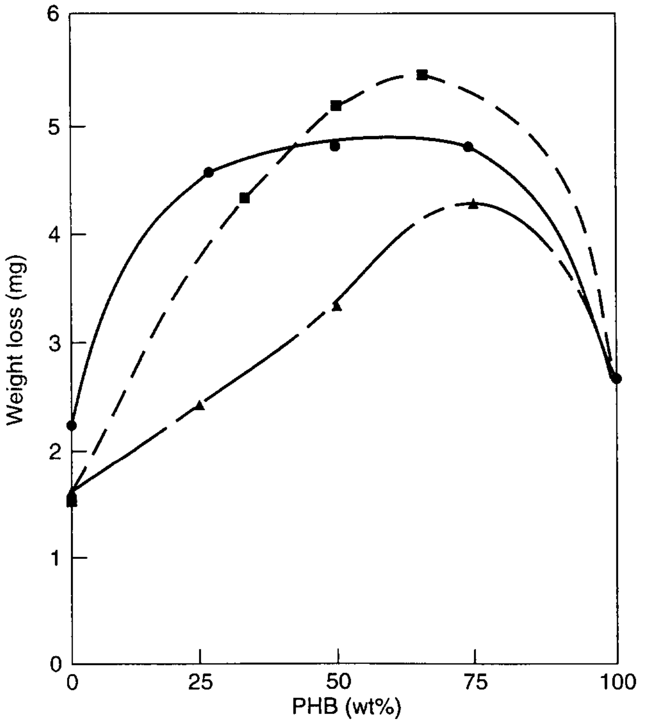


Figure 5 Weight loss of PHB-based blend films (initial weight 6–8 mg) after 19 h in an aqueous solution (pH 7.4) of PHB depolymerase (8 μg) at 37°C: (●) PHB/PPL; (▲) PHB/PEA; (■) PHB/P(HB-*co*-76% HV). (Reprinted with permission from ref. 75, © 1992 Elsevier)

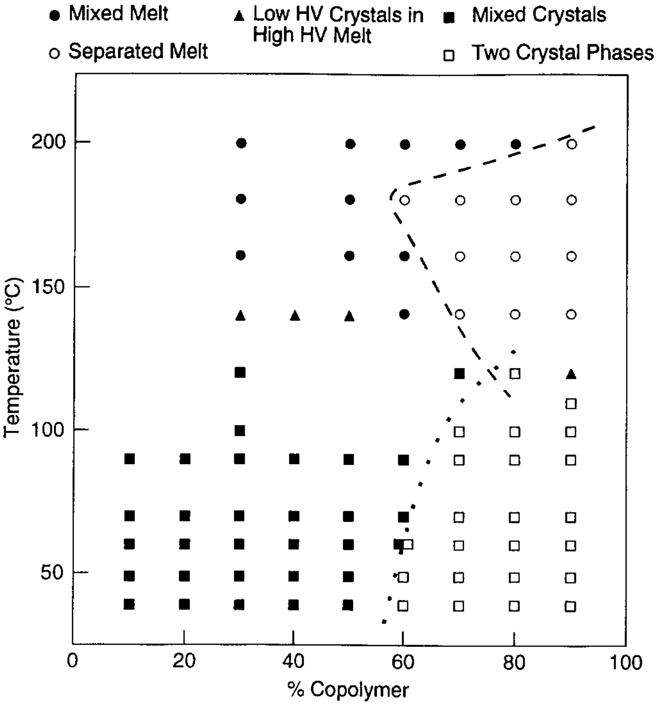


Figure 6 Summary of d.s.c. results of PHB/P(HB-*co*-18.4% HV) blends. The broken curve shows the approximate position of the boundary for liquid–liquid phase separation. The dotted curve shows the boundary between single- and two-phase crystallization. (Reprinted with permission from ref. 76)

Pullulan (linear α-linked D-glucan with 1,4-linked maltotriose and maltotetraose units connected by 1,6-linkages) and P(HB-*co*-16% HV) are immiscible as concluded from the presence of two T_g values in the blend (d.s.c. analysis)[80]. Films are opaque, with good strength and flexibility. Although no data were given, it has been reported that these blends may have increased biodegradability over P(HB-HV) alone in a marine environment.

P(HB-HV) copolymers, containing 12 or 20% HV, have been melt blended with 10 or 30 wt% amylose, dextran, dextrin or sodium alginate[81]. The presence of these polysaccharides drastically affects the hydrolytic degradation of the P(HB-HV) copolymers in buffer solutions. As in the PHA/starch composites, the incorporation of polysaccharide increases the rate of degradation of the P(HB-HV) matrix. This is caused by

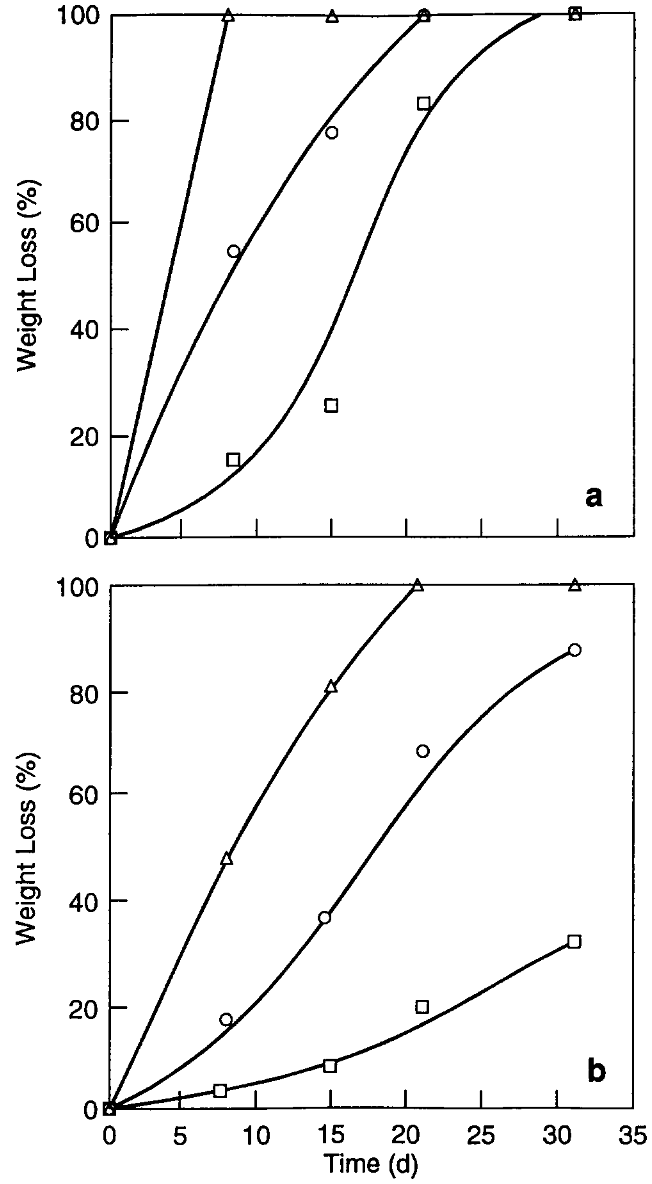


Figure 7 Percentage weight loss of blends of starch and P(HB-*co*-19.1% HV) having a thickness of (a) 150 and (b) 800 μm. The starch content (by weight) was 50% (△), 25% (○) and 0% (□). (Reprinted with permission from ref. 79, © 1993 American Society of Microbiology)

the dissolution and subsequent leaching of the polysaccharide out of the matrix, allowing increased enzyme access. The hydrolytic degradation of the P(HB-HV)/polysaccharide blends is affected by both pH and temperature, with a more rapid degradation under alkaline conditions at increased temperature (70°C).

Melt-blended mixtures of P(HB-*co*-10% HV) with CAB[82] and of P(HB-*co*-20% HV) with CAB or CAP[83] show composition-dependent miscibility. Blends with a P(HB-HV) content up to 50% are amorphous and miscible while those with more P(HB-HV) are partially crystalline. Two relaxation processes, a high-temperature glass transition, sensitive to blend composition, and a low-temperature transition, independent of composition, are observed, comparable with those of blends of PHB and cellulose esters[71,73]. ^{13}C n.m.r. analysis of the individual molten polymers and their molten 50/50 blend revealed that CAB and P(HB-*co*-10% HV) have different mobilities, even in a homogeneous melt[82]. This difference in mobility (or dynamic heterogeneity) is maintained in the solid state and is reflected by the two aforementioned relaxation processes. Blends containing 20–50% P(HB-*co*-10% HV) have shown such dynamic heterogeneity.

The tangent moduli and tensile strength decrease linearly with increasing PHA content for blends containing 20–50% P(HB-*co*-10% HV) while the tear strength remains largely unaffected. The 50% blend shows a five-fold increase in elongation at break in comparison with pure P(HB-*co*-10% HV). Above 50% P(HB-*co*-10% HV) where the crystallinity of P(HB-*co*-10% HV) is no longer suppressed, the tangent moduli, tear strengths and tensile strengths increase with increasing P(HB-*co*-10% HV) while the elongation at break drops significantly. ^{13}C n.m.r. and g.p.c. analyses show no transesterification during the melt blending and little change in molecular weight[82].

POLY(3-HYDROXYBUTYRATE) AND A SYNTHETIC BIODEGRADABLE POLYMER

Summary of blends discussed

Solution-blended (chloroform) mixtures of PHB and poly(β-propiolactone) (PPL) or poly(ethylene adipate) (PEA)[75] are immiscible. Immiscible blends of PHB and poly(ε-caprolactone) (PCL) are formed independent of the blending technique[45,84]. Miscibility is reported for solution-blended mixtures of PHB and PEO[85–88] or poly(vinyl alcohol) (PVA)[89]. Addition of synthetic, atactic PHB (P(*R*,*S*-HB)) to bacterial, isotactic PHB (P(*R*-HB)) results in immiscible systems when cast from a solvent[90]. However, melt-crystallized samples are miscible[91–93]. Synthetic, partially isotactic PHB is reported to be miscible with bacterial, isotactic PHB[90]. Extrusion-blended mixtures of PHB and PCL can be considered immiscible but are compatibilized by an *in situ* formed caprolactone/β-hydroxybutyrate copolymer[94].

Determination of miscibility

From measurement of the glass transition temperature T_g). No shift of the T_g values of PHB, PCL, PPL or PEA is observed in solution-blended mixtures of PHB and any of the other polymers[45,75]. Such blends can therefore be considered immiscible. A similar thermal behaviour is found for PHB/PCL blends prepared via melt blending/injection moulding, melt blending/compression moulding or solution blending/compression moulding[84].

A single T_g is found in PHB/PEO[85–88] and P(*R*-HB)/P(*R*,*S*-HB)[91] blends. A T_g–composition dependence is found in PHB/PEO blends, suggesting miscibility of these polymers. *Figure 8* shows good agreement between the experimental and theoretical (broken line) T_g values of the PHB/PEO blends.

Although P(*R*-HB)/P(*R*,*S*-HB) blends show one T_g, it is not possible to determine miscibility from these measurements because the individual T_g values are too similar (5°C for P(*R*-HB) and −2°C for P(*R*,*S*-HB))[90]. In another study[93] isotactic P(*R*-HB) and both atactic and partially isotactic P(*R*,*S*-HB) had indistinguishable T_g values of 4°C. Again the T_g measurements were of little use in miscibility determination.

From determination of a melting-point depression. A depression of the experimental melting point of PHB is reported for the PHB/PEO (*Figure 8*)[85,86], PHB/PVA[89] and P(*R*-HB)/P(*R*,*S*-HB) blends, with both synthetic, atactic and partially isotactic P(*R*,*S*-HB)[90–93].

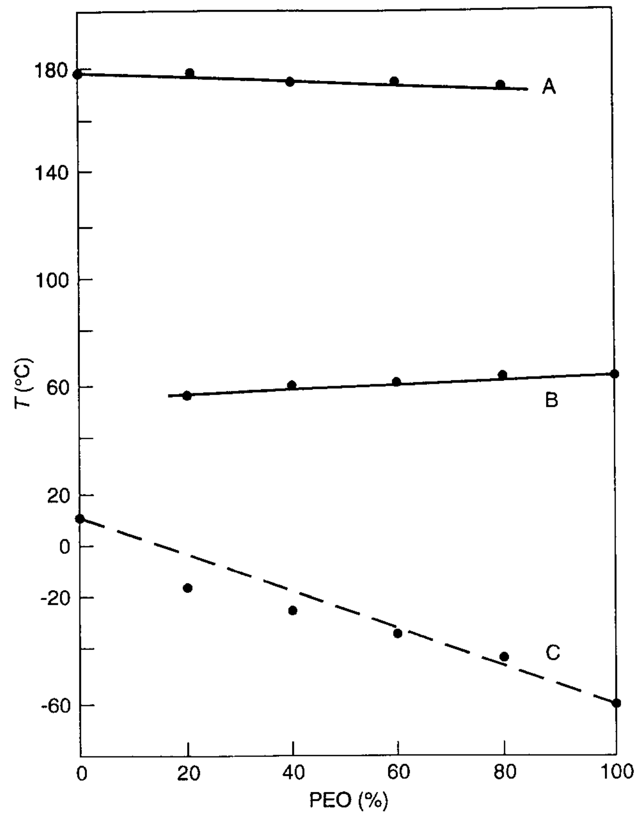


Figure 8 PHB/PEO phase diagram as determined with d.s.c.: (●) experimental points; (A) T'_m of PHB; (B) T'_m of PEO; (C) T_g(expt); (----) T_g as determined with the Fox equation. (Reprinted with permission from ref. 85)

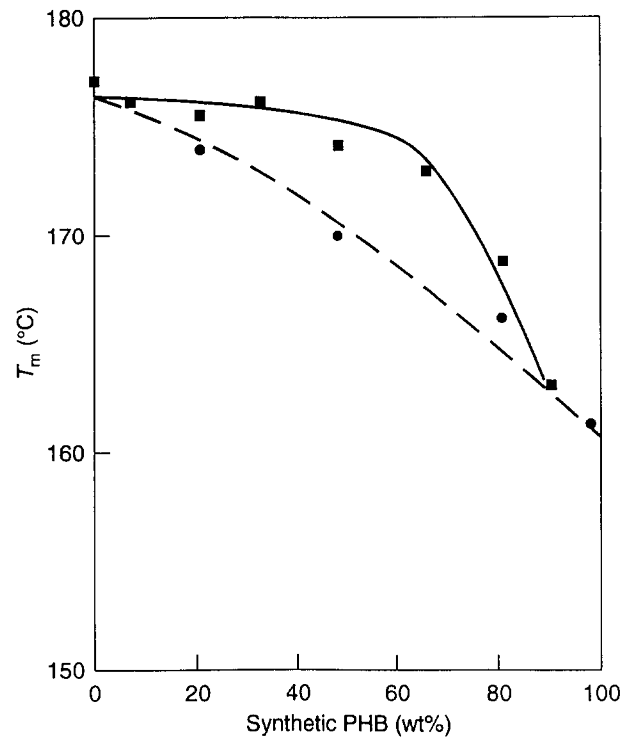


Figure 9 D.s.c. melting points of blends of bacterial PHB and synthetic atactic PHB (■) and partially isotactic PHB (●). (Reprinted with permission from ref. 91)

In the case of the PHB/PVA blends, the experimental melting point of PVA, T'_{mb}(PVA), remains almost unchanged when PHB is added[89]. Addition of glycerine to these blends results in a depression of T'_{mb}(PVA) but does not influence the T'_{mb} of PHB.

The addition of synthetic, atactic PHB to bacterial, isotactic PHB results in a slight decrease of the experimental melting temperature, T'_{mb}, of the bacterial PHB in solvent-cast blends[91] (*Figure 9*). A dramatic drop in T'_{mb}(P(*R*-HB)) is found for blends containing 60 wt% or more atactic PHB[91]. The effect of added atactic PHB can be ascribed to a decrease in the crystalline perfection of the isotactic material. The depression of the experimental melting point can therefore be attributed to morphological and dilution effects. A more pronounced decrease in the experimental melting point of P(*R*-HB) is found when the solvent-cast blends are melted and recrystallized[90,93].

Solution-blended (chloroform) mixtures consisting of synthetic, partially isotactic PHB and bacterial, isotactic PHB exhibit one melting point, intermediate between those of the pure components (*Figure 9*)[91]. This behaviour suggests co-crystallization of the two polymers. To obtain this behaviour it is necessary to co-precipitate the mixture rapidly into a non-solvent (diethyl ether). Slow evaporation of chloroform at room temperature results in two distinct melting points, one for each crystalline phase.

A decrease in the equilibrium melting point of PHB, T^0_{mb}, is found for solution-blended PHB/PEO mixtures[85] and blends of isotactic and atactic PHB[93] when the second component is added. These blends are therefore considered to be miscible in the melt and in the solid amorphous state. For the PHB/PEO blends the interaction parameter χ_{12}, as calculated with equation (2), is composition-dependent and always has a negative value, indicating strong interactions and miscibility[85].

The equilibrium melting points, T^0_{mb}, of PHB and PVA have not been determined for the PHB/PVA blends owing to decomposition of PHB before melting of the PVA[89].

From density measurements. Density measurements have been used to determine the miscibility of PHB and PVA in more detail[89]. For this method the assumption must be made that the polymers are immiscible. The crystallinity of the PVA phase can then be determined from the density of the blend and the crystallinity of the PHB phase. Crystallinity values of the PVA phase are reported to be larger than unity for some of the blend samples, indicating that these blends are at least partially miscible[89].

From n.m.r. measurements in the solid state. ^{13}C n.m.r. measurements have been used to determine the ^{1}H spin–lattice relaxation times in the laboratory frame (T_1^H) and in the rotating frame ($T_{1\rho}^H$) for PHB/PVA blends[89]. Crystalline and amorphous phases in semicrystalline polymers have, in general, different characteristic relaxation times (T_1^H, $T_{1\rho}^H$). Spin diffusion among protons can modify these relaxation times. If the domains of two contacting phases are small enough for effective spin diffusion, each phase will have the same T_1^H value. However, when domains are larger, each phase has different T_1^H values. T_1^H measurements make it possible to estimate the degree of homogeneity at a scale of several tens of nanometres. $T_{1\rho}^H$ measurement scales are smaller than those of T_1^H, so information can be obtained about the compositional homogeneity of blends on a scale of nanometres.

Table 4 T_1^{H} and $T_{1\rho}^{\mathrm{H}}$ values of PHB/PVA blends as obtained with ^{13}C n.m.r. in the rotating (at 6 kHz) and static (at 67.9 MHz) frame. (Reprinted with permission from ref. 89)

PHB	T_1^{H} (s)		$T_{1\rho}^{\mathrm{H}}$ (ms)			
(%)	PHB	PVA	PHB		PVA	
100	1.45		6.3	18		
75	1.43	2.6	7.0	18	0.22	3.3
50	1.47	2.1	4.5	15	1.00	5.0
25	1.70	1.8	n.d.	n.d.	1.20	5.0
0		2.7			0.25	3.5

Both PHB and PVA have a single T_1^{H} value, indicating that spin diffusion occurs between the crystalline and amorphous phases of these polymers (*Table 4*). Both polymers have two $T_{1\rho}^{\mathrm{H}}$ values (*Table 4*), which probably correspond to the crystalline and amorphous phases. However, it has not been reported which value corresponds to which phase. A blend with 25% PVA has T_1^{H} and $T_{1\rho}^{\mathrm{H}}$ values corresponding to those of the pure polymers, so this blend can be considered heterogeneous. Blends containing 50 and 75% PVA have T_1^{H} and $T_{1\rho}^{\mathrm{H}}$ values that differ from those of the individual homopolymers. In fact the two T_1^{H} values of the blend with 75% PVA are almost identical, which indicates that this sample shows homogeneity within several tens of nanometres. It has been suggested that the $T_{1\rho}^{\mathrm{H}}$ values of this blend indicate miscibility on a molecular scale, but further substantiation is required. The sample is actually heterogeneous, consisting of crystalline and amorphous phases.

Crystallization behaviour

PHB spherulites grow isothermally in equilibrium with a one-phase melt blend (PHB + PEO) at crystallization temperatures above the experimental melting point of PEO[85,86]. Such a blend can be characterized by the presence of a crystallized PHB phase, a liquid PEO + PHB phase and a phase of almost pure PEO. When further cooled to −100°C, PEO chains are crystallized. This crystallization occurs close to the crystallization temperature, T_c, of pure PEO (≈40°C) and at lower temperatures (−20 to −30°C). Thus, the PEO molecules that phase-separate during isothermal growth of PHB spherulites from the melt blend form interfibrillar intraspherulitic domains of almost pure PEO that crystallize at ≈40°C. The crystallization observed between −20 and −30°C can be attributed to that of PEO molecules trapped with amorphous PHB in the interlamellar regions of PHB spherulites. This fractionated crystallization phenomenon[88] can occur in two steps at different supercoolings, depending on the crystallization conditions, the thermal history and the cooling rate. Two different modes of PEO nucleation can be produced: homogeneous (at high supercooling), from a melt consisting of mainly PEO nuclei, and heterogeneous (at low supercooling), when nuclei, other than PEO nuclei, are present. Each results in a different morphology.

The processing technique influences the crystallinity of PHB in PHB/PCL blends[84]. Compression-moulded blends show the formation of a second endotherm for PHB at 190°C in addition to the first one at 175°C. The 190°C endotherm is not found in injection-moulded samples. This difference in crystallization is caused by the cooling rate, which is much faster in injection moulding than in compression moulding.

It has been found that volume-filling spherulites of isotactic PHB are present even in blends with a high level (>80 wt%) of atactic PHB[91–93]. The atactic PHB is found in the amorphous regions between individual lamellae within the spherulites of isotactic PHB[93]. The growth rate of the P(*R*-HB) spherulites is significantly retarded upon addition of the second component. Analysis of the growth-rate data with the Lauritzen–Hoffman model[95] shows that a regime II → III transition is present for the blends investigated (0–50 wt% atactic PHB) and that this transition occurs at a constant temperature of 140°C[93]. There are three distinct regimes of crystal growth depending on the relative rates of formation of secondary nuclei on the growth front and the rate at which the nuclei, once formed, spread along the growth front[96]. At high T (low undercooling), each surface nucleation occurrence leads to rapid completion of the growth strip prior to the next nucleation event (regime I). At lower T, multiple surface nuclei form and spread across the growth front together. The separation between them decreases as the undercooling increases (regime II). When crystallization occurs at a still lower T, the separation between the multiple nuclei characteristic of regime II reaches its minimum value (of the order of the molecular width) (regime III). The ratio of the nucleation constants for the regimes II and III is found to deviate from the theoretical value of 2.0 in the blend of isotactic and atactic PHB. This deviation is not due to entropic effects[93].

Bacterial PHB and partially isotactic PHB cocrystallize and the inclusion is essentially complete[91]. The decrease in the experimental melting point of bacterial PHB reflects the incorporation of synthetic PHB into the crystalline bacterial PHB lattice (isomorphism). Non-equilibrium crystallization conditions are necessary in order to obtain compatibility and can be obtained by the preparation method described above (in the previous subsection).

The crystallinity of PHB in PHB/PVA blends is reported to decrease with increasing amount of PVA[89] owing to a disturbance of PHB crystallization by the PVA crystalline phase.

Mechanical properties

Addition of PCL to PHB (via solution blending) decreases the Young's modulus and the tensile strength with increasing PCL amount[45]. Minimum values are reached for the 50/50 blends. These results indicate poor compatibility.

The *in situ* formed caprolactone/β-hydroxybutyrate copolymer (obtained by adding 1 phr catalyst (zinc acetic anhydride)) improves the elongation at break of 50/50 PCL/PHB films tested[94]. A copolymer content of at least 28 wt% is needed for optimum elongation.

Addition of atactic PHB to bacterial isotactic PHB results in more flexible and tougher materials with increasing atactic PHB content[90]. The Young's modulus and tensile strength are decreased. The elongation at break is increased from 5 to 500% for an increase of atactic PHB from 0 to 76 wt%.

Degradation tests

Weight-loss studies have been performed on solution-blended PHB/PEO[87], PHB/PCL[45], PHB/PPL, PHB/

PEA[75] and P(*R*-HB)/P(*R*,*S*-HB)[90] blends. The tests were carried out at 37°C in a 0.1 M phosphate buffer (pH 7.4) containing PHB depolymerase. All blends were tested for 19 h with the exception of the P(*R*-HB)/P(*R*,*S*-HB) blends (5 h).

PHB/PEO blends were completely degraded as measured by weight loss in a phosphate buffer containing extracellular PHB depolymerase[87]. Apparently the water-soluble PEO component dissolved in the buffer solution, allowing the PHB depolymerase increased access. Complete degradation was thus a combination of the solubilization of PEO and degradation of PHB[45].

PHB/PPL and PHB/PEA films also proved susceptible to enzymatic degradation by the PHB depolymerase and an acceleration of the degradation was observed for these blends (*Figure 5*). Again the phase-separated morphology of the blends allowed the formation of large cavities owing to the degradation of the dispersed phase, allowing greater access of the PHB depolymerase to the matrix material[75].

The degradation of PHB/PCL films in the presence of extracellular PHB depolymerase is greatly influenced by the morphology of the blends[45]. When PCL is the matrix (at concentrations of 60–100%) a low weight loss is observed. The weight loss increases for the blends with a dispersed PCL phase (0–40%). Weight loss is greater for 25/75 PCL/PHB blends than for pure PHB. PCL films should not be degraded by PHB depolymerase, so it is likely that the PCL dispersed phase is simply released from the film surface into the buffer solution. As a result, the surface area increases and the degradation of the PHB by the PHB depolymerase is accelerated.

P(*R*-HB)/P(*R*,*S*-HB) blends show a higher rate of enzymatic degradation than either of the individual components when exposed to PHB depolymerase[90]. The acceleration of the degradation may be caused by a decrease in the overall crystallinity of the blends relative to the pure polymers.

Immiscible PCL/PHB films prepared by different techniques have also been tested for degradability in a soil environment[84]. The influence of crystallinity on biodegradation was demonstrated. Extruded/injection-moulded samples showed a greater weight loss for the 50/50 blend than the solution-blended/compression-moulded and extruded/compression-moulded samples. The latter have newly formed crystalline regions (at 190°C) that are less susceptible to degradation[56]. No data have been shown to confirm an influence of the blend morphology on biodegradability of these blends.

POLY(3-HYDROXYBUTYRATE-*co*-3-HYDROXYVALERATE) AND A SYNTHETIC BIODEGRADABLE POLYMER

Solution-blended (chloroform) combinations of P(HB-*co*-16% HV) and PCL, poly(L-lactide) (PLL) and poly(D-lactide) (PDL) are reported to be immiscible[59–62]. No shift of the T_g values of the PHA or the other polymers nor a depression of the P(HB-HV) melting point have been reported.

Weight-loss studies were only performed on PCL/P(HB-HV) films[59,61,62]. They were exposed to a supernatant containing PHA depolymerase at 28°C for 2 and 4 days. Weight loss was about 45% for both the 50/50 and the 20/80 PCL/P(HB-HV) films after 4 days. This is relatively low when it is considered that degradation of PCL by the micro-organism used (*Penicillium funiculosum*) has been reported by Cook *et al.*[97]. This was attributed to the fact that the culture had been grown using PHB as the sole carbon source and that the presence of PCL may be necessary to stimulate the presence of the enzymes responsible for PCL hydrolysis[59,61,62].

CONCLUDING REMARKS

Many studies performed on PHA-containing blends have focused on miscibility of the polymers. It has been shown that PHA polymers exhibit possibilities for interaction with other polymers. This has been demonstrated in blends with PVC and PEO, via intermolecular hydrogen bonding, and in blends with PVDF, presumably via dipole–dipole interactions. The interactions in these blends are strong enough to render them miscible.

The crystallinity of PHA polymers is greatly influenced by the presence of the other component for both miscible and immiscible blends. In most cases the other component is rejected into interlamellar or interfibrillar regions. Co-crystallization can be observed in P(HB-HV) blends and seems to depend on the method of blend preparation, copolymer composition and other processing parameters.

Blending of PHAs with other polymers also influences the overall rate of biodegradation. Increased miscibility of PHAs with non-biodegradable thermoplastics decreases the apparent biodegradability (weight loss) of PHAs due to restriction of enzymatic access. Immiscible blends frequently show improved degradation rates, but the morphology of these blends must be well controlled for this to be reproducible. The release into the environment of the dispersed non-biodegradable polymer of an immiscible blend may be ecologically undesirable. It is therefore recommended to blend biodegradable components only. Promising biodegradable blend components for PHAs are natural biopolymers, such as starch and cellulosic materials, as well as synthetic polymers, such as aliphatic polyesters, including PCL and certain synthetic PHAs.

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APPENDIX

List of symbols

$T_g(i)$	glass transition temperature of polymer i
$W(i)$	weight fraction of polymer i
T^0_{mb}	equilibrium melting point of a semicrystalline polymer in a blend
T^0_m	equilibrium melting point of a semicrystalline polymer in the pure state

ΔH^0	heat of fusion of a semicrystalline polymer
V_i	molar volume of the repeat unit of polymer i
ϕ_i	volume fraction of polymer i
R	gas constant
χ_{12}	interaction parameter
T'_{mb}	experimental melting point of the crystalline phase in a blend
T'_{m}	experimental melting point of a semicrystalline polymer in the pure state
m_i	degree of polymerization of polymer i
C	proportionality constant for morphological contributions
E	modulus of elasticity
σ_{R}	tensile strength
ε_{R}	elongation to break
T_1^{H}	^{1}H spin–lattice relaxation time in the laboratory frame
$T_{1\rho}^{\mathrm{H}}$	^{1}H spin–lattice relaxation time in the rotating frame

List of abbreviations

ABS	acrylonitrile–butadiene–styrene copolymer
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
DBP	di-n-butyl phthalate
EPR	ethylene–propylene rubber
EPR-*g*-DBM	EPR grafted with dibutyl maleate
EPR-*g*-SA	EPR grafted with succinic anhydride
EVA	ethylene–vinyl acetate
EVAL	EVA polymer containing OH groups
PBA	poly(1,4-butylene adipate)
PC	polycarbonate
PCHMA	poly(cyclohexyl methacrylate)
PCL	poly(ε-caprolactone)
PDL	poly(D-lactide)
PE	polyethylene
PEA	poly(ethylene adipate)
PECH	poly(epichlorohydrin)
PEG	poly(ethylene glycol)
PEO	poly(ethylene oxide)
PET	poly(ethylene terephthalate)
PGA	poly(glycolic acid)
PHA	poly(3-hydroxyalkanoate)
PHB	poly(3-hydroxybutyrate)
P(HB-HV)	copolymer of 3-hydroxybutyrate and 3-hydroxyvalerate
P(*R*-HB)	bacterial PHB, isotactic
P(*R*,*S*-HB)	synthetic PHB, atactic or partially isotactic
P(*R*,*S*-HB-*b*-EG)	block copolymer of atactic poly((*R*,*S*)-3-hydroxybutyrate) and poly(ethylene glycol)
PHO	poly(3-hydroxyoctanoate)
PLA	poly(lactic acid)
PLL	poly(L-lactide)
PMMA	poly(methyl methacrylate)
PP	polypropylene
PPL	poly(β-propiolactone)
PS	polystyrene
PTMG	poly(tetramethylene glycol)
PVA	poly(vinyl alcohol)
PVAc	poly(vinyl acetate)
PVC	poly(vinyl chloride)
PVDF	poly(vinylidene fluoride)
SAN	styrene–acrylonitrile copolymer
SMA	poly(styrene–maleic anhydride)