Study of the Behavior of Blends of a Poly(hydroxybutyrate-valerate) Copolymer, Polypropylene, and SEBS

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ABSTRACT: Polyhydroxyalkanoates are a type of polymers with a clear renewable origin, as different types of microorganisms can produce them. Unfortunately, their mechanical properties are not usually as good as those of conventional polymers and for a moment their price is relatively higher; these are two of the reasons why it is suggested in the bibliography that they can be employed forming part of blends with conventional polymers. In the present work, blends of a poly(hydroxybutyrate-valerate) (PHBV) copolymer and a polypropylene resin have been successfully processed using PHBV concentrations up to 20 phr with internal mixer and a hot plate press. Processability and applicability of such blends logically depend on their properties, and for this reason morphology, rheological, thermal properties, and tensile strength

INTRODUCTION

Polyolefins are the most widely employed family of plastics. In fact, according to a report issued by the Association of Plastics Manufacturers on 2008 ("The Compelling Facts about Plastics-An analysis of plastics production, demand and recovery for 2006 in Europe"), more than 40% of the plastic demand in Europe in 2006 was for polyethylene and polypropylene. Packaging, building, and construction are the main fields of applicability. However, once plastics have covered the consumers' demand they usually conclude their service life, and according to the same report, it has been estimated that around 50% of these plastics are disposed of, around 30% are employed for energy recovery, and only 20% of them are recycled. This means that conventional plastics, derived from oil, involve a direct contribution to the carbon dioxide emissions.

However, there exist other types of plastics, not so frequently employed, which are obtained from

for all samples have been evaluated. Ternary blends, incorporating a poly(styrene-ethylene-butylene) copolymer have also been obtained and the influence of the blends properties has been analyzed. Results have shown that the rheological behavior and crystallization process of the system is markedly dependent on the blend composition. Although tensile strength significantly decreases with PHBV concentration, the use of low concentrations of the styrene-ethylene-butylene-styrene copolymer could improve the elongation at break to a certain extent. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3187–3195, 2009

Key words: blends; poly(hydroxybutyrate-valerate); polypropylene

renewable sources, as is the case of polyhydroxyalkanoates. This type of plastic is produced by certain microorganisms,1-5 such as energy and carbon storage, when they are cultured in stress conditions. Depending on the culture conditions and the selected microorganism, it is possible to find granules constituted by polyhydroxybutyrate (PHB) or poly(hydroxybutyrate-polyhydroxyvalerate) in the microorganism. Although pure PHB is a brittle and rigid polymer with a relative high melting point, poly(hydroxybutyrate-valerate) (PHBV) copolymers offer better mechanical properties and a lower melting temperature that facilitate their processing⁶; in addition, Choi et al.⁷ also reported a slight increase in the elasticity of the copolymer with the polyhydroxyvalerate content.

This type of plastic presents two advantages over conventional plastics: they are obtained from renewable sources and are biodegradable, which means, bacteria in landfills can degrade them. However they have serious disadvantages, as their relative high price and the fact that from several points of view, their properties are not comparable with those of conventional polymers. This could be the reason why it is possible to find different works in the bibliography dealing with polymeric blends, where conventional polymers have been partially substituted

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by polyhydroxyalkanoates. For example, Choe et al.⁸ prepared films by dissolving PVC and two PHBV copolymers (8 and 18% of valeriate), Rodrigues et al.9 studied the behavior of films containing PHB and polyethylene glycol, Chiu et al.¹⁰ described the behavior of PHB-PVA-poly(vinyl acetate)-blends, and Choi and coworkers^{11,12} reported the rheological behavior of PHB-PEO-poly(ethylene oxide)-blends. In all cases, the miscibility between the polymers considered and its influence on the blend properties are two of the most important factors to bear in mind. It is worth mentioning that most of the polymers tested have a marked polarity, similar to that of PHB whose carboxylic groups are expected to confer certain polarity to these polymers. This polarity could present a problem from the point of view of compatibility and blending with other types of polymers with a lower polar nature, as in the case of polyolefins. Oxidation reactions could improve compatibility between PHBs and polyolefins, and in this sense Arcana et al.¹³ reported that the properties of PHB blend with oxidized polypropylene-PPO-.

Although limited compatibility between PHB's and polyolefins is expected, the questions that arise are how relevant could the likely detriment of mechanical properties in such binary blends be and whether it is possible to improve such miscibility by alternative methods to chemical modification.

On the other hand, it is possible to find, in bibliography that in some cases polypropylene is blended with other polymers, such as example SEBS, poly (styrene-ethylene-butylene), in order to improve the impact strength of polypropylenes.¹⁴ SEBS copolymers have a bivalent nature; they present low polarity domains (corresponding to ethylene) as well as high polarity domains (corresponding to styrene). This is the reason why these types of copolymers have been simultaneously employed as compatibilizers, as suggested by Chirawithayaboon and Kiatkamjornwong¹⁵ in order to compatibilize HDPE and HIPS.

The aim of the present work has been the study of the behavior of ternary and binary blends of a commercial polypropylene (PP), a PHBV copolymer and a SEBS copolymer. Tensile strength, crystallization temperature (by differential scanning calorimetry), morphology (by scanning electron microscopy), and the rheological properties of some formulations have been characterized to evaluate their likely processability and application fields.

EXPERIMENTAL

Materials and samples preparation

The heterophasic copolymer of polypropylene ISPLEN PB 180 G2M from RepsolYPF (Madrid, Spain) has been employed with a PHBV copolymer (12% of

valeriate) supplied by GoodFellow (Lille, France). The SEBS resin Calprene H6110 from RepsolYPF has also been included in some formulations; according to the supplier, this SEBS copolymer has a Shore A hardness of 76 and a melt flow index of 1.5 at 230°C (2.16 kg). Different formulations with different PHBV and SEBS content were prepared expressing concentrations in terms of parts in weight per hundred of resin of polypropylene (phr). PHBV concentrations ranged from 0 to 20 phr (concentrations of around 40% cannot be processed under the conditions employed), while SEBS ranged from 0 to 10 phr.

All formulations were blended in a Brabender (Duisburg, Germany) internal mixer at 170°C for 10 min and then processed at the same temperature in a hot plates press for 10 min under a pressure of 10 atm. Then, the mould was transferred to a water-cooled press at 10°C for 15 min (under a pressure of 10 atm), obtaining plastics sheets with a thickness of around 1.5 mm.

Methods

Morphological analysis

Samples were introduced in liquid nitrogen, and immediately broken. Fractured surfaces were analyzed in a scanning electronic microscope JEOL (Tokyo, Japan) JSM 840.

Mechanical properties

Tensile strength was measured in an Instron (Barcelona, Spain) 4411 extensometer using an extension rate of 25 mm/min. Test specimens were prepared from compression processed formulations by using a cutting die with the shape of multipurpose specimens for tensile strength testing, which allowed the obtaining of test samples with the following dimensions: Width of narrow section: 5 mm, length of narrow section: 30 mm, width overall: 10 mm, length overall: 75 mm, and distance between grips: 50 mm. Ultimate tensile strength (UTS) and elongation at break (EB) of at least 15 specimens have been determined.

Thermal analysis

Different samples were analyzed in a Perkin-Elmer (Waltham, MA) Pyris 6 Differential Scanning Calorimeter. Successive heating (from 20 to 200°C at 10° C/min) and cooling runs (from 200 to 20°C at 5° C/min) have been performed.

Rheological properties

Rheological properties were obtained in a 20-mm parallel plates rheometer ARES, TA Instruments (New Castle, DE). Frequency sweep tests were performed at 180°C using a strain amplitude of 1%.



Figure 1 Microphotography of (a) pure PP (4000 magnifications); (b) pure PP (1500 magnifications); (c) PP + 5 phr of PHBV (4000 magnifications); (d) PP + 5 phr of PHBV (1500 magnifications); (e) PP + 5 phr of PHBV + 5 phr SEBS (4000 magnifications); (f) PP + 5 phr of PHBV + 5 phr SEBS (1500 magnifications).

RESULTS AND DISCUSSION

Morphological analysis

On the one hand, as reported by the manufacturer, the PP resin consists of a heterophasic system [Fig. 1(a,b)], but the presence of PHBV even at very low concentrations (5 phr) increases the proportion of the disperse phase [Fig. 1(c,d)], thus reflecting certain incompatibility between both polymers. When SEBS is included in the formulation [Fig. 1(e,f)], the apparent effect is to decrease the disperse phase size; it is relatively difficult to find disperse phase particles larger than 1 μ m, in contrast to samples where SEBS is not present.

Mechanical properties

Figure 2(a,b) show the UTS and EB, respectively, versus the concentration of PHBV at three SEBS concentrations.

When PHBV is added, UTS decreases with PHBV concentration, as observed in Figure 2(a). At 20 phr of PBHV, samples exhibited poor mechanical properties and processability, making the production of

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Figure 2 (a) Ultimate tensile strength of samples with different PHBV concentrations and 0 phr SEBS, 5 phr SEBS, 10 phr SEBS. (b) Elongation at break of samples with different PHBV concentrations and 0 phr SEBS, 5 phr SEBS, 10 phr SEBS.

samples with the adequate characteristics difficult for this type of test. The effect of the SEBS copolymer concentration on UTS is similar and for a constant PHBV concentration, it decreases again when the SEBS concentration increases.

Concerning EB, it is important to bear in mind the highest standard deviations calculated. In spite of this, it is possible to draw the following conclusions. When the SEBS copolymer is included in the PP-PHBV system, at very low concentrations (5 phr), the polymeric blends increase their ductility [Fig. 2(b)], since UTS slightly decreases, while EB tends to increase in all the formulations (except 20 phr of PHBV) with respect to pure PP. At 10 phr of SEBS, both magnitudes decrease, revealing a significant deterioration of tensile strength. The improvement, with such a low SEBS concentration is in good agreement with results reported by Chirawithayaboon and Kiatkamjornwong,¹⁵ who concluded that low SEBS concentrations were optimal for the case of HDPE and HIPS.

Then, considering both UTS and EB results, it is possible to state that 5 phr of SEBS is an optimal concentration, and concentrations equal or below 10 phr of PHBV could be of practical interest, from the point of view that, although UTS has decreased, elongation at break has been improved, indicating that the system has increased its ductility.

Thermal analysis

The crystallization process was analyzed in thermograms corresponding to cooling runs, as shown in Figure 3, where the behavior of binary blends of PP and PHBV is shown. It is possible to observe that crystallization of PP appears at higher temperatures as PHBV increases, very probably due to the fact that both polymers are immiscible even at the lowest concentrations, and the droplets of PHBV embedded in PP matrix could act as a nucleating agent.

Similar thermograms were obtained for the rest of formulations, although the effect of SEBS on the crystallization process is apparently different. As it is possible to observe in Figure 4, the presence of the SEBS modifies the crystallization pattern; the crystallization peak becomes wider and is slightly shifted to lower temperatures; this could be due to the fact that both polymers are at least partially miscible and molecular chains of SEBS present in the polypropylene phase could modify the spherulite size and crystal perfection degree of PP.

Then, it is expected that both phenomena could coexist in ternary blends (i.e., the nucleating effect of PHBV and the hindering effect of SEBS). Thus, the behavior of different samples is strongly dependent on the composition of the system. In Figure 5, the crystallization peak temperature is represented versus the PHBV concentration for different formulations. In the case of binary blends of PP-PHBV [Fig. 5(a)] it is possible to observe the trend mentioned



Figure 3 Thermograms of PP-PHBV binary blends: ----, Pure PP; ----, 5 phr PHBV; ---, 10 phr PHBV.



Figure 4 Thermograms of blends containing 5 phr of PHBV and different SEBS concentrations: —, 0 phr SEBS; _____, 5 phr SEBS; ----, 10 phr SEBS.

above, in spite of the fact that it is clear that there exist certain saturating effects, and above 10 phr of PHBV, the crystallization peak temperature exhibits a plateau. When SEBS is present in the formulations,

124 Crystallization temperature (°C) 123 122 121 120 119 118 117 5 10 15 0 20 а PHBV concentration (parts per hundred of PP) 123 122 Crystallization temperature (°C) 122 121 121 120 120 119 119 118 10 15 20 0 b PHBV concentration (parts per hundred of PP)

Figure 5 (a) Evolution of the crystallization peak temperature for binary blends of PP-PHBV. (b) Evolution of the crystallization peak temperature for blends containing different SEBS concentrations: \blacksquare , 1 phr; ●, 5 phr; \blacklozenge , 10 phr.

different profiles with progressively lower temperatures are obtained, as SEBS concentration increases [Fig. 5(b)]. At the same time, the effect of PHBV is also readily observable and the crystallization temperature shows an upward trend with PHBV concentration.

Rheological properties

Results obtained reveal that all rheological magnitudes measured (i.e., elastic modulus, viscous modulus, loss tangent, and complex viscosity) markedly depend on the formulation employed.

In the case of complex viscosity, a pseudoplastic behavior with oscillation frequency is observed for all samples. In Figure 6(a) the behavior of PP-PHBV binary blends is represented as an example; it is possible to observe a slight increase of the low shear rates viscosity with PHBV concentration. When SEBS is present, a pseudoplastic behavior is also noticed, but it is markedly affected by the concentration of both materials (PHBV and SEBS). In order to achieve a comparison between all the complex viscosity curves, they have been analyzed by following



Figure 6 (a) Complex viscosity of binary blends of PP-PHBV: ◆, Pure PP; ×, 1 phr PHBV; ■, 5 phr PHBV; ▲, 10 phr PHBV. (b) Complex viscosity curve of pure PHBV.

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TABLE I						
Parameters	Calculated	for	the	Carreau's	Mode	

	0 phr PHBV		1 phr PHBV		5 phr PHBV		10 phr PHBV					
	η ₀ (Pa s)	λ (s ⁻¹)	п	η ₀ (Pa s)	λ (s ⁻¹)	п	η ₀ (Pa s)	λ (s ⁻¹)	п	η ₀ (Pa s)	λ (s ⁻¹)	п
0 phr SEBS	613	1.44	0.71	942	2.07	0.72	836	3.39	0.74	959	5.84	0.74
1 phr SEBS	1234	1.63	0.67	1290	2.14	0.70	1334	2.51	0.67	1432	9.97	0.73
5 phr SEBS	1541	3.01	0.70	1879	3.52	0.67	2070	6.85	0.70	5001	47.1	0.71
10 phr SEBS	3053	8.98	0.69	3581	12.94	0.70	4429	36.9	0.71	5456	55.2	0.70

a similar procedure as that reported in the bibliography.^{16,17} Lim et al.¹⁶ and Hyun et al.¹⁷ correlated their experimental results by means of the Carreau model in order to investigate the dependence of viscosity on the parameters studied:

$$\eta = \frac{\eta_0}{\left[1 + \left(\dot{\gamma}t_1\right)^2\right]^{(1-n)/2}}$$

where η is the viscosity, $\dot{\gamma}$ is the shear rate, η_0 is the zero shear rate viscosity, n is a dimensionless parameter, and t_1 is the characteristic relaxation time (available as the inverse of the critical shear rate at which the shear thinning behavior begins), which is approximately the longest time that the elastic structures require to relax.¹⁸ As is known, the Cox-Merz rule establishes equivalence between viscosity-shear rate and complex viscosity-oscillation frequency, and for this reason the Carreau model has been adapted:

$$\eta^* = \frac{\eta_0^*}{\left[1 + (\varpi t_1)^2\right]^{(1-n)/2}}$$

where ϖ is the oscillation frequency expressed in s^{-1} , η^* is the complex viscosity, and η^*_0 the zero oscillation frequency viscosity.

The characteristic parameters of the model have been obtained by minimising an objective function calculated from the j values of experimental (η^*_{exp}) and calculated complex viscosities (η^*_{calc}) corresponding to each formulation:

$$OF = \sum_{j} \left(\eta_{\exp,j}^* - \eta_{\operatorname{calc},j}^* \right)^2$$

In order to evaluate the fit quality, a variation coefficient has been calculated:

VC (%) =
$$\sqrt{\frac{\text{OF}}{(J-N)\left(\bar{\eta}^*\right)^2}} \times 100$$

where *J* is the number of experimental points in a curve whose average viscosity is η^* and *N* is the

number of parameters to optimise (in this case, N = 3). In this way, the V.C. describes the degree of deviation between experimental and calculated data.

Parameters calculated and variation coefficients are shown in Tables I and II. The low variation coefficients calculated (the highest value is around 6%) indicate a good fit of experimental results. While the dimensionless parameter (n) seems to adopt a similar value in all cases (around 0.70), the zero oscillation frequency viscosity and characteristic relaxation time markedly increase with PHBV and SEBS concentrations. Concerning zero shear rate viscosity, it surprisingly increases with PHBV concentration, in spite of its relatively low viscosity [Fig. 6(b)]; this could probably be due to the fact that PP and PHBV exhibit certain immiscibility, and the presence of droplets of PHBV in the PP matrix may contribute to increase viscosity, the same as Einstein's equation predicts for diluted suspensions of hard spheres.¹⁹

Nevertheless, the effect of the SEBS copolymer is more prominent, since viscosity undergoes more marked changes than in the case of the PHBV. This could probably be due to two different reasons: the first one, SEBS is more viscous than PP, and any fraction dissolved in PP will also contribute increasing viscosity of the blend (the SEBS copolymer has such a high viscosity that it cannot be determined with the available parallel plates rheometer), and the second one, if a part of SEBS is not incorporated to polypropylene, but remains as droplets embedded in polymeric matrix, these will also contribute to the increase in viscosity.

These results are concordant with those obtained in the thermal analysis section. The presence of PHBV increases the PP viscosity [in spite of the fact

TABLE II Variation Coefficients Calculated

	0 phr	1 phr	5 phr	10 phr			
	PHBV	PHBV	PHBV	PHBV			
	VC (%)	VC (%)	VC (%)	VC (%)			
0 phr SEBS	2.3	2.2	3.6	3.5			
1 phr SEBS	3.1	2.1	2.1	2.5			
5 phr SEBS	2.7	2.7	3.9	6.0			
10 phr SEBS	5.2	5.0	5.6	6.1			



Figure 7 Viscous modulus obtained from frequency sweeps for samples with 5 phr of PHBV and different SEBS concentrations: \blacksquare , 0 phr SEBS; \blacklozenge , 1 phr SEBS; \blacklozenge , 5 phr SEBS; \bigstar , 10 phr SEBS.

that the PHBV copolymer has a lower viscosity, Fig. 6(b)], due to the fact that both polymers exhibit certain immiscibility, but at the same time, the droplets of the PHBV phase act as a nucleating agent for PP crystallization. On the other hand, the presence of SEBS seems to hinder crystallization, indicating that PP and SEBS show a certain degree of interaction and miscibility, causing a more marked increase in viscosity.

Although complex viscosity curves offer very valuable information, the degree of miscibility of different polymers can be studied more deeply by the analysis of the behavior of other rheological properties. The study of elastic and viscous modulus properties reveals that for high SEBS concentrations, the elastic modulus presents a shoulder at low frequencies, in contrast to viscous modulus curves, as is possible to observe when comparing Figures 7 and 8. This shoulder in elastic modulus has already been described in bibliography²⁰ in cases where immiscible polymer are studied; this is attributed to the fact that at low frequencies, the droplets of the discrete phase are deformed, but they are able to recover their original shape, storing energy as interfacial energy, and contributing in increasing elastic modulus with respect to the expected trend.

Although elastic and viscous modulus curves facilitate very useful information, the shoulder in elastic modulus is not readily observed in all cases. However, alternative procedures can be employed, and in this regard different researchers^{21–24} have suggested the utilization of the Cole–Cole plots, diagrams where the loss viscosity ($\eta'' = G'/w$) is represented versus the elastic viscosity ($\eta' = G''/w$). For compatible or very fine dispersed samples,²⁵ a semicircular shape chart is expected, but if a tail or drift from this shape is observed, it indicates that the sys-

tem studied presents phase segregation and a non homogeneous dispersion. In Figure 9 it is possible to observe the Cole–Cole plots for all the formulations tested.

Although morphological, rheological, and thermal analysis results have permitted us to elucidate that in PP-PHBV-SEBS ternary blends different phases could coexist, it is worth mentioning that in most of the Cole-Cole plots, a nearly semicircular shape is observed. This could indicate that at least there exists a good degree of dispersion in such samples. Thus, in Figure 9[(b) 10 phr SEBS; (c) 10 phr SEBS; and (d) 5 and 10 phr SEBS] it is possible to notice a clear drift, with a higher immiscibility or a poorer dispersion between the phases. The case of the 5 phr SEBS sample in Figure 9(c) should be remarked; although the deviation from the semicircular shape is not very relevant, it is already observable and it could correspond to a formulation where poor dispersion of both phases starts to become incipient; at the same time, thermal analysis and viscosity results indicate the possibility that a part of SEBS is incorporated to the PP phase. In consequence, this justifies why these samples exhibit a relatively high elongation at break: SEBS is incorporated to the PP phase, contributing in increasing elasticity (andEB) of the blends; a higher SEBS concentration (10 phr) does not yield a further improvement, as this effect is overrun by the negative effect of the increasingly prominent immiscibility and phase segregation.

CONCLUSIONS

In this work, blends of PP with a PHBV copolymer have been processed in concentrations up to 20 phr of the latter. The influence of the presence of a SEBS



Figure 8 Elastic modulus obtained from frequency sweeps for samples with 5 phr of PHBV and different SEBS concentrations: \blacksquare , 0 phr SEBS; \blacklozenge , 1 phr SEBS; \blacklozenge , 5 phr SEBS; \bigstar , 10 phr SEBS.

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Figure 9 (a) Cole–Cole plots for samples with 0 phr PHBV and different SEBS concentrations: \blacklozenge , 0 phr SEBS; \blacktriangle , 1 phr SEBS; \blacksquare , 5 phr SEBS; \bigstar , 10 phr SEBS. (b) Cole–Cole plots for samples with 1 phr PHBV and different SEBS concentrations: \diamondsuit , 0 phr SEBS; \times , 1 phr SEBS; \blacksquare , 5 phr SEBS; \bigstar , 10 phr SEBS; \blacksquare , 5 phr SEBS; \bigstar , 10 phr SEBS; \blacksquare , 5 phr SEBS; \bigstar , 10 phr SEBS.

copolymer has also been analyzed. The presence of PHBV and SEBS notably affects properties of blends (mechanical, thermal, and rheological properties).

Concerning mechanical properties, it is possible to state that although PHBV concentration causes a progressive decrease in UTS, a low concentration of SEBS (5 phr) improves EB, but this improvement vanishes at higher concentrations.

Regarding calorimetric analysis, both SEBS and PHBV seem to modify crystallization pattern of PP and in general terms it is possible to conclude that they cause opposite effects: while PHBV could act as a nucleating agent, shifting crystallization temperatures to higher values; when SEBS is present, crystallization occurs at lower temperatures.

In relation to rheological properties, complex viscosity curves have been correlated by the Carreau model in order to study the influence of the presence of PHBV and SEBS on blend flow properties. Furthermore, Cole–Cole plots have revealed the

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presence of a clear immiscibility in certain formulations, mainly at high SEBS concentrations, fact that could explain the poor tensile strength in formulations with 10 phr of SEBS.

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