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Polyolefins/Poly(3-hydroxybutyrate-*co*-hydroxyvalerate) Blends Compatibilization: Morphology, Rheological, and Mechanical Properties

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ABSTRACT: Polypropylene/poly(3-hydroxybutyrate-*co*-hydroxyvalerate) blend (PHBV) and polyethylene/PHBV blend were prepared by twin screw extruder using preformed copolymer (EVOH-*g*-PHBV) as compatibilizer or with functional polyolefins that can react *in situ* with the PHBV phase to form POs-*g*-PHBV. Scanning electron microscopy shows that by using either EVOH-*g*-PHBV preformed copolymer or formed copolymers *in situ* both emulsify the phase interface and reduce the interfacial tension, which result in an enhancement on the mechanical properties of compatibilized blends. Enhancement is more or less pronounced depending on the used PO matrix. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: blends; compatibilization; polyolefins; biodegradable; mechanical properties

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INTRODUCTION

Nowadays, most plastics are derived from nonrenewable crude oil and natural gas resources. Although some plastics are being recycled and reused, the majority are disposed in landfills due to end-use contamination. As one of the solutions to alleviate solid waste disposal problems and to lessen the dependence on petroleum-based plastics, there has been a sustained research interest on compostable polymers derived from renewable sources.[1] Polymers from renewable resources (PFRR) have attracted an increasing attention over the last 2 decades, predominantly due to two major reasons: first, environmental concerns, and second, the realization that petroleum resources are finite.[2] Generally, PFRR can be classified into three groups: (i) natural polymers, such as starch, protein, and cellulose; (ii) synthetic polymers from natural monomers, such as poly(lactic acid); and (iii) polymers from microbial fermentation, such as polyhydroxyalkanoates family.[2,3] PHAs attract much attention because they can be produced from a variety of renewable resources and are truly biodegradable and highly biocompatible thermoplastic materials. The most representative member of this family is poly(3-hydroxybutyrate) (PHB).[4] However, practical application of PHB has often been limited by its brittleness and narrow processing window. Therefore, blending of PHB with other polymers has been often reported in literature.[5–9] Another method to improve the mechanical and other physical properties of PHB is the development of copolymers of PHB. Among such copolymers poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) is characterized by better impact resistance and offers the possibility of processing at lower temperatures than PHB. Their properties (melting temperature, glass transition temperature, and crystallinity) are very similar to some widely used polyolefins (POs), and they can be processed using conventional extrusion and molding process.[4] The drawbacks of PHBV are the still high cost compared with that of petroleum-based commodity plastics, and a relatively low impact resistance.[10,11] Blending PHBV with POs can offer an alternative to minimize the generation of plastic waste. However, most of the polymer blends are immiscible, and the multiphase blends show poor mechanical performance because of the low interfacial adhesion between the polymer phases. Thermoplastic POs have been extensively used as toughening agents in numerous polymer blending systems, including polyester[12–14] and nylon.[15] These polymer blends are immiscible because of the high polarity difference between the polymer components. To solve the problem of immiscibility, compatibilizing agents, such as (i) premade block or graft copolymers that bear constitutive segments that are miscible with the blend components[16,17] or (ii) polymers with complementary reactive groups that can link the matrix

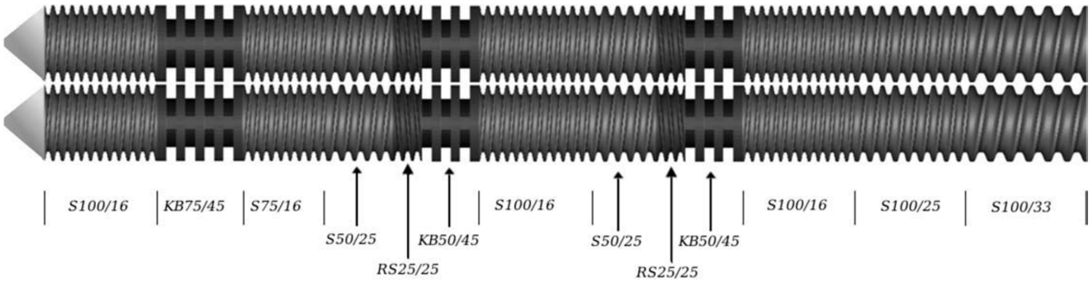

Figure 1. Screw profile used in POs/poly(hydroxybuturate-*co*-hydroxyvalerate) blends compatibilization.

with the dispersed phase via covalent bonds formed *in situ* during melt blending process are used to reduce the interfacial tension and elevate interface adhesion between the immiscible phases.[18,19]

In this study, the effects of poly[ethylene-*co*-(vinylalcohol)](EVOH)-*g*-PHBV and functionalized POs [such as EVOH and functional polypropylene (PP)] as compatibilizing agents for POs/PHBV blends were investigated. Physical and reactive blends were prepared using a twin screw extruder. Reactive extrusion (REX) is an interesting route for cost-effective one-step preparation of polymer materials, and also prepolymers, by polymerization, copolymerization, and grafting reactions.[20–24] An extensive study of the influence of compatibilization on the mechanical properties and morphology of the blends was done using various compatibilizers at different concentrations.

EXPERIMENTAL

Reagents

SABIC® PP 108MF97 high impact copolymer was purchased from SABIC and contains 22% ethylene-propylene rubber (EPR) and also a fraction of polyethylene. Two kinds of polyethylene (PE) were used in this study: Lupolen 4261 AG Q469 high-density polyethylene and Lupolen 1840D nonadditivated low-density polyethylene. Both used PE were kindly provided by LyondellBasell. PHBV (PHI 002) was supplied by NaturePlast (melting point = 145–155°C, glass transition temperature, T_g = 5°C (NaturePlast data)). EVOH was E105B purchased from EVAL Europe (melting point = 165°C, glass transition temperature, T_g = 55°C (EVAL data)) with an ethylene content of 44 mol%, given by EVAL data and determined by ^{1}H NMR spectroscopy in dimethyl sulfoxide (DMSO). 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) was purchased from Aldrich and used as received.

Melt Blending

Before any blend extrusion, PHBV was dried overnight at 80°C. For the blank blends or the compatibilized ones with EVOH-*g*-PHBV, pellets of different components of the blends were shaken before being introduced in the hopper. For the blends compatibilized with a functional PO (EVOH or functional PP), compatibilizer pellets were previously coated with TBD before mixing with the other components. Then, the polymer blends were processed with a Clextral BC 21 modular fully intermeshing corotating twin screw extruder. The screw diameter was 25 mm, the total barrel length 900 mm, and the centerline distance 21 mm. The obtained polymers were extruded through a cylindrical die. The extruder screw and temperature profiles are given in Figure 1.

Each zone of the screw profile in the extruder was chosen according to the desired functions. A relatively long compression step, 300 mm, was needed to assure a correct feeding and melting of the reactants introduced by the volumetric feeder. Three kneading blocks areas with a neutral configuration (staggering angle: 90°) were used, the first and the second disc areas were directly followed by reverse pitches screw elements to fill these zones. This relatively severe screw profile was chosen to obtain an intensive mixing. Screw rotation speed was fixed at 160 rpm for all prepared blends, only the extrusion temperature changes depending on the used PO and was fixed at 200°C for PP/PHBV and PE low density (PELD)/PHBV blends and at 220°C for PE high density (PEHD)/PHBV blends because of the high viscosity of the PO phase.

Once the blends were extruded, the extrudates were pelletized and then injection molded through a BABYPLAST 610 injection molding machine to produce test specimens. The temperature of the screw was set to 220°C for blends that contains PEHD and 200°C for all the other blends.

Characterizations

Rheology at Molten State. The rheological measurements were performed using a Rheometric Scientific ARES N_2 with parallel plate geometry (25 mm). Tests were carried out in the dynamic frequency mode at 180 or 200°C according to the PO matrix. Stress sweeps were performed to ensure that all data were acquired within linear viscoelastic conditions. The strain amplitude was kept constant at 5%.

Dynamic Mechanical Thermal Analysis. Specimens ($30 \times 2 \times 10$ mm^3) were subjected to a sinusoidal deformation in tension mode analysis at a frequency of 1.0 rad s^{-1}, strain amplitude of 0.03%, and heating rate of 3°C.min^{-1} from −100°C to 120°C in a Rheometric Scientific ARES N_2.

Scanning Electronic Microscopy. The morphologies of the polymer blends were observed by means of scanning microscopy using a Hitachi S-3000N. Prior to observations, samples were cryofractured in liquid nitrogen to avoid any plastic deformation and morphology alteration. The cryofractured surfaces were covered by a gold-palladium layer prior to analysis.

Tensile Tests. Tensile tests were carried out on an MTS 2/M tester at a speed of 10 mm/min. Ten dumb-bell shaped were tested for each polymer blend to check the good reproducibility

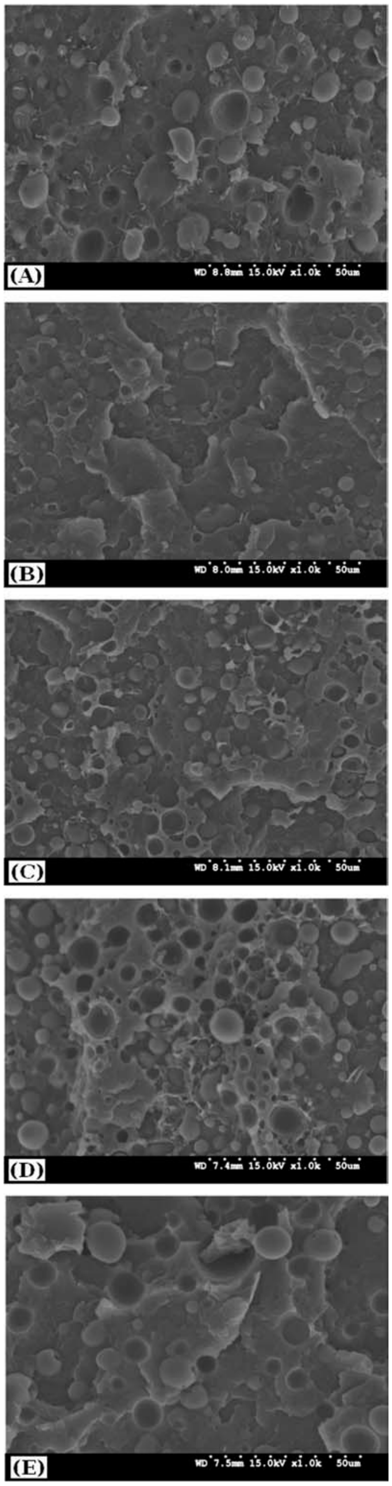

Figure 2. SEM micrographs of cryofractured surface of A: PP-PHBV 75–25 wt %, B: +5% PP-*g*-HEMA, C: +5% PP-*g*-MAH, D: +5% PP-*g*-AP, E: +5% PP-*g*-IAC.

of the experiments. Young's modulus, tensile strength, and elongation at break were determined.

Impacts Tests. Notched Charpy impact tests were performed on injected samples (80 × 10 × 4 mm) at a temperature of

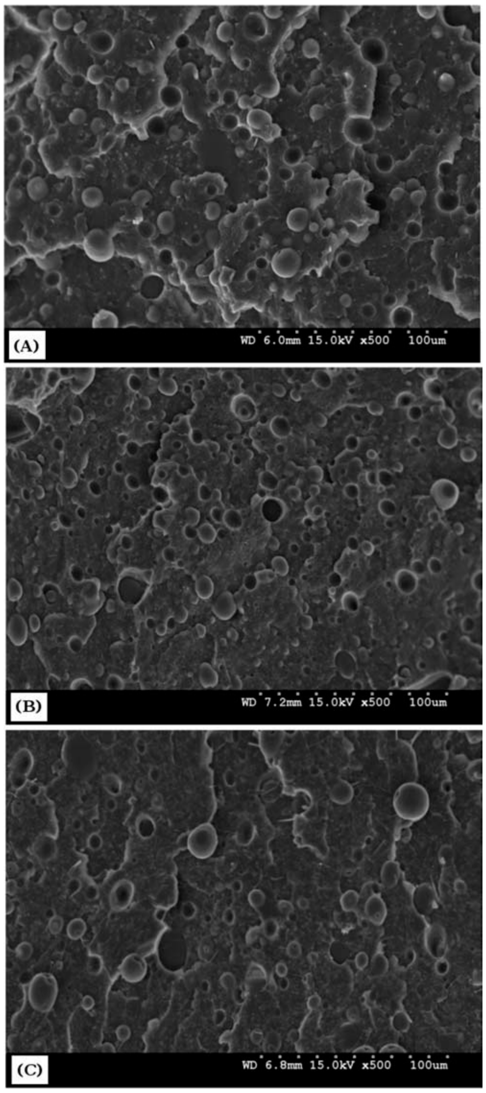

Figure 3. SEM micrographs of cryofractured surface of A: PP-PHBV 75–25 wt %, B: +5% EVOH-*g*-PHBV, C: +5% (EVOH/PHBV/TBD).

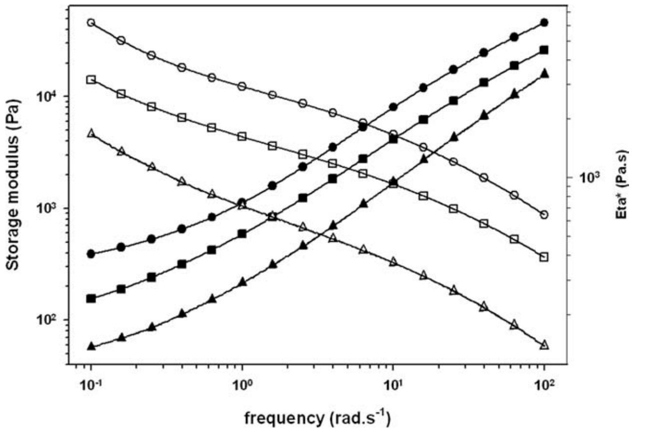

Figure 4. The storage modulus evolution of: (●) Neat PP, (■) PP/PHBV 75/25 wt %, (▲) PP/PHBV 50/50 wt %, and complex viscosity of: (○)Neat PP, (□)PP/PHBV 75/25 wt %, (Δ) PP/PHBV 50/50 wt %, at 180°C, the strain amplitude = 5% and the frequency fixed at 1 rad s^{-1}.

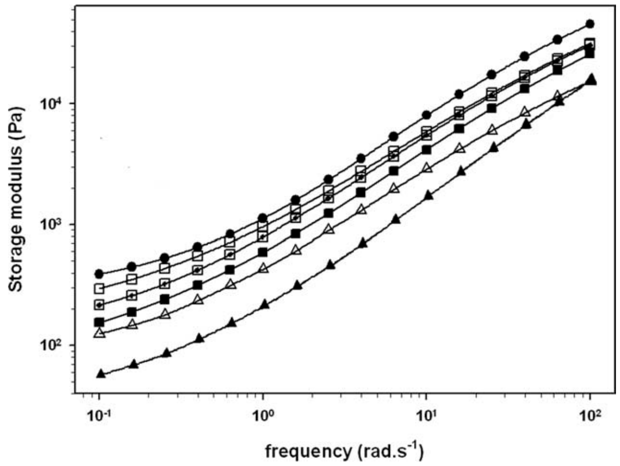

Figure 5. Storage moduli evolution of: (●) Neat PP, (■) PP/PHBV 75/25 wt %, (□) PP/PHBV 75/25 wt % with 5% EVOH-*g*-PHBV, (⊡) PP/PHBV 75/25 wt % with 5% EVOH (*in situ*) (▲) PP/PHBV 50/50 wt %, (Δ) PP/PHBV 50/50 wt % with 5% EVOH-*g*-PHBV at 180°C, the strain amplitude = 5% and the frequency fixed at 1 rad s^{-1}.

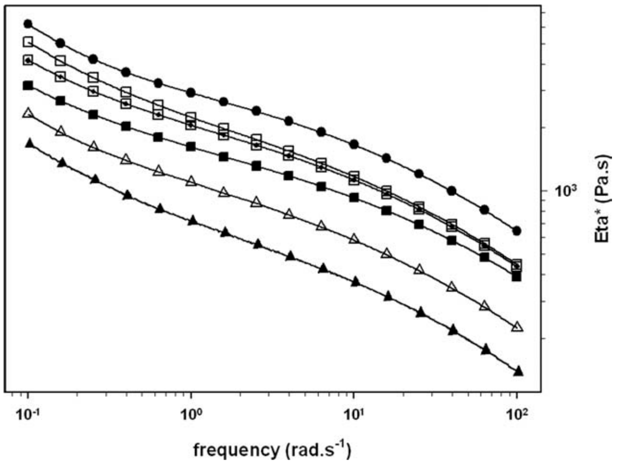

Figure 6. The complex viscosity evolution of: (●) Neat PP, (■) PP/PHBV 75/25 wt %, (□) PP/PHBV 75/25 wt % with 5% EVOH-*g*-PHBV, (⊡) PP/PHBV 75/25 wt % with 5% EVOH (▲) PP/PHBV 50/50 wt %, (Δ) PP/PHBV 50/50 wt % with 5% EVOH-*g*-PHBV at 180°C, the strain amplitude = 5% and the frequency fixed at 1 rad s^{-1}.

23°C. Ten samples were realized for each blend to evaluate the good reproducibility and an average value was determined.

RESULTS AND DISCUSSION

PP/PHBV Blends Compatibilization

Three kinds of compatibilizer were used to compatibilize PP/PHBV blend; as the used PP contains a fraction of PE, the compatibilization can be performed through the PP matrix or the PE fraction. The first compatibilizer is based on PP containing polar functions, namely PP-*g*-(maleic anhydride) (PP-*g*-MAH), PP-*g*-(itaconic acid) (PP-*g*-IAC), PP-*g*-(2-hydroxyethyl methacrylate) (PP-*g*-HEMA), and PP-*g*-(3-allyloxy-1,2-propanediol) (PP-*g*-AP). Only PP-*g*-MAH was a commercial grade, all the other modified PP were synthesized by REX in the melt as presented in our previous work.[25] The other compatibilizer was EVOH. Functional groups of these two polymers should allow, in the presence of an efficient transesterification catalyst, to form *in situ* graft copolymers bearing constitutive segments that are miscible with the PHBV dispersed phase and the matrix. The third used compatibilizer was EVOH-*g*-PHBV premade copolymer. This copolymer was obtained by grafting PHBV onto EVOH by REX as described in the previous work.[26] It is well accepted that the presence of the copolymers with similar blocks structure to that of the parent homopolymers not only emulsifies the phase interface, reducing the interfacial tension as a result, but also allows interpolymer polar interactions across phase boundaries, thus favoring growth of the interfacial layer and finally stabilizing a well-dispersed morphology. This morphology change has a favorable effect on enhancing mechanical properties.

Morphological Analysis. The phase morphologies of the blank PP/PHBV blend and its compatibilized samples using modified PP as the compatibilizer are displayed in Figure 2. All samples present typical sea-island morphologies, where the minor PHBV phase is dispersed in the PP matrix as spherical domains. With addition of both PP-*g*-HEMA and PP-*g*-MAH, the average size of the PHBV domains reduces sharply from 10.7 to 4.1 μm. This indicates that the presence of copolymers compatibilized the blend. Less dramatic particle size decrease is also observed when the other functional PPs were added to the blend and the average particle size reaches 6.0 and 7.6 μm for PP-*g*-AP and PP-*g*-IAC, respectively, [Figure 2(D-E)].

Figure 3 depicts the morphology of the phase morphologies of the blank PP/PHBV blend and its compatibilized samples with EVOH-*g*-PHBV or EVOH. As compatibilized blends with functional PPs, all samples exhibit matrix-droplet morphology, the particles of PHBV are dispersed in the PP matrix as spherical

Table I. Mechanical Analysis Results: Tensile and Impact Properties of PP/PHBV Blank Blend and Blends Compatibilized with Functional PPs

PP (wt %)	PHBV (wt %)	Compatibilizer	PHBV Average particle size (μm)	Tensile modulus (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Charpy notched impact, 22°C (kJ/m^2)
75	25	–	8.4 ± 2.6	476 ± 19	15.0 ± 1.1	8.4± 0.6	8.7 ± 1.2
75	25	PP-*g*-HEMA	4.1 ± 1.3	570 ± 15	18.3 ± 0.8	6.8 ± 0.2	5.0 ± 0.2
75	25	PP-*g*-MAH	4.1 ± 1.2	531 ± 20	18.0 ± 0.6	7.4 ± 0.7	3.7 ± 0.3
75	25	PP-*g*-AP	6.0 ± 2.2	544 ± 5	16.1 ± 0.5	6.9 ± 0.6	5.5 ± 0.4
75	25	PP-*g*-IAc	7.6 ± 2.3	535 ± 13	16.2 ± 1.5	7.2 ± 0.6	5.0 ± 0.3

Table II. Mechanical Analysis Results: Tensile and Impact Properties of PP/PHBV Blank Blend and Blends Compatibilized with EVOH-*g*-PHBV or EVOH (*In Situ*), Compatibilizer 1: EVOH-*g*-PHBV, compatibilizer 2: EVOH (*In Situ*)

PP (wt %)	PHBV (wt %)	Compatibilizer 1	Compatibilizer 2	Tensile modulus (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Charpy notched impact, 22°C (kJ/m^2)
75	25	–	–	477 ± 19	15.0 ± 1.1	8.4 ± 0.6	8.8 ± 1.6
75	25	3	–	595 ± 27	14.6 ± 2.0	6.7 ± 0.9	13.1 ± 1.0
75	25	5	–	591 ± 49	14.5 ± 0.9	6.5 ± 0.8	13.7 ± 0.9
75	25	7	–	567 ± 36	12.4 ± 1.2	5.5 ± 0.7	12.7 ± 0.6
75	25	–	3	572 ± 49	15.0 ± 0.8	6.6 ± 0.9	12.6 ± 1.0
75	25	–	5	570 ± 23	15.0 ± 1.0	5.6 ± 0.4	13.1 ± 0.8
75	25	–	7	597 ± 27	12.6 ± 0.8	5.5 ± 0.7	12.1 ± 1.0
50	50	–	–	855 ± 65	16.5 ± 4.3	2.8 ± 0.6	4.0 ± 0.7
50	50	5	–	755 ± 41	16.9 ± 2.3	2.7 ± 0.5	4.1 ± 0.3

domains. With addition of both compatibilizers, the average size of the PHBV domains reduces respectively from 10.7 to 8.7 and 9.7 μm EVOH-*g*-PHBV and EVOH. Compared to the compatibilized blends with functional PP, this decrease remains relatively low.

Rheological properties. The evolution of storage modulus and complex viscosity of blends compared with neat PP is given in Figure 4. As expected, storage moduli and viscosities decrease with the PHBV content increase, as a result of lower viscosity and storage modulus of PHBV compared with the used PP.

Figure 5 and Figure 6 give the curves of storage modulus and complex viscosity, respectively. It is notable that with adding copolymer, the low-frequency modulus as well as the complex viscosity increase gradually. This indicates that the compatibilized blend samples show higher interfacial elasticity than that of blank blend due to the reduced domain size. In other words, the emulsification by the added copolymers changed interfacial structure, such as size and thickness, which is closely related to the viscoelasticity of phase.

Mechanical properties. The mechanical properties as well as the impact strength of the blends with and without compatibilizer were characterized. As the morphology was dependent on the compatibilizer concentration and its nature, the mechanical properties should also be impacted.

Results of tensile tests for the blank PP/PHBV blend and its compatibilized samples using modified PP as the compatibilizer are summarized in Table I. Even containing rigid PHBV, the blank blend shows lower strength than that of the neat PP. This is attributed to the poor interfacial adhesion between matrix PP and minor PHBV phase. With addition of the copolymers, as expected, the strength of the blends increases remarkably because the enhanced phase adhesion and the increased interfacial area enhance load transfer between both phases. The highest strength was obtained for both compatibilized blends with PP-*g*-HEMA and PP-*g*-MAH. Strength enhancement was also accompanied with a tensile modulus increase for all compatibilized blends compared with the blank and then the formation of a rigid phase limiting the elongation at break and the impact strength as shown in Table I.

For the compatibilized blends with EVOH-*g*-PHBV or with EVOH, the obtained values of tensile test are listed in Table II. With addition of the copolymers, as expected, the strength of the blends increases because the enhanced phase adhesion and the increased interfacial area improve load transfer between two phases. Strength increase is generally accompanied with a tensile modulus growth unlike break elongation that decreases as a result of a rigid phase formation. Impact strength for these compatibilized blends shows an outstanding increase especially when 5% of compatibilizer was added as reported in Figure 7, where a maximum at 5% is observed for PP/PHBV 75/25 wt % blends for both used compatibilizers.

Generally, for compatibilized blends with functional PP, both tensile strength and tensile modulus increase showing a strengthening effect while, for the compatibilized blends with EVOH-*g*-PHBV and EVOH, rather the impact strength that shows a pronounced improvement and then, the compatibilization presents a toughening effect.

Dynamic mechanical analysis. Figure 8 displays the variation of storage moduli with temperature for neat polymers and

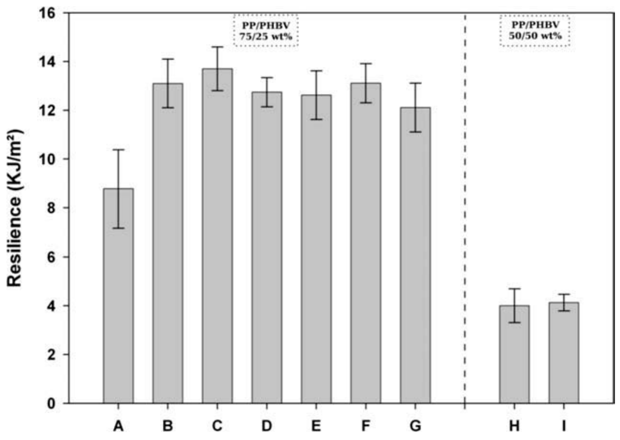

Figure 7. Mechanical properties at room temperature: Impact Strength of A: PP-PHBV 75–25 wt %, B: +3% EVOH-*g*-PHBV, C: +5% EVOH-*g*-PHBV, D: +7% EVOH-*g*-PHBV, E: +3% EVOH, F: +5% EVOH, G: +7% EVOH, H: PP-PHBV 50/50 wt %, I: +5% EVOH-*g*-PHBV.

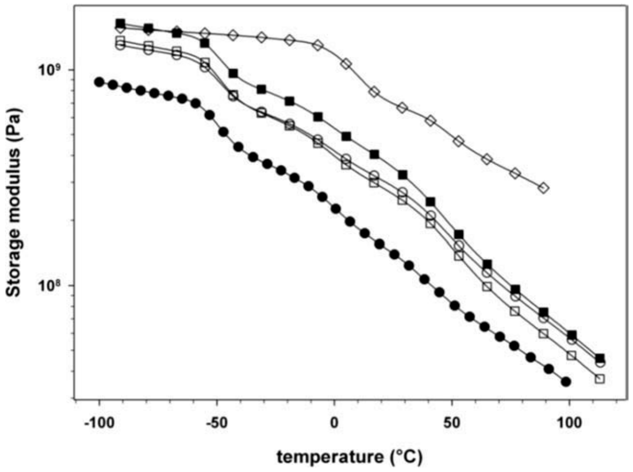

Figure 8. Storage modulus (G′) as a function of temperature (●) Neat PP, (○) PP/PHBV blend without compatibilizer, (■) PP/PHBV blend with 5% EVOH-g-PHBV, (□) PP/PHBV blend with 5% (EVOH/PHBV/TBD), (◊) Neat PHBV.

blends with and without compatibilizer. For the blend without compatibilizer, G′ lies between that of PP and PHBV. However, the addition of compatibilizer had a positive effect on G′, especially at temperatures below T_g of EPR contained in PP (−50°C). The phase boundary between the incompatible constituents was modified by compatibilizer and, thus, allowed efficient stress transfer at the interface.

Figure 9 displays the variation of loss modulus with temperature for neat polymers and blend with and without compatibilizer. PHBV showed a sharp transition around 8°C corresponding to its T_g, whereas PP showed two different transitions around −1°C, corresponding to its T_g, and −50°C, related to the EPR phase. The PP/PHBV blends with and without compatibilizer show the same observed transition for neat PP. Because the T_g of PP and that of PHBV are close to each other, the distinction of the T_g of PHBV is quite difficult.

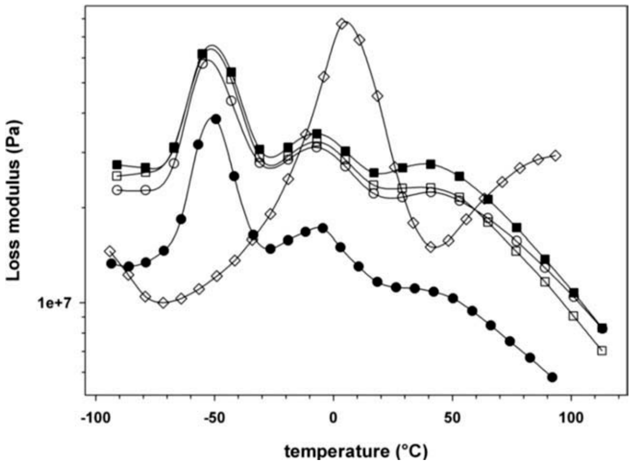

Figure 9. Loss modulus (G″) as a function of temperature (●) Neat PP, (○) PP/PHBV blend without compatibilizer, (■) PP/PHBV blend with 5% EVOH-*g*-PHBV, (□) PP/PHBV blend with 5% (EVOH/PHBV/TBD), (◊) Neat PHBV.

Polyethylene/PHBV Blends Compatibilization

Low Density PE/PHBV

Morphological properties. Figure 10 depicts the phase morphologies of the blank PE/PHBV blend and its compatibilized samples with 5% EVOH-*g*-PHBV or 5% EVOH. As for compatibilized PP/PHBV blends, all samples exhibit matrix-droplet morphologies, the particles of PHBV are dispersed in the PE matrix as spherical domains. With the addition of a compatibilizer, the average size of the PHBV domains reduces from 6.4 μm for blank blend to 4.0 μm for the blends compatibilized with EVOH-*g*-PHBV and to 5.3 μm for the one compatibilized with EVOH. That proves one more time that EVOH-*g*-PHBV is more efficient to reduce interfacial tension.

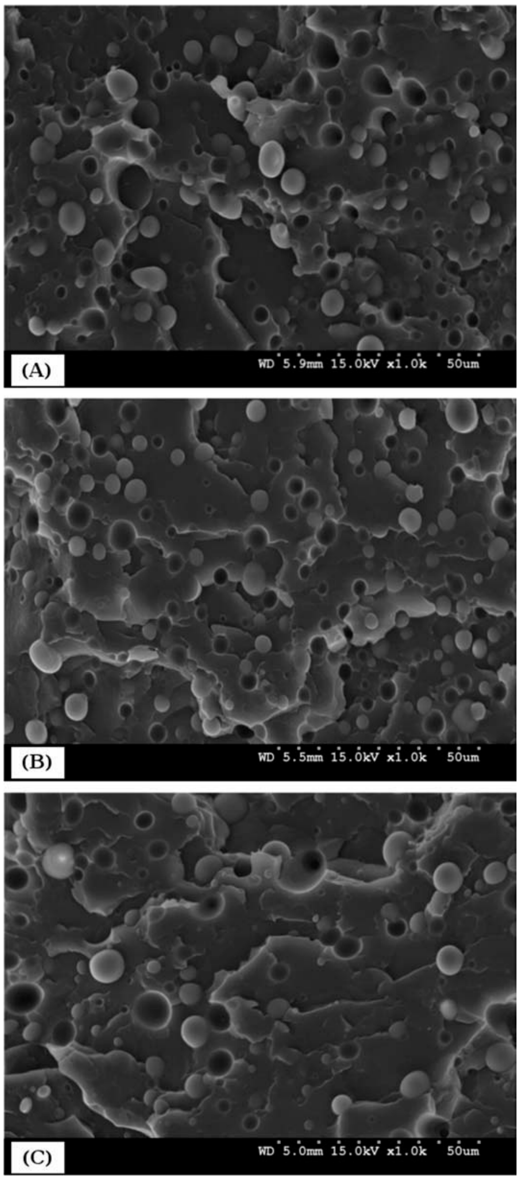

Figure 10. SEM micrographs of cryofractured surface of A: PE-PHBV 75–25 wt %, B: +5% EVOH-*g*-PHBV C: +5% (EVOH/PHBV/TBD).

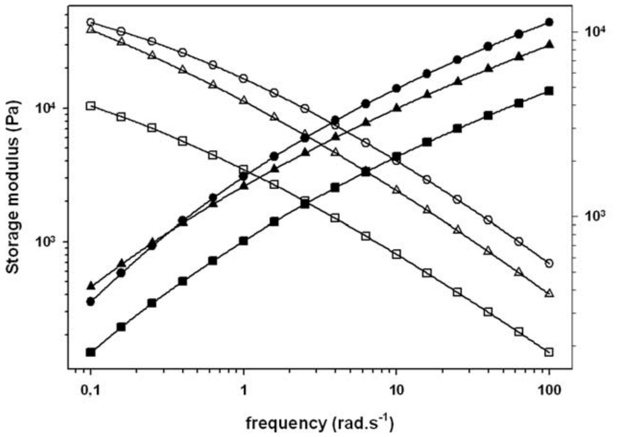

Figure 11. The storage modulus evolution of: ●) Neat PELD, (■) PELD/PHBV 75/25 wt %, (▲) PELD/PHBV 50/50 wt %, and complex viscosity of: (○)Neat PELD, (□) PELD/PHBV 75/25 wt %, (Δ) PELD/PHBV 50/50 wt %, at 180°C, the strain amplitude = 5% and the frequency fixed at 1 rad s^{-1}.

Rheological properties. Figure 11 displays the evolution of storage modulus and complex viscosity of blends compared with neat PE. As for the PP/PHBV blends, storage modulus and viscosity decrease with the PHBV content increase following blends rules.

Figure 12 and Figure 13 give the curves of storage moduli and complex viscosities, respectively. By adding both EVOH-*g*-PHBV and EVOH, a small storage modulus and viscosity increase is observed for blends with 25 wt % PHBV while for blend with 50 wt % PHBV compatibilized with EVOH-*g*-PHBV, the storage modulus and the viscosity present the same rheological behavior as the blank blend.

Cole-Cole plots are usually used for the description of viscoelastic properties of the systems with a relaxation time distribution. For many immiscible polymer blends, Cole-Cole plots yield with two arcs, which were interpreted by the simultaneous occurrence of two processes with largely differing relaxation times.[27]

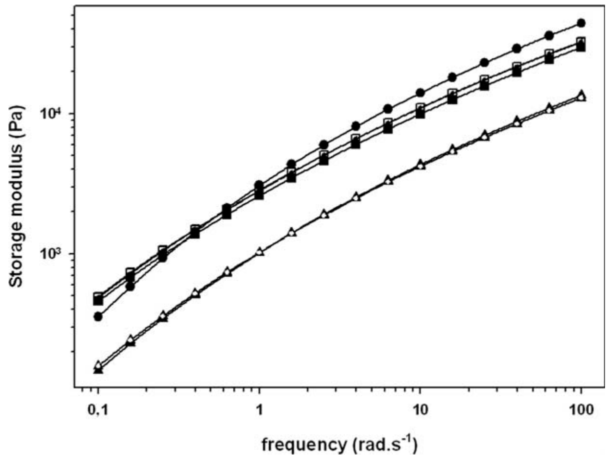

Figure 12. The storage modulus evolution of: (●) Neat PELD, (■)PELD/PHBV 75/25 wt %, (□) PELD/PHBV 75/25 wt % with 5% EVOH-*g*-PHBV, (⊡) PELD/PHBV 75/25 wt % with 5% EVOH (*in situ*) (▲) PELD/PHBV 50/50 wt %, (Δ) PELD /PHBV 50/50 wt % with 5% EVOH-*g*-PHBV at 180°C, the strain amplitude = 5% and the frequency fixed at 1 rad s^{-1}.

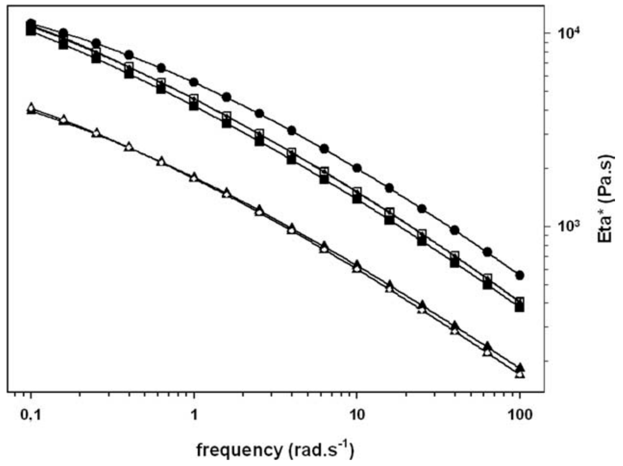

Figure 13. The complex viscosity evolution of: (●) Neat PELD, (■)PELD /PHBV 75/25 wt %, (□) PELD/PHBV 75/25 wt % with 5% EVOH-g-PHBV, (⊡) PELD /PHBV 75/25 wt % with 5% EVOH (*in situ*) (▲) PELD /PHBV 50/50 wt %, (Δ) PELD /PHBV 50/50 wt % with 5% EVOH-*g*-PHBV at 180°C, the strain amplitude = 5% and the frequency fixed at 1 rad s^{-1}.

Figure 14 gives the Cole-Cole plots for the PE/PHBV blends. Blends without compatibilizer present two relaxation arcs, which are corresponding to different relaxation mechanisms. With addition of the compatibilizer, the relaxation arc is broadened and shifts up to high-viscosity region indicating that the presence of copolymers retards the overall relaxation of the PE/PHBV blend systems. However, the Cole-Cole plots cannot provide additional information on the interfacial relaxation because the relaxation arc cannot fully appear in the experimental ranges of frequency.

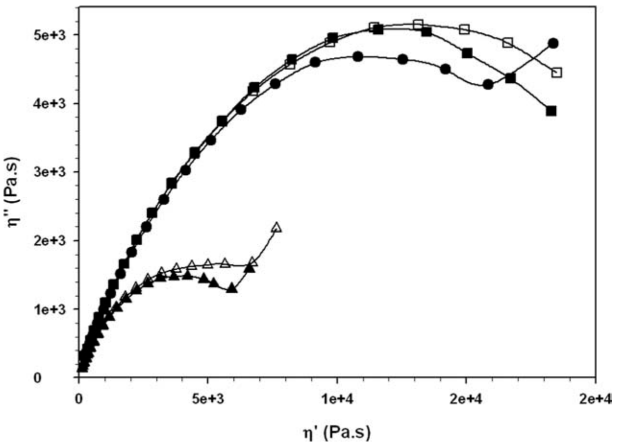

Figure 14. The Cole-Cole plots of imaginary viscosity (η'') versus real viscosity (η') at 180°C for the blank and the compatibilized blend samples. (●) PE/PHBV 75/25 wt % without compatibilizer (■) with 5% EVOH-*g*-PHBV (□) compatibilization *in situ* (▲) PE/PHBV 50/50 wt % without compatibilizer (Δ) with 5% EVOH-*g*-PHBV.

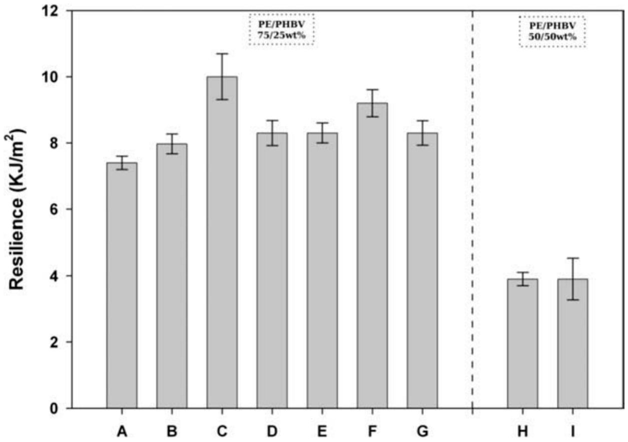

Figure 15. Mechanical properties: Impact Strength of A: PELD-PHBV 75–25 wt %, B: +3% EVOH-*g*-PHBV, C: +5% EVOH-*g*-PHBV, D: +7% EVOH-*g*-PHBV, E: +3% EVOH, F: +5% EVOH, G: +7% EVOH, H: PELD-PHBV 50/50 wt %, I: +5% EVOH-*g*-PHBV.

Mechanical properties. The impact properties obtained by means of notched Charpy impact tests are reported in Figure 15. The results of notched impact strength as well as tensile tests are summarized in Table III. For PE/PHBV 75/25 wt % blends, strength impact of the compatibilized blends enhances whatever the concentration of the added compatibilizer. This enhancement is more pronounced for the addition of 5 wt % compatibilizer, and it is noted that the highest impact strength was obtained for compatibilized blend with EVOH-*g*-PHBV, which is quite logical as this blend shows a finer morphology than the one obtained for compatibilized blend with EVOH. Even for obtained results from tensile test, blends with 5 wt % of compatibilizer stand out from the blank blend by a higher tensile strength and elongation at break and the blend compatibilized with 5% EVOH-*g*-PHBV shows once again the highest mechanical properties. For 3 and 7% of compatibilizer, the concentration is too low or in excess to ensure an improvement in the mechanical properties. For PE/PHBV 50/50 wt % blends, the mechanical properties of compatibilized blend either remain almost unchanged or decrease compared with the blank blend.

High Density PE/PHBV. Because of the high viscosity of this PEHD, only the compatibilization with a concentration of 5 wt % of EVOH-*g*-PHBV was investigated. The mechanical properties of these blends are summarized in Table IV. It is clearly shown that the addition of the compatibilizer is very effective for overcoming the brittleness of blends, resulting in a significant increase in the elongation at break. Indeed, with the addition of 5% of compatibilizer, the elongation at break remarkably increased to over 80% against 47% for the blank blend. It was also shown that this elongation at break increase was accompanied by a decrease in the tensile modulus while ultimate tensile strength presents a slight increase by adding the compatibilizer. The impact resistance also increases strongly and rises from 14 KJ/m for the blank blend to 24.4 KJ/m for the compatibilized blend. This enhancement in the mechanical properties can be explained by the presence of the compatibilizer that emulsifies the phase interface and reduces significantly the interfacial tension, consequently, much finer phase domain size was obtained as shown in Figure 16 allowing this improvement in the mechanical properties.

Table III. Tensile and Impact Properties of PELD/PHBV Blank Blend and Blends Compatibilized with EVOH-*g*-PHBV or EVOH (*In Situ*), Compatibilizer 1: EVOH-*g*-PHBV, compatibilizer 2: EVOH (*In Situ*)

PE (wt %)	PHBV (wt %)	Compatibilizer 1	Compatibilizer 2	Tensile modulus (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Charpy notched impact, 22°C (kJ/m^2)
75	25	–	–	239 ± 17	7.5 ± 0.7	13.4 ± 1.1	7.4 ± 0.2
75	25	3	–	233 ± 13	7.4 ± 0.6	12.5 ± 1.1	8.0 ± 0.3
75	25	5	–	249 ± 19	8.9 ± 1.0	16.9 ± 1.0	10.0 ± 0.7
75	25	7	–	257 ± 24	6.6 ± 0.7	12.9 ± 0.8	8.3 ± 0.4
75	25	–	3	282 ± 14	6.4 ± 0.8	9.6 ± 0.9	8.3 ± 0.3
75	25	–	5	262 ± 15	8.1 ± 0.7	15.9 ± 1.9	9.2 ± 0.4
75	25	–	7	265 ± 14	7.3 ± 0.4	11.8 ± 1.1	8.3 ± 0.4
50	50	–	–	481 ± 34	9.1 ± 1.4	2.7 ± 0.4	3.9 ± 0.2
50	50	5	–	380 ± 52	4.4 ± 2.3	1.6 ± 0.4	3.9 ± 0.6

Table IV. Tensile and Impact Properties of PEHD/PHBV Blank Blend and Blends Compatibilized with EVOH-*g*-PHBV

PE (wt %)	PHBV (wt %)	Compatibilizer 1 (wt %)	Tensile modulus (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Charpy impact notched, 22°C (kJ/m^2)
75	25	–	377 ± 7	15.8 ± 0.1	47 ± 9	14 ± 0.9
75	25	5	331 ± 12	16.3 ± 0.2	84 ± 12	24.4 ± 1.8

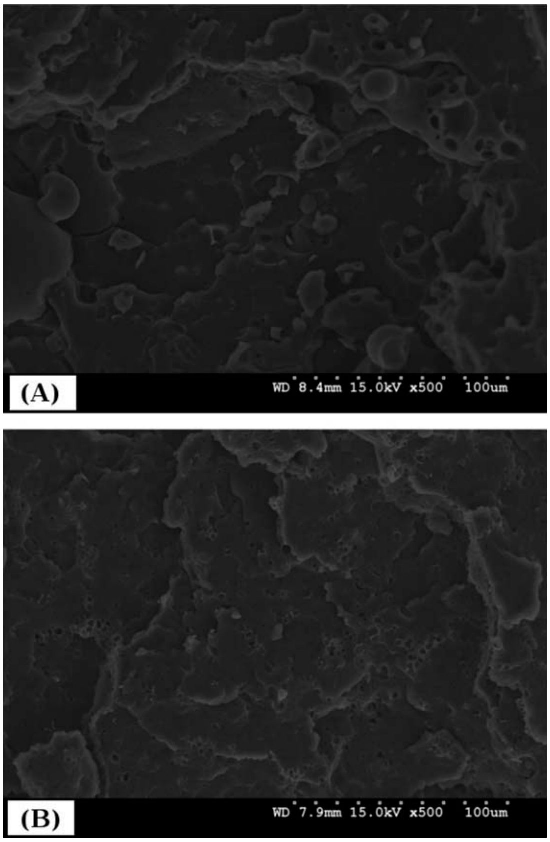

Figure 16. SEM micrographs of cryofractured surface of A: PEHD-PHBV 75–25 wt %, B: +5% EVOH-*g*-PHBV.

CONCLUSION

In this study, various copolymers were used as compatibilizers to improve interfacial and mechanical properties of the immiscible PP/PHBV and PE/PHBV blends. PP/PHBV blend was compatibilized using functional PPs or EVOH that react *in situ* to form PP-*g*-PHBV or EVOH-*g*-PHBV, respectively. Compatibilization was also performed by using EVOH-*g*-PHBV preformed copolymer. For PP/PHBV compatibilized blends with functional PP, both tensile strength and tensile modulus increase showing a strengthening effect while for the compatibilized blends with EVOH-*g*-PHBV and EVOH, rather the impact strength that shows a pronounced improvement and then, the compatibilization presents a toughening effect.

The compatibilization of PELD/PHBV 75/25 wt % blends was achieved successfully using either EVOH-*g*-PHBV or EVOH that act as compatibilizer, reducing interfacial tension and improving interfacial adhesion, and finally enhancing mechanical properties regardless of the copolymer concentration, although the highest mechanical properties were obtained with 5% of compatibilizer. Compatibilization of PEHD with PHBV was also achieved with 5% of EVOH-*g*-PHBV and the compatibilized blend shows outstanding mechanical properties compared with the blank blend.

All blends with 50/50 wt % ratio regardless of the PO used keep poor mechanical properties. This suggests that the used concentration of compatibilizer is not high enough to reduce interfacial tension and enhance mechanical properties.

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