Improvement of the Thermal Properties of Poly(3-hydroxybutyrate) (PHB) by Low Molecular Weight Polypropylene Glycol (LMWPPG) Addition

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ABSTRACT: In this work, blends of poly(3-hydroxybutyrate) (PHB) with 5, 10, 15, and 20 wt % low molecular weight poly(propylene glycol) (LMWPPG) have been prepared and characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) with attenuated total reflectance (ATR) accessory and simultaneous thermal analysis (TG/DTA). FTIR and thermal analyses suggested that the presence of LMWPPG led to a maximum crystallinity for the blend PHB/PPG (90/10) blend. The presence of LMWPPG also caused a significant increase of the PHB processability window, i.e., the difference of the melting and degradation temperature, of PHB from 105 to 134°C, which is extremely important for the industrial uses of PHB. This PHB stabilization effect is discussed in terms of an intermolecular interaction of the PHB carbonyl with LMWPPG methyl groups which probably hinders the classical radon β-scission PHB intramolecular decomposition mechanism. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is a naturally occurring polyester produced from renewable sources by different bacteria in nature.[1–4] The PHB biodegradability is a key feature for its use to replace the conventional petrochemical plastics and other uses in agriculture, food packaging, and storage.[5–9] Because of its biocompatibility the PHB can also be used in biomedicine as a surgical sutures, drug delivery vehicles and also investigated as scaffolds for tissue engineering.[7] On the other hand, high crystallinity and processability have been mentioned as the main barriers for the commercial uses of PHB.[1–4] Different approaches have been used to improve the PHB processability such as copolymerization, use of plasticizer, production of composites, and blends.[3,9–16] Different copolymers containing PHB have been investigated for different applications, e.g., multiblock poly(ester urethane)s PHB-PEG or PPG,[17] poly(ether-ester-urethanes) containing segments of PEG, PPG and PHB.[18,19]

The research on PHB blends has been focused mainly on crystallinity and miscibility studies due to the importance of these phenomena on the thermal, physical, biodegradability and mechanical properties.[8,20]

PHB blends have been produced with different polymers, such as poly(vinyl alcohol), polyesters, e.g., poly(L-lactide), poly(ester ethers), polyacrylates, polysaccharides cellulose, and starch derivatives.[20-26] Polyethers such as polyethylene oxide (PEO), polyethylene glycol (PEG), poly(methylene oxide), and its chloride derivatives[20,27] have shown good compatibility and some effect on the thermal, morphological, physical–chemical, and biodegradability properties.[16,28,29] On the other hand, blends of PHB with LMWPPG (low molecular weight PPG) have not been described in the literature. Low molecular weight

Additional Supporting Information may be found in the online version of this article.
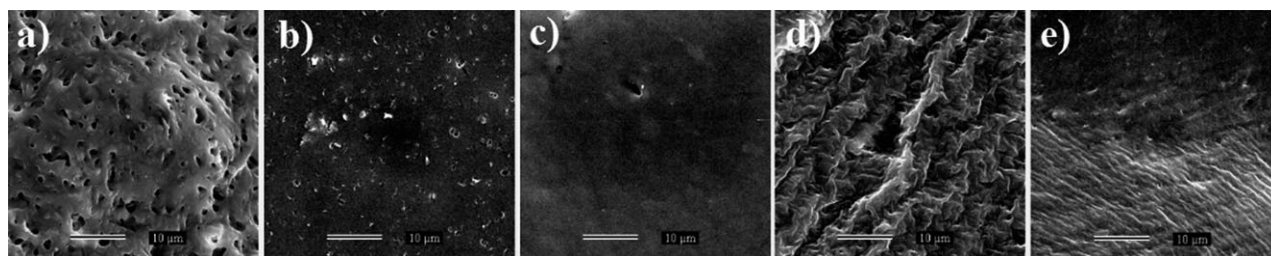
Figure 1. SEM images surface of the PHB neat (a); PHB/PPG (95/05) (b); PHB/PPG (90/10) (c); PHB/PPG (85/15) (d); and PHB/PPG (80/20) (e).

polypropylene glycol is a liquid polymer with hydroxyl terminal groups which should interact with the PHB chains producing a plasticizer effect.[23,30,31]

In this work, the effect of LMWPPG on the crystallinity and thermal properties of PHB was investigated. The results suggest that LMWPPG interacts with PHB at the molecular level to form a homogeneous material with a significant improvement of the thermal properties and processability window widening its industrial uses.

EXPERIMENTAL

The PHB (ca. 600 kDa) was purchase from PHB Industrial S/A. (Serrana, SP-Brazil). The LMWPPG (ca. 1 kDa) was obtained from Aldrich (St. Louis, MO). The blends were prepared by solution blending. PHB was solubilized in chloroform (Vetec, 99.8%—Duque de Caxias, RJ, Brazil) at 40°C through constant stirring until complete dissolution of the polymer. The LMWPPG was added to obtain the concentrations of LMWPPG in the blends of 5, 10, 15, and 20 wt %. The polymer solutions were stirred for 3 h and transferred to an appropriate glass mold for solvent evaporation for 48 h at room temperature.

The morphological study of PHB/PPG blends was carried out by scanning electron microscopy (SEM) using a JEOL instrument, model 840A, operating at 15 kV or SHIMADZU model SSX 550. The samples were immersed in liquid nitrogen to produce the fractures.

The blends with 5, 10, and 20 wt % have been subjected to selective extraction by deionized water for 5 days at room temperature and dried in oven by for 24 h at 50°C.

Fourier transform infrared (FTIR) measurements of the blends were carried out with a Nicolet FT–IR 380 spectrophotometer equipped with an attenuated total reflectance (ATR) accessory. The spectra of the samples were obtained in the region from 4000 to 400 cm^{-1} using a ZnSe crystal. The TG/DTA curves were obtained under nitrogen atmosphere (50 mL min^{-1}) at 20°C min^{-1} in a simultaneous thermoanalyzer DTG 60 Shimadzu.

RESULTS AND DISCUSSION

The PHB/PPG films with LMWPPG contents of 5, 10, 15, and 20 wt % were obtained by casting and the obtained blends showed homogeneous aspect. Figure 1 shows SEM images of the film surfaces and cryofractures for the PHB/PPG prepared blends. Pure PHB showed a typical surface with the presence of

pores, likely produced during the evaporation of the solvent chloroform used for casting. The addition of LMWPPG to PHB gradually changed the texture of the blends producing smoother surfaces with a decrease on the number of pores.

This effect is likely related to LMWPPG that minimizes the stresses produced in the polymer during drying and crystallization favoring more regular surface and less pores. On the other hand, for higher LMWPPG contents, SEM images showed an increase on the surface roughness. In this case, migration of LMWPPG to the blend surface might be responsible for the different morphologies. Probably, after a critical concentration, LMWPPG starts to migrate to the surface whereas the bulky LMWPPG concentration remains approximately constant. For many blends, the miscibility depends on the composition and it is driven by interactions among side groups or polymer segments.[32,33] SEM images did not show any significant difference on the fracture pattern for the different blends with the cracks formed in similar direction suggesting a brittle structure with low resistance to fracture.

The morphology of the PHB/PPG blends was also evaluated by SEM after the LMWPPG phase was extracted using water as selective solvent. The neat PHB and PHB/PPG (95/05) images before and after selective extraction were similar suggesting that up to 5 wt % PPG the system behaves as a diluted solution, i.e., high miscibility. On the other hand, the fracture images of the blend PHB/PPG (90/10) revealed the presence of small submicrometric cavities distributed homogeneously over the PHB matrix, due to the extraction of the LMWPPG. For the blends 5 and 10 wt % the miscible PPG can act as a nucleating agent or provide greater mobility to the chains favoring crystallization. This crystallization is likely responsible for the fragile fracture observed in Figure 2. On the other hand, the blend PHB/PPG (80/20) presents larger cavities and features of a more ductile fracture (Figure 2). This result is likely related to a critical miscibility limit of PPG in PHB which is reached above 10 wt %. After this critical limit the LMWPPG segregated can be extracted by water to form large cavities. Moreover, the different fracture patterns observed for the blend PHB/PPG (80/20) also suggest an important modification of the interactions of the PPG and PHB chains.

The polymers and the blends were also investigated by FTIR–ATR (Figure 3). The main IR bands observed for LMWPPG were: at about 3000 cm^{-1} associated with —CH groups, 1090 cm^{-1} related to C—O—C group and deformation of methyl group at about 1373 cm^{-1}. For the PHB were observed bands
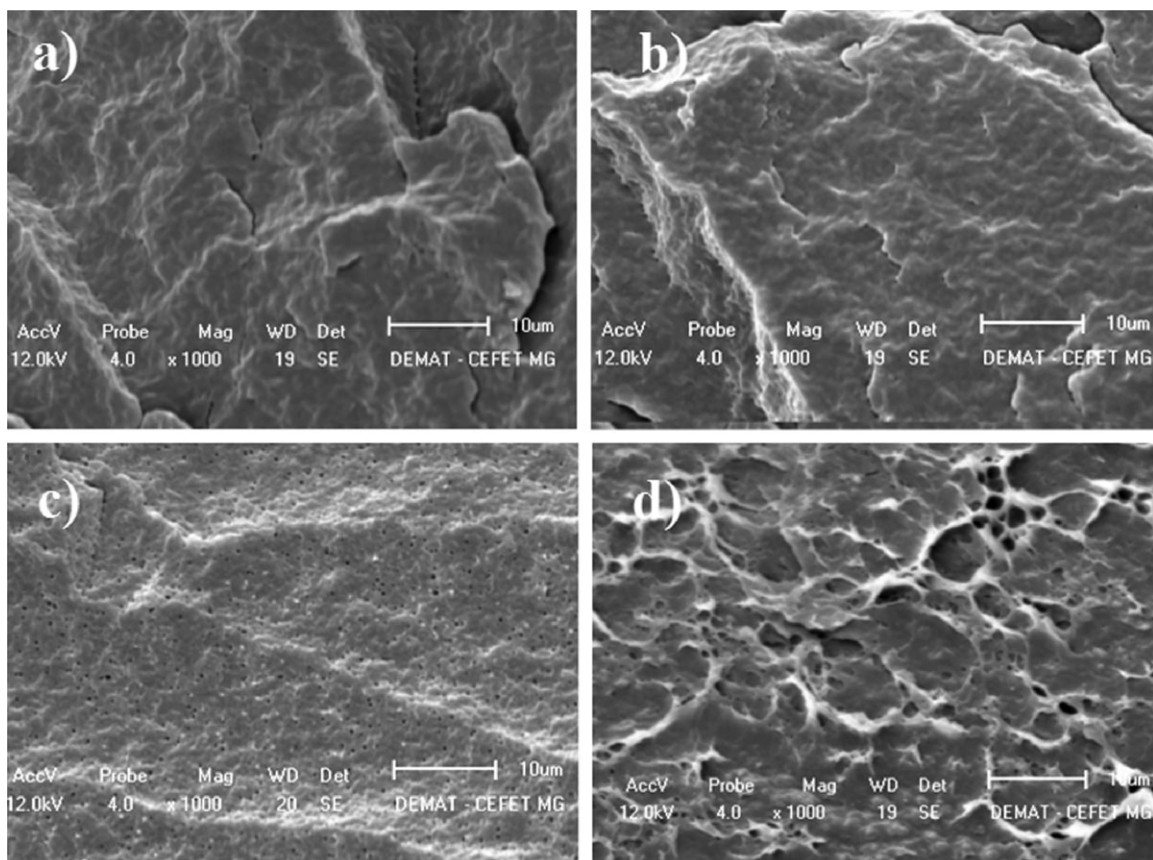
Figure 2. SEM images after solvent extraction. PHB neat (a); PHB/PPG (95/05) (b); PHB/PPG (90/10) (c) and PHB/PPG (80/20) (d).

at 3000–2900 cm^{-1} and 1460–1350 cm^{-1} associated with CH$_3$, CH$_2$ asymmetric and CH$_2$ symmetric stretching and deformation modes, respectively. Multiple bands within 1300–1100 cm^{-1} are related to C—O—C groups in crystalline (1276 and 1226 cm^{-1}) and amorphous phases (1261 and 1183 cm^{-1}).[33] All blends showed FTIR spectra similar to PHB with a slight increase on the intensity of the carbonyl peak (1716 cm^{-1} for the PHB and 1718 cm^{-1} for the blends).

The PHB carbonyl IR peak about 1720 cm^{-1} showed asymmetric stretching vibrations between 1760 and 1680 cm^{-1}. The presence of shoulders in the IR carbonyl band is related to contributions of C=O free or hydrogen bonded existing in the crystalline and amorphous phases. The assignment of these amorphous and crystalline phases by IR has been extensively studied for PHB and others PHAs. It has been suggested that these intramolecular carbonyl interactions are important for the PHB crystal structure organization.[32–37]

A deconvolution of the carbonyl IR band in the different components was carried out by a Gaussian fitting (Figure 4). The obtained fitting showed the presence of three main components identified as: (i) the shoulder at 1742 cm^{-1} related to free C=O amorphous phases, (ii) the shoulder at 1732 cm^{-1} likely associated with the intermolecular interactions of C=O with the methyl groups (likely a transition state between crystalline and amorphous phase), and (iii) the peak at 1718 cm^{-1}, related to crystalline phases involved in intramolecular bonding

interactions between carbonyl groups and CH$_3$ groups.[32–38] It was also observed a weak absorption at 1687 cm^{-1} associated with crystalline phases.

It is interesting to observe that the shoulder at 1732 cm^{-1} was modified but the addiction of LMWPPG to PHB (Figure 4) suggesting that methyl groups of LMWPPG are likely interacting with PHB carbonyl groups inducing the formation of a
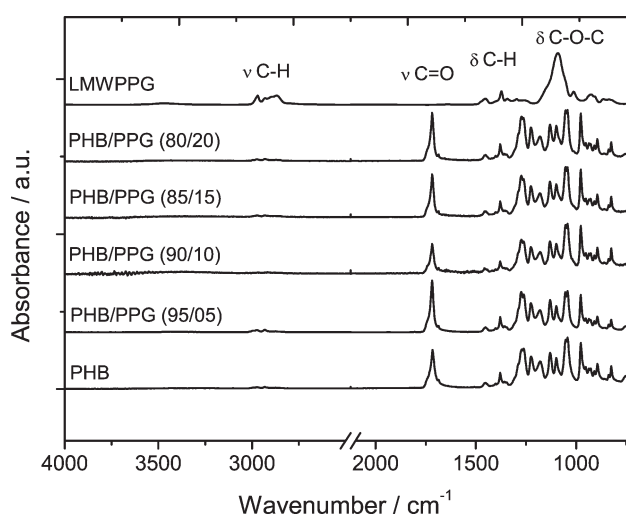

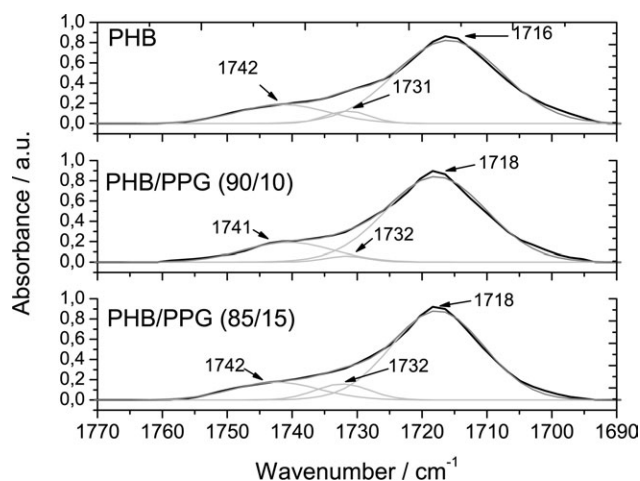**Figure 3.** FTIR–ATR spectra of the homopolymers and PHB/PPG blends.

Figure 4. Fitted Gaussian FTIR-ATR curves for carbonyl region.

Figure 5. DTA curves for the homopolymers and PHB/PPG blends.

crystalline/amorphous transition phase. Previous work for poly-hydroxyalcanoates suggests that the disappearance of the highly ordered crystalline component observed by the band at 1718 cm^{-1} of the polymer does not lead directly to the amorphous phase but produces an intermediate phase observed by the band at about 1732 cm^{-1}.[39] Similarly, the addiction of LMWPPG can interact with the crystalline phase of PHB induce modifications in the transition phase.

To study the effect of LMWPPG on the crystallinity of PHB two indexes were calculated from the IR spectra, i.e., the index of crystallinity (I_c) and the index of transition crystalline-amorphous region (I_t). The I_c calculated by the ratio of the band area at 1718 cm^{-1} (intra C=O crystalline) and the total carbonyl band area was used to obtain a PHB relative index of crystallinity, ($A_{1718}/A_{\text{carbonyl band}}$). Also, an index to express the relative quantity of carbonyl groups in the interface/transition crystalline-amorphous region was obtained by I_t, the ratio of the band at 1732 cm^{-1} and the total area of carbonyl band ($A_{1732}/A_{\text{carbonyl band}}$). These I_c and I_t for different blends are shown in Table I.

It can be observed that the I_t is inversely related to I_c (see plot in Supporting Information), i.e., a decrease of the crystallinity (I_c) is accompanied by an increase of the index I_t. The index I_c shows only slight changes for the blends. In general the presence of LMWPPG caused a decrease on the crystallinity of PHB, except for the blend with 10 wt % LMWPPG which showed a slight increase on the I_c.

Table I. Crystallinity Index (I_c) and Transition Index (I_t) for the PHB and PHB/PPG Blends

PHB/PPG	I_c (%)	I_t (%)
100/0	80	5.0
95/05	79	5.6
90/10	81	2.2
85/15	77	8.2
80/20	78	5.8

These results suggest that the crystalline fraction of PHB decreases in the presence of LMWPPG to form a transition/interface region between crystalline and amorphous phases which has been observed before.

A more significant variation can be observed in the spectra of PHB/PPG (90/10) and PHB/PPG (85/15) (Figure 4) which produced I_t of 2.2 and 8.2, respectively. These results indicate that the blend PHB/PPG (90/10) should have the highest crystallinity whereas the blend PHB/PPG (85/15) should be the less crystalline. These results have been confirmed by thermal analyses as discussed below.

The DTA curves were used to determine the melting enthalpy ΔH_m of the blends (Figure 5). This parameter is related to the crystallinity fraction (X_c) of the polymer used for semicrystalline polymer blends.[40]

$$X_c = \left(\frac{\Delta H_m}{\Delta H_m^0 W_{\text{PHB}}} \right) \cdot 100 \qquad (1)$$

The ΔH_m^0 for pure crystalline PHB is 146 J g^{-1} and W_{PHB} corresponds to the weight fraction of PHB in the sample.[41]

The obtained results suggested a decrease on the PHB crystallinity of about 60–50% with the addition of LMWPPG. The blend PHB/PPG (90/10) again showed a different behavior with higher crystallinity (ca. 64%) compared to PHB. Very important effects were observed with the addition of LMWPPG into PHB, especially a decrease of the melting temperature (T_m) and an increase in the onset temperature (T_{onset}) increasing the thermal stability of PHB blends compared to pure PHB. These effects are likely related to the weakening of the PHB intramolecular interactions due to an intermolecular interaction between PHB–LMWPPG. This difference between the maximum decomposition temperature (T_d) and T_m, described as ΔT. The ΔT is an important parameter for the processability of the blends. The addition of LMWPPG caused a remarkable increase in ΔT of about 30°C (Table II) for all blend compositions.

The TG/DTG curves, Figure 6, showed a decomposition of PHB at lower temperatures (289°C) whereas LMWPPG decomposes

Table II. Results of Thermal Analysis of PHB/PPG Blends

PHB/PPG	T_m (°C)	T_{onset} (°C)	T_d (°C)	ΔT^a (°C)	ΔH_m (J g^{-1})	$X_{c\ DTA}{}^b$
100/0	184	274	289	105	87	60
95/05	177	291	308	131	69	49
90/10	179	294	309	130	84	64
85/15	175	297	309	134	57	46
80/20	178	297	310	132	57	49
0/100	–	319	342	–	–	–

[a]ΔT difference between the temperature maximum decomposition and melting temperatures by DTA analysis, [b]Melt temperature and crystalline fraction measured by DTA, 1st run of heating at 20°C min^{-1}.

at about 342°C (Table II). The formation of the blends significantly affects the TG/DTG profiles of PHB. It can be observed that the presence of LMWPPG at 20 wt % thermally stabilizes PHB with an increase of T_d from 289 to 310°C (Table II). The decomposition peak of LMWPPG, DTG curves [Figure 6(b)], was not observed in the blends up to 20 wt % at high temperatures.

The thermal properties, such as T_{onset}, T_m, and T_d of the blends, suggest that LMWPPG affects the PHB properties in blends in

Figure 6. TG (a) and DTG (b) curves for the homopolymers and PHB/PPG blends.

two aspects: a slight decrease in the melting point and an increase in the thermal stability. The changes in crystallinity present a maximum in the blends in the composition with 10 wt % of LMWPPG. This maximum effect at an intermediate additive concentration in polymers has been observed in different materials such as PHB/PEG blend using cellulose nanocrystals in thermal and mechanical properties, with maximum thermal degradation temperature and elongation at break using only 0.45 wt % of cellulose nanocrystals.[42] Those effects were also observed in the crystallinity of nanocomposites using nanoclay, with maximum at 4 wt % of clay.[4] The PHB/PLA (25/75) blend exhibits significantly improvement of tensile properties if compared to pure PLA or another compositions of PLA in PHB/PLA blends.[43] Although this effect is not clear for the PHB/PPG blends one can speculate that it is related to a highest miscibility for the blend PHB/PPG (90/10).

The LMWPPG acts as a plasticizer increasing the PHB chains mobility and it can also promote an increase in the crystallinity. On the other hand, blends with LMWPPG concentrations higher than 15 wt % presented a phase separation. This separation can be related to the endothermic event present at high temperatures in the DTA curves for the blend with 20 wt % of LMWPPG, Figure 5, not observed for the other blends studied.

The result obtained in this work suggests that LMWPPG has some important effects on PHB, i.e., a decrease on the crystallinity and on the melting temperature with a simultaneous increase on the decomposition temperature. These effects can be discussed by a facile diffusion of the relatively small LMWPPG molecules and also by molecular interactions with PHB. The LMWPPG can diffuse easily acting as a plasticizer. The PPG molecules dispersed in the rich PHB phase are likely disturbing crystal formation and therefore reducing crystallinity and decreasing the melting point. The IR results suggest that these molecular interactions are likely related mainly to CH_3 groups with the C=O PHB groups. A schematic representation of the PHB intermolecular interactions that are replaced by the interactions with LMWPPG via CH_3 groups are illustrated in Figure 7.

The other remarkable effect of LMWPPG is on the increase of the decomposition temperature of PHB. Thermal degradation of PHB has been reported to take place by a random chain scission reaction. The mechanism described in the literature proposes the formation of the six-member ring transition state with carbonyl groups leading to an elimination of hydrogen
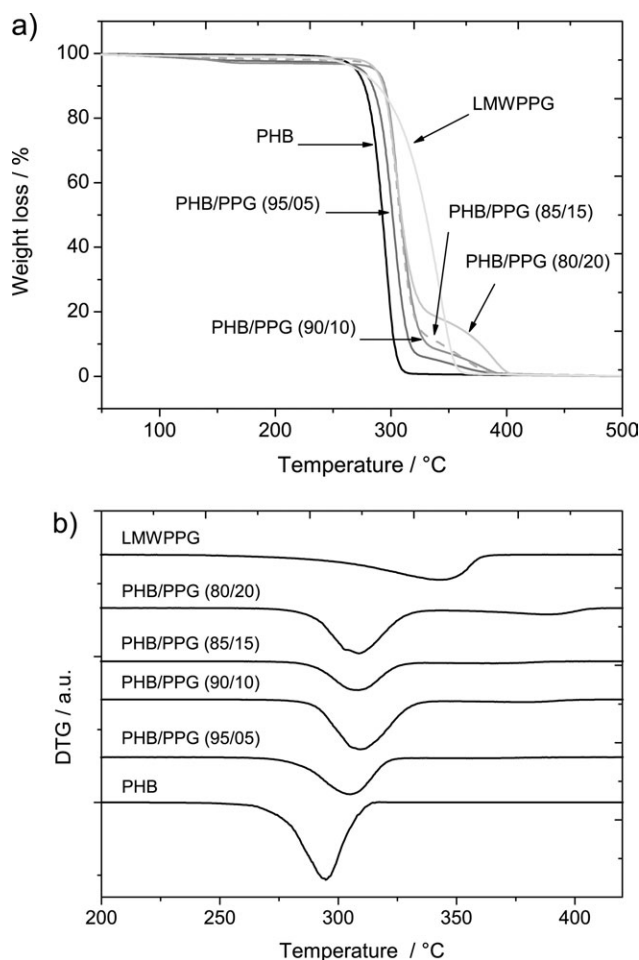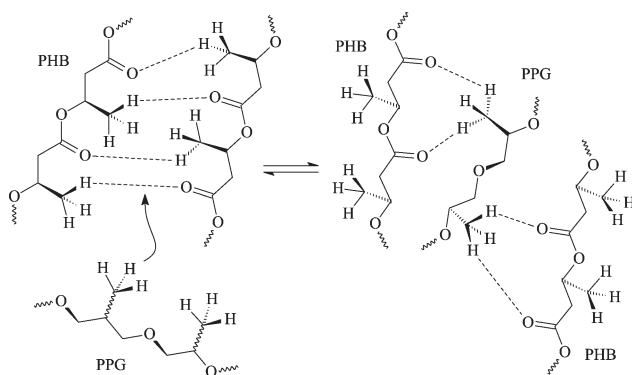
Figure 7. Schematic representation of interactions between PPG and PHB in blends.

atom from a β-carbon. The thermal stabilization observed by TG could be related to the intermolecular interaction of LMWPPG with PHB chains hindering the mechanism of β-elimination.[44] As discussed earlier, PHB C=O groups can interact with —CH$_3$ groups of PPG hindering the formation of the decomposition transition state which retards the degradation, as observed in Table II.

The presence of LMWPPG in the PHB matrix has an unique effect compared to the analogous PEG. While PEG decreases both temperatures, T_m and T_d,[40] the presence of LMWPPG has an effect of decreasing the T_m and increasing the T_d, which improves the processability window of PHB. This effect only occurs because of the PPG and PHB interactions which disturb the mechanism of degradation by random scission of the PHB by the methyl groups.[44]

CONCLUSIONS

The addition of LMWPPG produces significant changes in the PHB properties, i.e., a decrease in the crystallinity and on the melting temperature with a simultaneous increase on the decomposition temperature and significant morphologic changes. FTIR and TG/DTA results indicated that molecular interactions of LMWPPG groups, i.e., CH$_3$ and terminal OH, with C=O groups of PHB should be responsible for the decrease on the crystallinity and melting point of PHB. Moreover, these PPG–PHB molecular interactions should increase the PHB decomposition temperature by disfavoring the formation of a PHB intramolecular six-member ring transition state with the C=O. The LMWPPG effect of hindering the formation of this intermediate ring, unfavor the β-elimination process and consequently increases the decomposition of PHB.

As a result all blends studied showed improved thermal stability compared to neat PHB. The decrease on the T_m and increase on the decomposition temperature of PHB is extremely important for the industrial processing of PHB.

ACKNOWLEDGMENTS

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