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Thermo-Mechanical and Morphological Characterization of Plasticized Poly[(R)-3-hydroxybutyric acid]

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Summary: Blends of poly[(R)3-hydroxybutyryric acid) (PHB) with different plasticizers were investigated by TGA, DSC, OM and mechanical testing. Markedly hydrophilic plasticizers promote PHB thermal-degradation through a light alcoholysis reaction. All the used plasticizers were compatible with PHB up to a maximum load of 5 wt-%. Higher loads were recorded with increasing of plasticizer molecular weight.

Keywords: blend; factorial design; plasticizer; poly(3-hydroxybutyrate)

Introduction

Isotactic poly[(R)3-hydroxybutyryric acid] (PHB) can be obtained by microbial fermentation under stressed conditions as promoted by a variety of bacterial strains. This polymer gives rise to big spherulites with banded texture and crystallinity degree that can be higher than 55%. The secondary crystallization is a typical event in the course of storage after an initial crystallization. As a consequence this polymer results brittle with low deformability.[1-3] Besides, it was found to be vulnerable to thermo-degradation at around melt temperature with significant drop in the molecular weight.[4-6] Unsurprisingly, these intrinsic characteristics combined with the actual production cost slow down PHB applicability. Internal (copolymer formation)[1] and external plasticization[7-10] and blends preparations[11, 12] are the alternatives that have been considered and adopted in order to improve PHB processability window and mechanical properties of end manufacts.

Different family of plasticizers has been incorporated into poly(hydroxyalkanoate) (PHA) formulations during manufacture. Kauffman *et al.*[13] identified dioctyl phthalate, 1,4-cyclohexanedimethanol dibenzoate, tert-butylphenyl diphenyl phosphate, polyethylene glycols and phenyl ether of hydrogenated polyethylene glycol as compatible plasticizers for hot-melt adhesives formulations based on PHBV. Thermal and mechanical properties of PHB showed favorable results by the addition of triacetyl glycerol (TAG) and low molecular weight

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poly(adipate) (PA). PHB formulations containing both 30 wt-% of TAG and a mixture of 20 wt-% of PA and 10 wt-% of TAG were considered the best formulations with elongation at break of 15.5 % and 13.0 %, respectively.[7] Yoshie *et al.*[10] demonstrated that tributyrin, dodecanol, lauric acid, and trilaurin are suitable plasticizers for PHB and depending upon their relative load in the blends they can act as accelerators or retardants for enzymatic PHB degradation.

Regarding PHB blends comprising as second component a biodegradable polymer, several studies have been reported for the system PHB-PVA.[14-17] These blends were found to be partially miscible by FTIR, X-ray diffraction, solid-state ^{13}C NMR investigations and density measurements. The compatibility between the two components increases with increasing of the PVA content and/or PVA syndiotacticity and this behavior is attributed to hydrogen bonding in the amorphous phase. Besides, PHB crystallinity decreases when blended with PVA. PHB-PVA blends containing glycerol as third component highlighted the effect of this last component as nucleating agent leading to an effective increase of PHB crystallinity.[15]

On the other hand, it is well known that PVA in order to be processed in the melt needs to be plasticized.[18] In general, water and polyols are frequently used in PVA formulations. Consequently, if one intends to prepare PHB-PVA blends by melt processing it is needed to be aware of effect of these polyols on PHB.

The present work is aimed to investigating the thermo-mechanical and morphological characteristics of PHB-polyol plasticizer blends for formulations containing 5 wt-% and 20 wt-%.

Experimental

Materials. Poly(3-hydroxybutyrate) (PHB) (Mw = 344124 ± 4.0%, MWD = 2.8; MFI = 14.7 ± 1.2% g/10 min at 190 °C/2.16 kg) was kindly supplied by PHB Industrial S.A. (Brazil). Glycerol (Gly), poly(ethylene glycol) (Mw = 200) (PEG200), tri(ethylene glycol) bis(2-ethylhexanoate) (TEGB) and pentaerythritol (Penta) were commercial products and were used as received.

Sample processing. PHB-plasticizer blends were processed in a torque rheometer W 50 EHT (with roller blade) connected to a Plastograph Can-Bus Brabender at 180°C and 50 rpm by 7 minutes. Subsequently, films were prepared by compression molding at 170 °C by 2 min and 1bar in a laboratory mold press.

Characterization. A Mettler TA 4000 System instrument consisting of DSC-30 differential scanning calorimeter, TGA-50 thermogravimetric furnace with a M3 microbalance, and TA72 GraphWare software were used for thermal analyses. DSC samples of 10–15 mg were weighed in 40µl aluminum pan and an empty pan was used as reference. Measurements were carried out under 80 ml·min^{-1} nitrogen flow rate according to the following protocol: first and second heating from -30 to 210 °C at 10 °C·min^{-1}; first cooling (quenching after the first heating) from 210 to -30 °C at 100 °C·min^{-1}. TGA evaluations were performed on ca. 20 mg samples at 10 °C·min^{-1} rate from 25 to 700 °C, under 200 ml·min^{-1} nitrogen flow.

Optical morphology observations and micrographs, were recorded on a small film fragments inserted between two microscope cover glasses and allocated in a Mettler FP52 hot stage. The samples were heated up to 200°C, held at this temperature by 2 min, compressed to decrease film thickness and cooled down to 90 °C and maintained at that temperature for 30 min for crystallization.

Mechanical properties were obtained according to ASTM D1708-93 and D638M-93 standard test methods. Twelve replicate were tested in a Universal Testing Machine (Instron model 5564) at a speed of 1mm min^{-1} at room temperature. Samples were cut into microtensile test specimens and preconditioned for more than one week at 25°C and 50% RH inside desiccators containing saturated solutions of magnesium nitrate.

Results and Discussion

Thermal degradation of plasticized PHB data obtained by thermogravimetric analysis is shown in Table 1. The amount of volatile was determined from weight loss step in the range of 25-150°C. As the plasticizers used have boiling point over 150 °C and are hygroscopic, volatile was attributable to the adsorbed moisture. Samples were not conditioned prior measurements to emulate as near as processing environment.

Table 1. TGA data of plasticized PHB samples.[a]

Sample wt-% plasticizer	Volatile (%)	T_d (°C)	T_p (°C)
0	–	289	309
5 Gly	3.9	288	309
20 Gly	10.5	286	308
5 PEG200	1.8	289	311
20 PEG200	5.0	280	303
5 TEGB	1.2	290	311
20 TEGB	3.4	290	311
5 Penta	1.4	288	309
20 Penta	2.8	288	307

[a] T_d = onset decomposition temperature (slope =2%/K); T_p = peak temperature of the first derivative trace.

Both glycerol and poly(ethylene glycol) (Mw = 200) (PEG 200) decreased the thermal stability of PHB resulting 3°C and 9°C lower at concentration of 20 wt-%, respectively. PHB degrades thermally resulting in polymeric chains terminated with carboxyl and vinyl groups.[19] Carboxyl end groups of polyesters catalyze hydrolysis reaction.[20, 21] In the present study, it is feasible a synergistic effect on the acceleration of thermal degradation by both moisture and polyol. All samples left less than 0.6 wt-% of residue at 490 °C.

The determination of the molecular weight changes after melt processing by torque rheometer, followed by compression molding, were not recorded due to insolubility of the plasticized PHB films in chloroform (both at room and boiling temperatures). The structural changes and/or interactions in plasticized PHB are being studied by FTIR and solid state NMR.

Table 2. Transitions temperatures and degree of crystallinity of PHB in PHB-plasticizer blends.[a]

Sample wt-%plast.	T_g (°C)	T_{cc1} (°C)	T_{cc2} (°C)	T_m (°C)	X_c (%)
0	1	52	78	174	56
5 Gly	1	52	80	172	55
20 Gly	-1	52	78	166	62
5 PEG200	-8	44	78	171	57
20 PEG200	-23	26	70	158	57
5 TEGB	-7	41	79	170	56
20 TEGB	-23	26	79	163	56
5 Penta	-17[b]	nd	nd	163[c]	–
20 Penta	-10	nd	nd	167	–

[a] T_g, T_{cc}, and T_m represent glass transition, cold crystallization, and melting temperatures, respectively; X_c is the degree of crystallinity; nd = not detected; [b] A second T_g was observed at -2°C. [c] An overlapped peak was observed at 168°C.

Table 2 reports the transitions temperatures and degree of crystallinity of PHB in PHB-plasticizer blends as attained from the second heating after a quenching treatment. In general, only one glass transition temperature (T_g) was found for each blend that decreased with the addition of the plasticizer. The major effects were observed with PEG200 and tri(ethylene glycol) bis(2-ethylhexanoate) (TEGB). On the other hand, both unplasticized PHB and that plasticized with 5 wt-% of glycerol have the same T_g. Besides, PHB films plasticized with 20 wt-% of glycerol after about one week from its preparation displayed a clear exudation. These behaviors suggest that glycerol and PHB are immiscible. However, it was observed above in the TGA results that glycerol has a significant effect on PHB macromolecules. As a result of this thermo-hydroglycolysis reaction, two factors could contribute for the slight decrease of T_g of PHB blend with 20 wt-% of glycerol: a reduction of molecular weight and an increase of polydispersity.

The dependence of T_g on the composition of PHB-PEG200 blends follows Fox relationship[22] (Eq. 1) considering the values of 1 °C and –82.4 °C for PHB and PEG200, respectively. The theoretical $T_{g,\,blend}$ values of –4.7°C and –20.9°C were found for samples containing 5 wt-% and 20 wt-% of PEG200, respectively, in good agreement with the experimental values. Conversely, PHB-TEGB blends can be well described by the Kwei equation[23] (Eq. 2) where the constants k=6 and q=42 were found considering the values of 1 °C and –50 °C for PHB and TEGB, respectively. The behavior of T_g's in PHB-pentaerythritol blend suggests two opposing roles held by pentaerythritol that is plasticizer and filler at the same time.

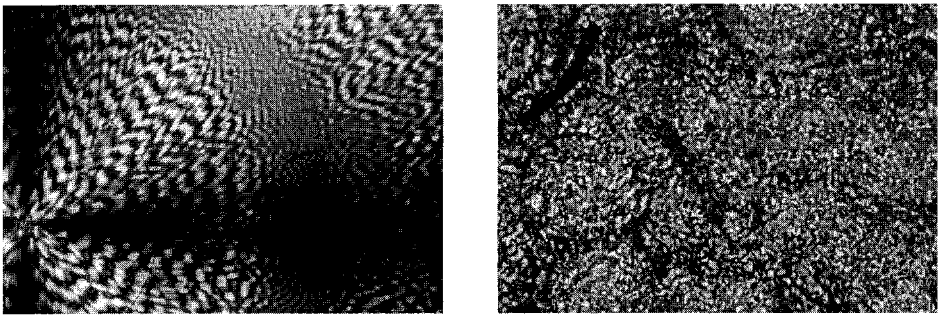
$$\frac{1}{T_{g,blend}} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}} \qquad \text{(Eq. 1)}$$

$$T_{g,blend} = \frac{(W_1\,T_{g,1} + k\,W_2\,T_{g,2})}{(W_1 + k\,W_2)} + qW_1W_2 \qquad \text{(Eq. 2)}$$

where W_1 and W_2 represent the mass fractions of the components and $T_{g,blend}$, $T_{g,1}$ and $T_{g,2}$ are the T_g's of the blend component 1 and component 2, respectively and k and q are adjustable parameters.

The temperature of the first peak of cold crystallization (T_{cc1}) decreased with increasing of plasticizer relative content in the blends containing PEG200 and TEGB. However, cold crystallization was not detected in blends containing pentaerythritol probably due to a nucleation effect. The second peak of cold crystallization (T_{cc2}) appeared to be independent of the kind and amount of plasticizer.

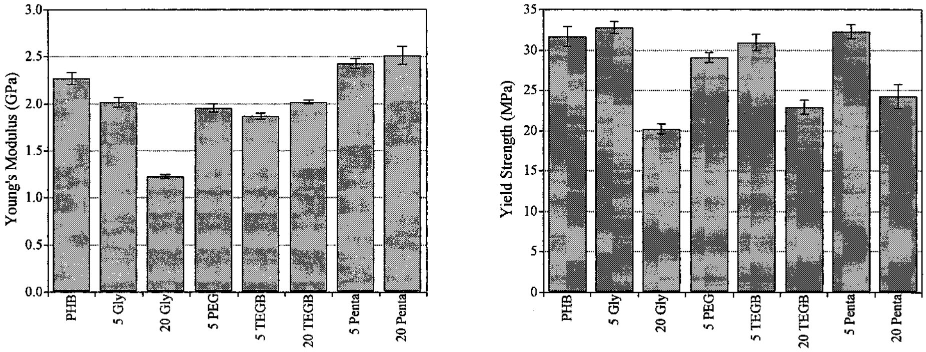
The melting enthalpy of 146 J/g was used to determine the degree of crystallinity.[24] Melting temperature of PHB (T_m) decreased in the PHB-plasticizer blends thus confirming the compatibility of the polymer and plasticizer components. The degree of crystallinity (X_c) of PHB was basically invariable. A higher value of X_c was observed for PHB-20 wt-% glycerol blend in accordance with Azuma *et al.*[15] Janigová *et al.*[8] explained that an increase in crystallinity are due to a higher chain mobility and a better packing of segments. However, in the present study the same behavior was not observed for the blends with plasticizers displaying a good compatibility with PHB and therefore with higher possibility to increase its chain mobility. Accordingly, others explanations can be inferred as for example the overestimation of melting peak area considering the results shown in Table 1. PHB-20 wt-% glycerol blend presented the higher value of volatile. Consequently, there will be an overestimation of enthalpy in the basis of prepared composition for evaluations after the first heating. Besides, the interface interactions between PHB and glycerol phase can indeed influence nucleation as supported by the morphologies presented in the optical micrographs of Figure 1. Characteristic concentric rings are detectable for plasticized free PHB (Fig. 1 (a)) whereas the presence of 5 wt-% of glycerol (Fig. 1 (b)) crystals are lower and Maltese cross is not clear.



(a) (b)

Fig. 1. Optical micrographs of (a) PHB (160x) and (b) PHB-5wt%Glycerol blend (400x).

Young's modulus (*E*) and yield strength (σ) mean values from twelve measurements performed on the differently plasticized PHB samples are presented in Figure 2. Error bars correspond to a 95 % of confidence. The sample consisting of PHB and 20 wt-% of PEG200 after compression molding resulted brittle and hence unfeasible for mechanical testing.



(a) (b)

Fig. 2. Effect of type and amount of plasticizers on PHB Young's modulus (a) and yield strength (b).

PHB modulus decreased about 0.3 GPa for samples plasticized with 5 wt-% of glycerol, PEG200 and TEGB. A more significant decrease was detected for PHB blends containing 20 wt-% of glycerol. Apparently, TEGB plasticizer concentration has little effect on the modulus of PHB blends. Conversely, pentaerythritol increases PHB modulus confirming its filler role.

All PHB-plasticizer blends presented elongation at break lower than 20% and necking did not occurred after yielding thus characterizing these blends as brittle materials. For this kind of materials yield stress is indeed somewhat ill defined. Anyway, some indication of the level of the strength needed to fracture PHB-plasticizer as a function of composition can be drawn. The addition of 5 wt-% of plasticizer has little effect on yield stress of PHB blends. However, lower values were found for blends containing PEG200 and TEGB in agreement of the relevant T_g data indicative of a better plasticization effect. Further decrease of yield strength of about 8 MPa was observed at 20 wt-% of plasticizer.

Conclusion

PHB was blended with polyols containing different amounts and type of hydroxyl group. Glycerol and poly(ethylene glycol) (PEG200) decreased thermal stability of PHB probably as a consequence of hydro-alcoholysis. Tri(ethylene glycol) bis(2-ethylhexanoate) (TEGB) and pentaerythritol indicated have no effect on thermal stability of PHB. Apparently, PEG200 and TEGB are more compatible with PHB with a significant influence on both glass transition and melting temperatures. Pentaerythritol appears to play also the additional role of filler. The mechanical testing of the plasticized PHB blends evidenced the brittleness of all samples with a major effect in the case of PHB containing 20 wt-% of PEG200.

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