Thermal Properties and Morphology of Poly(3-Hydroxybutyrate-*co*-3-Hydroxyvalerate) with Poly(Caprolactone Triol) Mixtures

Katiusca Wessler,[1] *Maurício Hajime Nishida,*[1] *João da Silva Jr.,*[1]
Ana Paula Testa Pezzin,[2] *Sérgio H. Pezzin**[1]

Summary: Aiming the development of new ductile and porous biodegradable materials, blends of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), P(3HB-*co*-3HV), and polycaprolactone triol, PCL-T, with compositions varying from 100/0 to 70/30 P(3HB-*co*-3HV)/PCL-T (w/w), were obtained by casting. The phase behavior, the morphology and the crystallinity of P(3HB-*co*-3HV)/PCL-T blends were studied by differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy and X-ray diffraction. DSC analyses showed that the glass transition temperature of P(3HB-*co*-3HV) decreases with the addition of PCL-T up to 15 wt%, evidencing that mixtures with higher PCL-T contents provide more flexible films, acting as a plasticizer, but the porosity and onset degradation temperature of P(3HB-*co*-3HV) are not affected.

Keywords: biodegradable; morphology; thermal properties

Introduction

Polyhydroxyalkanoates (PHAs) are thermoplastic polyesters made from bacterial fermentation using renewable resources. The polymers are produced as an intracellular storage polymer of carbon and energy under various nutritional and environmental conditions.[1] In the past two decades, PHAs have been the focus of extensive research considering their potential application as biocompatible and biodegradable thermoplastics, due to their hydrolyzability in the human body as well as in natural circumstances.[2] The polymers of PHAs family more extensively studied are poly(3-hydroxybutyrate), P(3HB) and the copolymer poly(3-hydroxybutyrate)-*co*-(3-hydroxyvalerate) (P(3HB-*co*-3HV)). P(3HB) can in principle be used in many applications, however, since P(3HB) is highly crystalline and forms large spherulites and also has a relatively high glass transition temperature in comparison with polypropylene, polyethylene, etc., the material itself is regarded as unacceptable brittle. Furthermore, P(3HB) suffers from an economic disadvantage and limited processing temperatures. These drawbacks have restricted the widespread application of P(3HB).[3] In order to obtain a material with better characteristics, many different physical mixtures of P(3HB) with other biodegradable polymers have been studied.[4–7] On the other hand, poly (caprolactone – triol), PCL-T, is a semi-crystalline polymer with melting point around 30 °C and glass transition temperature (T_g) around $-68\,^{\circ}C$, being potentially interesting to be used in biomaterials.[8] Thus, it seems that PCL-T (**1**) can be a good choice to plasticize P(3HB-*co*-3HV), maintaining its biodegradability and bioreabsorption properties.

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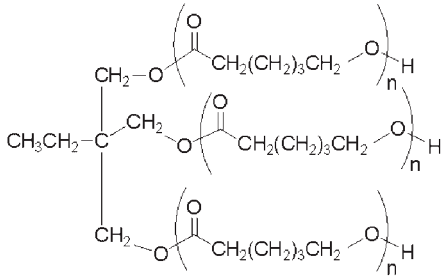
[1] Universidade do Estado de Santa Catarina – Centro de Ciências Tecnológicas – CP631 – 89223-100 Joinville-SC, Brazil
E-mail: pezzin@joinville.udesc
[2] Universidade da Região de Joiville – UNIVILLE – Joinville-SC, Brazil



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Experimental

P(3HB-*co*-3HV), presenting 10% of HV units in its composition and a numerical average molecular weight of 3.0×10^5g/mol, was kindly supplied by PHB Industrial S.A and purified prior to use by dissolution in chloroform and recrystallization in *n*-hexane. The PCL-T with 900g/mol was purchased from Aldrich.

The mixtures were prepared by the following procedure. P(3HB-*co*-3HV) have been dissolved in chloroform with a concentration of 5wt%, at 80 °C, under constant stirring. Then, different amounts of a 5wt% solution of PCL-T in chloroform were added to the PHA solution. The resulting solution was stirred for 6 h and casted on a glass plate (10cm of diameter). The solvent evaporation was carried out in a glass box with a dry chloroform-saturated atmosphere.

The P(3HB-*co*-3HV)/PCL-T blends were analyzed by X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

X-ray diffraction analyses were carried out in a Shimadzu LABX - XRD 6000 diffractometer, using Cu Kα1 radiation ($\lambda = 154.06$ pm), in the scan range of 2θ between 5° and 70°. DSC measurements were carried out in a 2920 MDSC TA Instruments, under argon atmosphere. In the first run, the samples were heated from 25 to 190 °C, at 10 °C/min. After that, they had been cooled at 15 °C/min from 190 °C to −100 °C and kept at this temperature for 2 minutes. Then, a second heating was carried out from −100 to 190 °C at 10 °C/min. Thermogravimetric analyses were performed on a Netzsch STA 449C apparatus. The samples were heated from 25 to 600 °C under argon atmosphere at 10 °C/min. FTIR spectra were recorded on a Perkin Elmer Spectrum One B spectrometer, in transmission mode, between 480 and 4000 cm^{-1}. The morphologies of the casted films were observed by scanning electron microscopy, using a Zeiss DSM 940A equipment operated at 5 kV. The samples were previously coated with gold in a sputtering device.

Results and Discussion

The DSC data are summarized in Table 1. It was observed that the glass transition temperatures of P(3HB-*co*-3HV) decreased from 2 °C to ca. −10 °C with the addition of 15 wt% of PCL-T. Further addition of PCL-T does not modifies the T_g of P(3HB-*co*-3HV). It is also noticed that the melting tempera-

Table 1.
DSC data for P(3HB-*co*-3HV)/PCL-T mixtures.

P(3HB-*co*-3HV) /PCL-T	T_g (°C) P(3HB-*co*-3HV)	T_m (°C) PCL-T	T_c (°C) P(3HB-*co*-3HV)	T_m (°C) P(3HB-*co*-3HV)
100/0	2	–	53	172
90/10	−9	31	–	170
85/15	−11	20	53	169
80/20	−10	25	47	166
70/30	−10	24	50	164

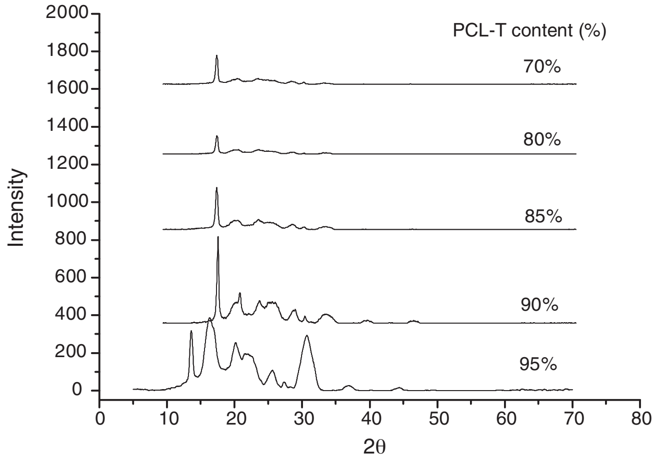

Figure 1.
X-ray diffractograms of the P(3HB-*co*-3HV)/PCL-T mixtures.

tures of P(3HB-*co*-3HV) and PCL-T decreases gradually as the PCL-T content is increased. The T_g of the samples are best defined with higher PCL-T contents, suggesting that the PCL-T addition decreases the crystallinity of the sample.

The diffraction profile for the P(3HB-*co*-3HV)/PCL-T mixtures is shown in Figure 1. It is possible to observe that the diffraction peaks in 2θ equal to 13.5; 16.9; 20; 22; 25.5; 27 and 30, characteristic of P(3HB-*co*-3HV) is being diminishing with the increasing amount of PCL-T.

The decrease of 13 and 23.7% on the crystallinity degree with the addition of 10 and 30% of PCL-T, respectively, deter-

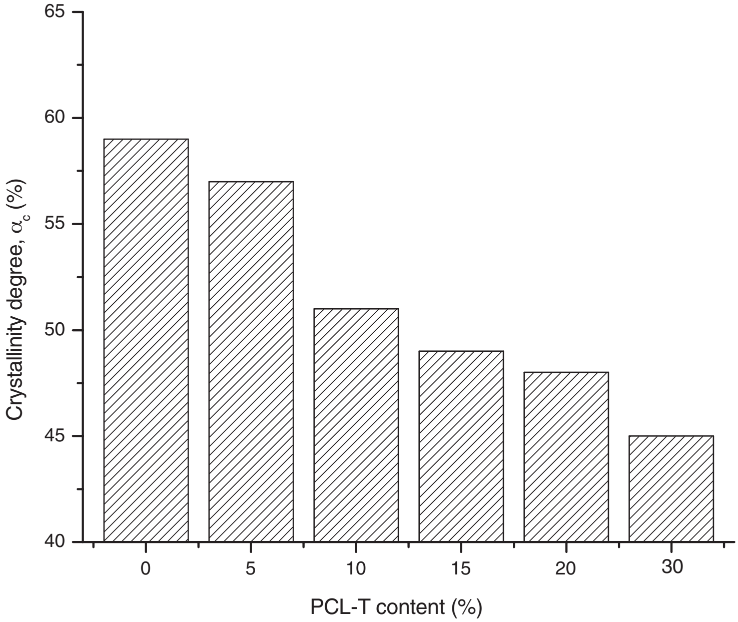

Figure 2.
Crystallinity degree (α_c) of P(3HB-*co*-3HV) varying the PCL-T content, obtained from XRD measurements.

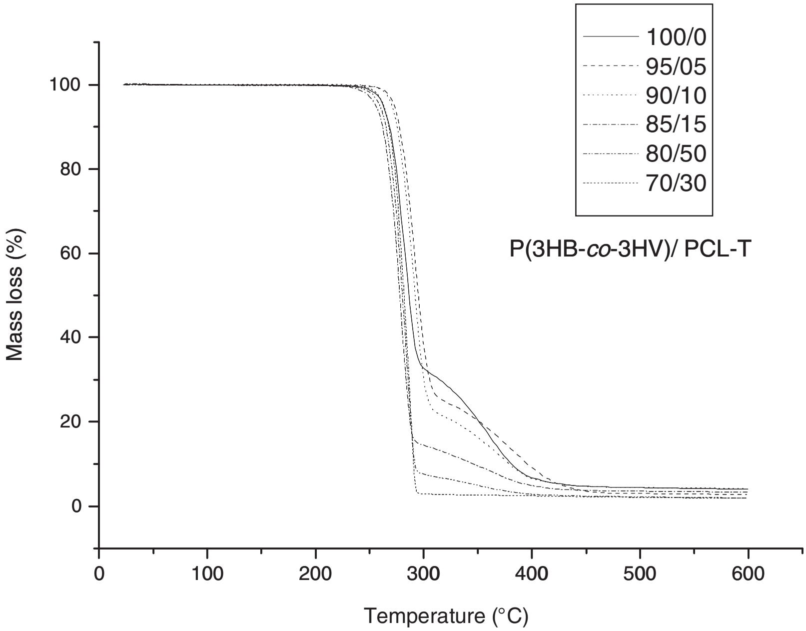

Figure 3.
TG curves of P(3HB-*co*-3HV)/PCL-T mixtures with different content of PCL-T.

mined by XRD analysis (Figure 2), confirms the DSC results.

Figure 3 shows thermogravimetric curves of the P(3HB-*co*-3HV)/PCL-T mixtures. Thermal degradation studies show that the onset temperature of the P(3HB-*co*-3HV) degradation varies very little with the addition of PCL-T ($T_{onset} = 272\,°C$ for P(3HB-*co*-3HV) and 268 °C for P(3HB-*co*-3HV) with 30% of PCL-T). Thus, the use of PCL-T, that acts as a plasticizing additive, does not interfere in the P(3HB-*co*-3HV) thermal degradation.

Figure 4 shows SEM micrographs of the cryo-fractured surfaces of P(3HB-*co*-3HV)/PCL-T mixtures. The micrographs reveal that the morphology of the mixtures practically does not change according to concentration of PCL-T. Dense films were obtained for all compositions.

It was also observed that the transparency of these films did not change with the

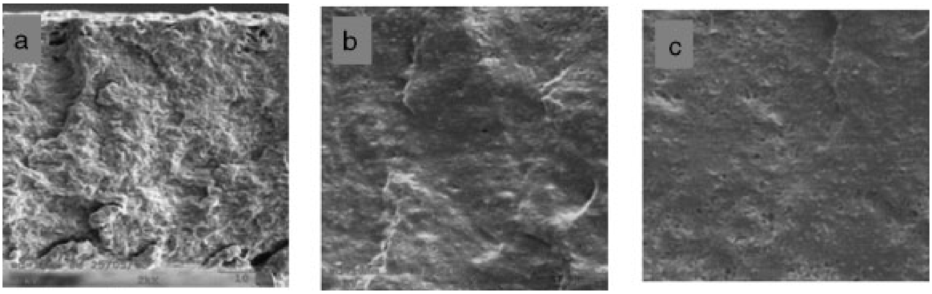

Figure 4.
SEM micrographs of P(3HB-*co*-3HV)/PCL-T mixtures: (a) 90/10; (b) 85/15; (c) 70/30. Magnification: 2000×.

PCL-T content. On the other hand the flexibility of the films seems to increase with the addition of PCL-T.

Conclusion

The results showed that the T_g of P(3HB-*co*-3HV) decreases with the addition of PCL-T up to 15wt%, suggesting that higher PCL-T ratios results more flexible films, lowering the crystallinity degree of P(3HB-*co*-3HV), but the porosity and onset degradation temperature of P(3HB-*co*-3HV) are not affected. It is suggested that PCL-T can be used to plasticize P(3HB-*co*-3HV) and that these materials have great potential to biomedical applications and packings.

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