Blends of Poly(hydroxybutyrate) and Poly (ε-caprolactone) Obtained from Melting Mixture

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Abstract: Poly(3-hydroxybutyrate) (PHB) is a thermoplastic polyester with a great potential owing to its biodegradability, bioreabsorbation and biological synthesis from a renewable source. Despite these characteristics, the applications of this polymer are very restricted due to its poor mechanical properties and thermal instability at temperatures above its melting point (around 175 °C). Among the possibilities of improvement of these materials, the development of blends is a relatively fast and inexpensive option. Poly(ε-caprolactone) (PCL) is a semi-crystalline polymer that may be used as a biomaterial. It presents good mechanical properties, a low melting point (around 55 °C), and could be a good option to develop PHB blends, maintaining the biodegradability and bioreabsorption properties. The objective of the present work was to obtain blends of PHB and PCL by melting mixture in an internal mixer. The compositions varied from 0 to 30 wt% of PCL. DSC, DMA, and SEM were used to characterize the blends. The blends were found to be imiscible with no indication of interaction either the amorphous or crystalline state. The morphology shows PHB as the matrix and PCL as the dispersed phase.

Keywords: *Polymeric blends, poly(hydroxybutyrate), poly(ε- caprolactone).*

Introduction

Poly(3-hydroxybutyrate) (PHB) is a thermoplastic polyester, that presents great potential because of features like biodegradation, bioreabsorbation and biological synthesis from a renewable source[1]. Despite these characteristics, the applications of this polymer are very restricted, due to its high crystallinity, its crystalline phase morphology and the secondary crystallization that occurs after processing, which leads to a material with poor mechanical properties[2]. Another restriction of this material is the thermal instability above the melting point, around 175 °C[3].

Among the possibilities to improve this material, the development of blends is a relatively fast and inexpensive option[4]. Poly(ε-caprolactone) (PCL) is a semi-crystalline polymer with potential to be used as biomaterial, it presents good mechanical properties, and has a melting point around 55 °C [5] and, thus, be a good option to develop PHB blends maintaining its biodegradability and bioreabsorption properties.

Blends of PHB and PCL prepared from chloroform solution have been described as imiscible, based on analysis of glass transition using DSC and viscosimetry measurements[6,7]. Blends prepared from a polymer mixture followed by compression molding were also considered imiscible[5].

A fascinating feature for polyesters blends is the potential for transreactions. This kind of reaction depends strongly on the initial polymer miscibility and blending conditions. These include temperature, mixing time, preparation method and presence of catalyst. Kotliar has reviewed interchange reactions involving the condensation polymers, polyester and polyamides[8]. In polyesters blends the possible reactions are intermolecular alcoholysis or transesterification (involving hydroxyl end-groups), intermolecular acidolysis (involving carboxyl end-groups) and interchange reactions between ester groups. In the literature there is few reports on the transreactions in the molten state involving PHB, probably due to its thermal instability at temperatures above 180 °C and its narrow window of processability. The thermal degradation is accompanied by decrease in the molar mass and consequently in mechanical properties of the polymer. Due to this fact, the majority of the PHB blends had been prepared in solution to avoid thermal degradation[9]. Recently we studied the transreactions between PHB and amorphous PET, PETG conducted in an internal mixer and in presence of catalyst. The extension of transreactions was found to be more dependent on the catalyst concentration than the processing time[10].

The purpose of this work is to obtain blends of PHB and PCL with several compositions, using an internal mixer, and to study the miscibility, morphology and physical-chemical properties of these systems.

Experimental

Materials. PHB (M_w = 450,000 g/mol, melting point ~176 °C) was kindly supplied by PHB do Brasil. PCL ($\overline{M}_n$ = 80,000 g/mol, melting point ~60 °C) was purchased from Aldrich. Both polymers were used without further purification.

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Blend preparation. Blends were prepared using a Haake Rheomix 600 internal mixer according to the following process parameters: temperature of mixture chamber of 200 °C; 5 minutes of mixing time; rotor speed of 80 rpm. The samples were named according to their PCL proportion in weight, which varied from 0 to 30%, e.g. the blends with 10 wt% of PCL were named as PCL10. The pure polymers were processed using the same conditions as for the blends.

Characterization. The samples were analyzed by differential scanning calorimetry DSC-2910 from TA Instruments, according to the following procedure: heating from 30 °C to 200 °C, isothermal for 2 minutes, cooling to -40 °C, isothermal for 2 minutes and heating to 200 °C. All these procedure steps were made using a rate of 10 °C/min.

Dynamical Mechanical Analysis (DMA) was made using a DMTA V – Rheometric Scientific equipment using the tension mode in the temperature range of –100 °C and 200 °C with a frequency of 1 Hz, strain amplitude of 0,01 % and heating rate of 2 ^{o}C/min.

Scanning electroning microscopy (SEM) was made with a JEOL 6360 microscope. The samples were obtained directly from the internal mixer, the fracture was made in liquid nitrogen and the surface was coated with carbon. The scan voltage was 20 kV.

Results and Discussion

Figure 1 shows the torque curves as a function of processing time for pure polymers and blends obtained during processing in the internal mixer. All curves have a similar profile, presenting a peak related to the material loading in the mixture chamber followed by polymer plastification. The PCL processing torque stabilizes around 5.5 Nm, just after the loading peak. From analysis of the curves for PHB and blends it is possible to observe a continuous reduction in the torque value during the processing period, a fact that can be attributed to the PHB molar mass reduction related to its thermal instability at temperatures above its melting point. Figure 2 presents the torque and the mixture chamber temperature at a processing time of 5 minutes. The PCL torque under these conditions is around 5.5 Nm while PHB presents the torque value around 2.25 Nm. The torque value is directly related to viscosity. Based on this it is possible to conclude that PCL is more viscous than PHB, despite the fact that PHB has a higher molar mass than PCL. All the blends, with the exception of that containing 5 wt% of PCL, presented a torque value between those of pure polymers. The processing temperature was kept around 195 °C in all samples.

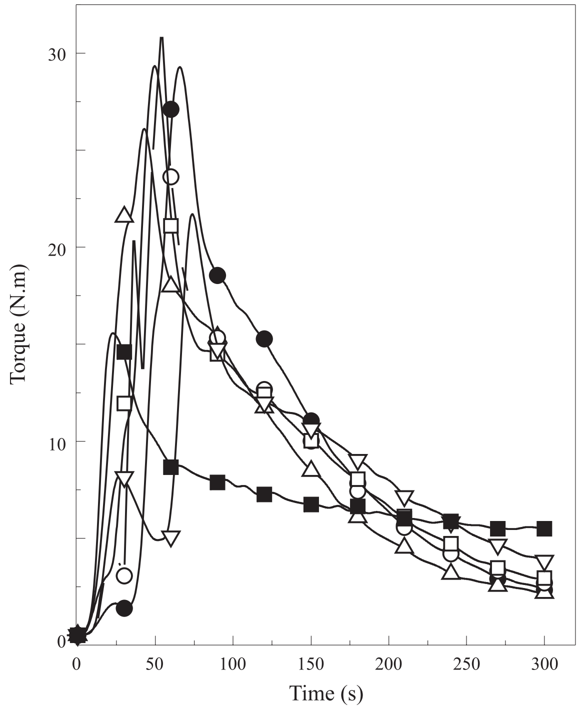

Figure 1. Torque *versus* processing time of pure polymers and their blends: (λ) PHB, (Δ) PCL5, (μ) PCL15, (□) PCL 20, (∇)PCL30, (ν) PCL.

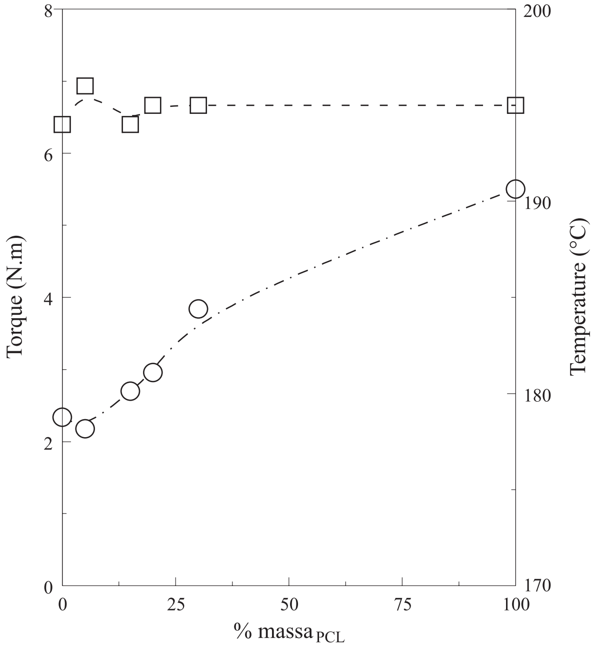

Figure 2. Torque (μ) and internal chamber temperature (□), considering a processing time of 5 minutes, *versus* blend composition.

Figure 3 shows the curves obtained from differential scanning calorimetry normalized based on sample weight. These data are based on the cooling step, starting from the melting state just after the isothermal period at 200 °C for pure polymers and blends. Both PHB and PCL pass through partial crystallization is this step. This fact can be confirmed by the exothermic peaks observed in the DSC curves of both polymers. The PCL crystallization peak is sharper than PHB peak with a maximum temperature at T_{c1} = 26 °C. The PHB crystallization peak is less sharp with a maximum temperature at T_{c1} = 55 °C. All blends presented exothermic signals in the cooling step related to crystallization that occurs during this stage. The blends composition has clearly an influence on the crystallizations. The blends containing up to 20 wt% of PCL present a crystallization peak around 55 ^{o}C, probably because of PHB crystallization. These blends present still

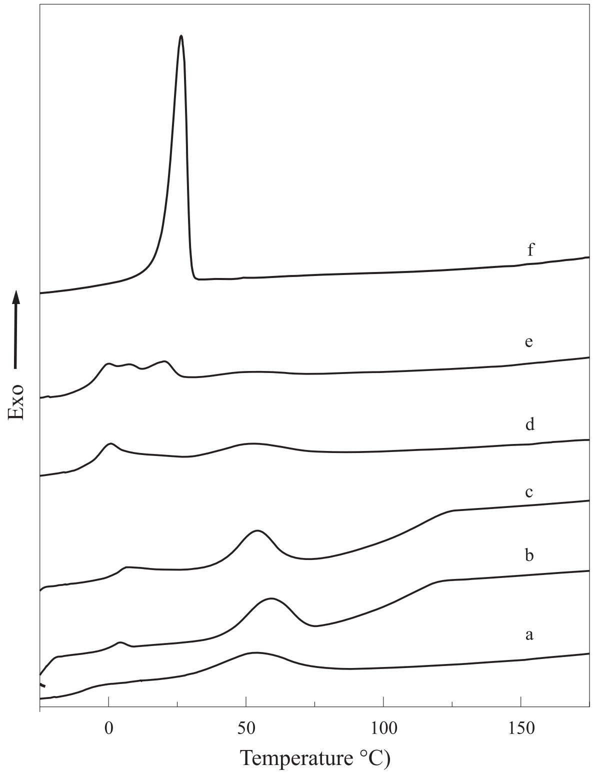

Figure 3. DSC curves corresponding to the cooling step of PHB, PCL and their blends, cooling rate of 10°C/min: (a) PHB, (b) PCL5, (c) PCL15, (d) PCL20, (e) PCL30, (f) PCL.

another less sharp peak around 0 °C, possibly because of PCL crystallization. The crystallization of the blend containing 30% of PCL is characterized by multiple poorly defined exothermic peaks at temperatures below 30 °C.

The DSC curves in the region above the glass transition temperature are presented in Figure 4. These data refer to the second heating step. The PCL curve presents only one sharp endothermic peak with a minimum at 57 °C, related to the melting process. Exothermic phenomena related to crystallization were not observed, indicating that PCL reaches maximum crystallization during the cooling step. PHB presents a sharp crystallization peak with a maximum temperature at $T_{c2} = 48$ °C, and a endothermic peak related to melting process with a minimum temperature at $T_m = 175$ °C. The blends containing up to 15 wt% did not present crystallization peaks, the only transition observed was polymer melting. In the blends containing 20 and 30 wt% of PCL, it is possible to verify three different thermal effects: the first one is an exothermic peak around 50 °C related to additional crystallization of both polymers, the second one is an endothermic peak around 55 °C related to PCL melting, and the third one is the PHB melting at 172 °C. It seems that PCL melting shifts to lower temperatures in the presence of PHB. However, this fact could be related to the overlay of thermal transitions such as crystallization and melting. Shape changes or shifts in the peaks related to the PHB melting were not detected. This fact indicates that PHB and PCL crystallized in two different phases and that these polymers are probably immiscible in the melted state.

Table 1. Data obtained from DSC

Blends	T_{c1}^{a} (°C)			T_{c2}^{b} (°C)	T_m (°C) PHB	ΔH_m (J/g_{PHB})	T_m (°C) PCL
PHB	—	—	53	48	172	106	—
PCL5	—	5	59	—	173	90	55
PCL15	—	7	54	—	172	90	57
PCL20	—	-1	52	48	172	91	56
PCL30	-2	6	19	49	172	107	56
PCL	—	—	26	—	—	—	57

a – crystallization temperature from the cooling step
b – crystallization temperature from the heating step.

Table 1 presents crystallization temperatures (T_{c1}, T_{c2}), melting temperature (T_m) and melting enthalpy (DH_m) related to pure PHB and in the blends. It was not possible to determine the PCL melting enthalpy because of the overlay of this process with PHB crystallization occurring during the heating step. The PHB melting enthalpy was normalized with respect to mass content of PHB in the blends. PHB melting enthalpy is lower when this polymer is present in the blends, indicating a reduction of the degree of crystallinity as a consequence of PCL influence on the kinetics of PHB crystallization. The crystallization temperature of PHB (T_{c1}) in the blends containing up to 20 wt% of PCL remains practically the same, even though PCL crystallization seems to be strongly affected by the presence of PHB.

In order to evaluate miscibility of the amorphous phase dynamical mechanical analysis (DMA) was carried out. Both

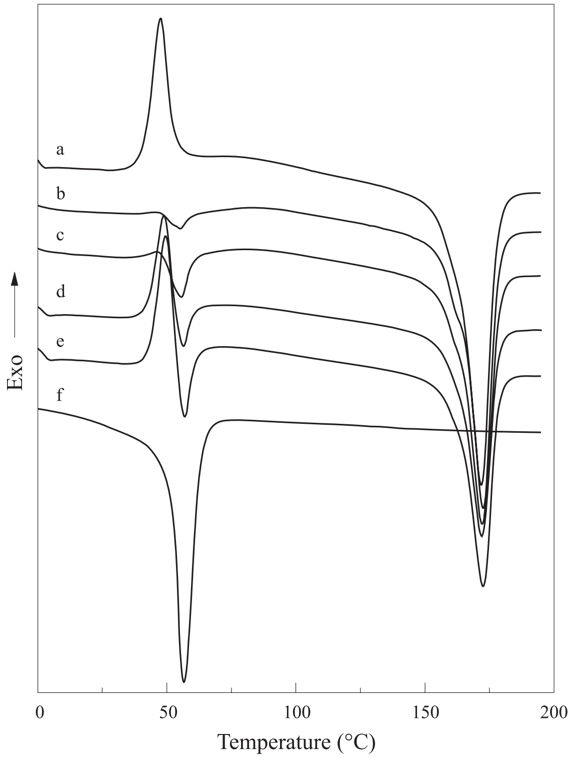

Figure 4. DSC curves corresponding to the second heating step of PHB, PCL and their blends, heating rate of 10°C/min: (a) PHB, (b) PCL5, (c) PCL15, (d) PCL20, (e) PCL30, (f) PCL.

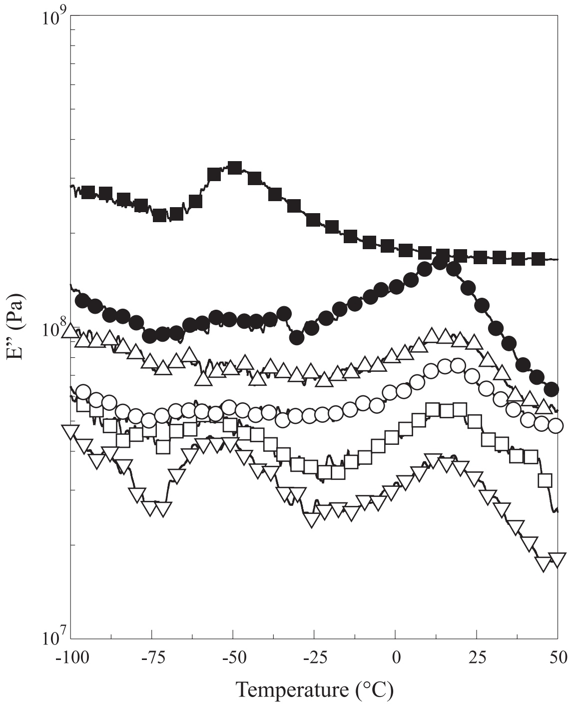

Figure 5. Loss modulus (E") *versus* temperature in the region of the glass transition of PHB, PCL and their blends: (λ) PHB, (Δ) PCL5, (μ) PCL15, (□) PCL 20, (∇)PCL30, (ν) PCL.

blend components are semi-crystalline, so the amorphous phase constitutes only a fraction of the polymers in the blend. Based on this, the blend containing 20 wt% of PCL has an amorphous fraction of this component of around 10 wt% or even smaller and the detection of the PCL glass transition by DSC can be difficult because of its low concentration and the presence of crystalline phase that change this transition. It is important to point out that in dynamical mechanical analysis the thermal history of polymers and their blends is not extinguished, which means that the observed transitions are functions of the previous treatment of the materials.

The loss modulus (E") *versus* temperature in the PHB and PCL glass transition region obtained by DMA are shown in Figure 5. It is possible to verify in this curve peaks representing polymer relaxation. The E" x T curve presents a peak with a maximum at –50 °C, corresponding to the PCL glass transition. The peak corresponding to PHB glass transition occurs at 15 °C. Blends containing up to 15 wt% of PCL presented two peaks located at the same temperatures as pure polymers. This fact indicates the existence of two distinct amorphous phases. The blend containing up to 5 wt% of PCL presents only one peak related to the glass transition of PHB, probably because of low concentration of PCL and the small fraction of amorphous phase which is responsible for the relaxations in the glass transition region. The immiscibility of this system is irrefutable, because the PHB glass transition temperature shows no alteration. Based on data from DSC and DMA is possible to conclude that the PHB/PCL blends are immiscible in both the amorphous and the crystalline phases, and that there is no interaction between these phases detectable by the techniques used.

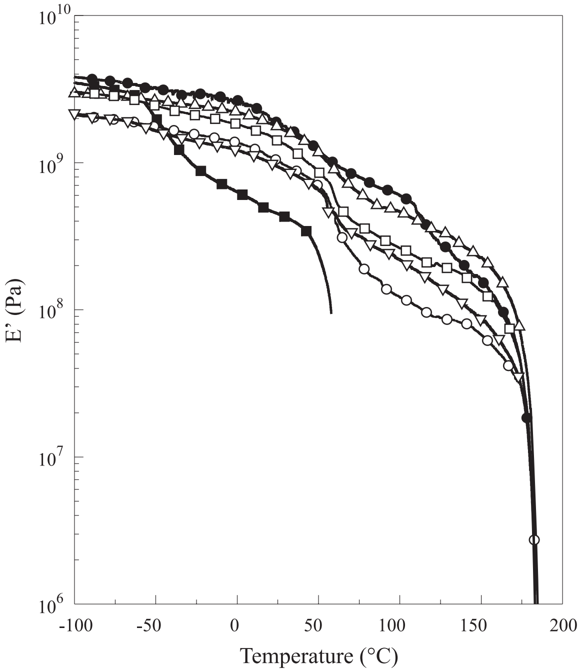

Figure 6. Storage moduli (E') *versus* temperature of PHB, PCL and their blends: (λ) PHB, (Δ) PCL5, (μ) PCL15, (□) PCL 20, (∇)PCL30, (ν) PCL.

Transreactions in these polyester mixture are possible, but in this case the extension of these reactions were not enough to change the miscibility and the crystallization and melting behavior, may be because the melting mixture were conducted at low time and temperature and in absence of catalyst. Transreactions between PHB and PETG, for example, were observed only for long processing time and in presence of catalyst[10].

Based on the curves of storage modulus (E') *versus* temperature of the pure polymers and their blends (Figure 6) it is possible to obtain information about morphology. The PCL curve presents two reductions in E' value at –50 °C and 50 °C, corresponding to glass transition and melting respectively. At temperatures above the PCL melting point there is flowing of this material, which makes continuation of analysis impossible. PHB presents a similar profile when compared with PCL, two reductions in E' value corresponding to glass transition and melting. In the blends the PHB glass transition is easily visualized, which does not happen with the PCL phase. Analyzing the blends it is possible to verify that E' values remain around 1x10^8 Pa even at temperatures where PCL flows (T > 50 °C). This fact indicates that PHB is the matrix while PCL is the dispersed phase.

The proposed morphology is confirmed based on the microscopy obtained by SEM, presented in Figure 7. From these micrographs it is possible to observe that the PHB matrix and PCL dispersed domains are mostly spherical. The PCL domains are visualized as the holes from which the material was pulled out. The diameters of the dispersed phase are around 2 μm in the PCL5 and PCL15 blends. The PCL20 blend presents a wider size distribution of the domains,

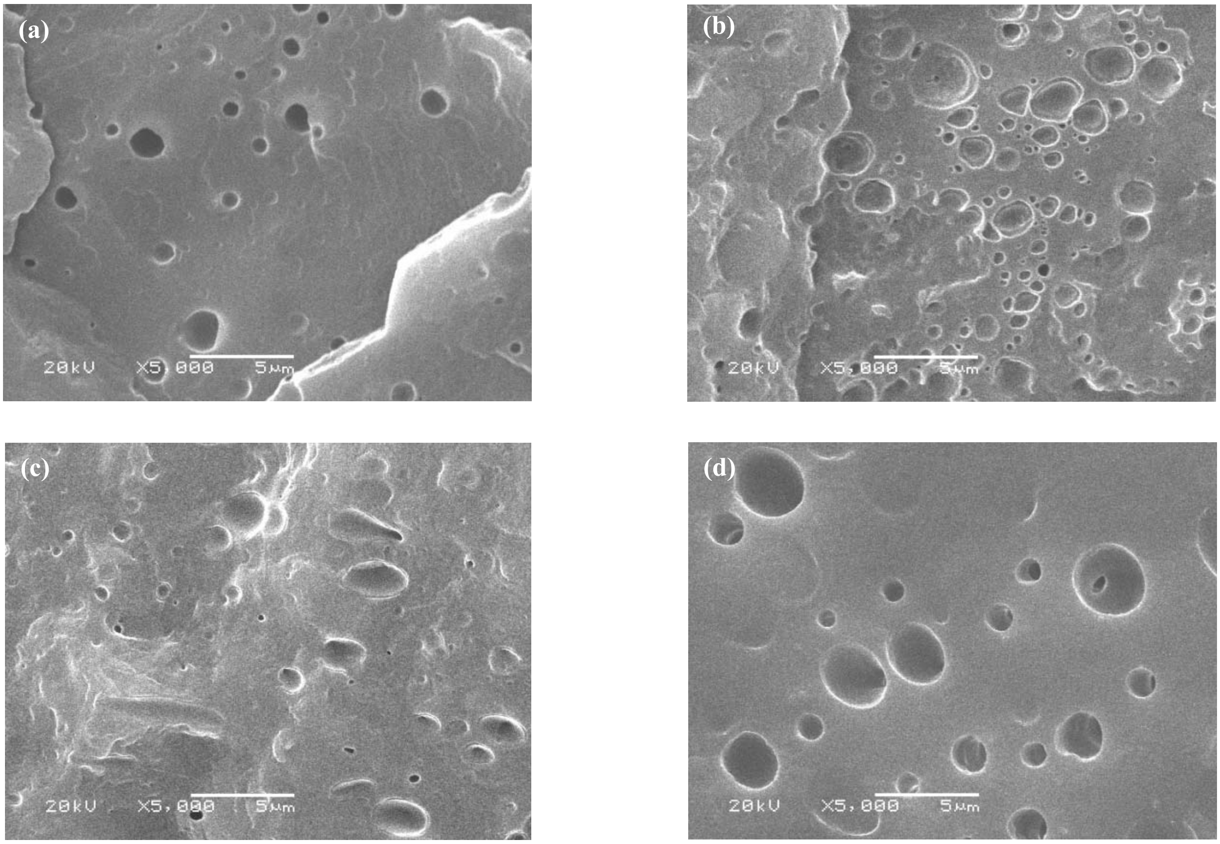

Figure 7. Scanning electronic microscopy: (a) PCL5, (b) PCL15, (c) PCL20, (d)PCL30.

varying from 0.5 to 4 µm and PCL 30 has domains with even larger diameters (between 3 and 5 µm). The interfacial adhesion between phases can be considered weak, since the PCL domains are easily pulled out from the PHB matrix.

Conclusions

PHB/PCL blends obtained from melting mixture can be considered an efficient way of processing these polymers without a considerable degradation of PHB and transreactions. The blends obtained are immiscible for compositions varying from 5 to 30 wt% of PCL. For these compositions, a system constituted of four distinct phases, amorphous and crystalline regions of both PHB and PCL was observed. The blend morphologies are characterized by a PHB matrix and dispersed domains of PCL.

Acknowledgements

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