Introduction

Nowadays the world faces many environmental problems. One, among the most serious ones is the production and the accumulation of urban waste. Biodegradable films based on biopolymers have been developed, for important environmental purposes, e.g. to control the gas permeability, preservation of surface integrity of products, restriction of moisture loss, etc. [1].

Biocompatible polymers, polysaccharide and gelatin based edible films were prepared with a plasticizers and analyzed by DSC techniques [1–4]. Blends of biopolymers, like starch, gelatin, cellulose derivatives, caseinates and others were plasticized with polyols and reported in [5, 6]. Decrease of biopolymer crystallization after gelatinization is an evidence of loss of the organized structure. Addition of small mobile molecules also decreases the degree of crystallization and improves the flexibility of the biopolymer chains [7]. PHB polyester (poly(3-hydroxybutyrate) is an interesting biodegradable polymer and intensively investigated as cast and sheet films with applications in food industry or in medicine. The films obtained are typically brittle and many scientists have attempted to reduce this brittleness by blending with other polymers.

PHB from Usina da Pedra was blended with PEG poly(ethyleneglycol) 300 resulting in blend 1 and blend 2. The two mixtures were melted at 200 and quenched at 0°C. TG curves showed that the thermal stability of the blends and the PHB are identical. For these blends the crystallization temperature decreased compared to the pure PHB, which is probably due to the lower nucleation density.

Keywords: biodegradable polymers, DSC, PHB

Materials and methods

The PHB was provided by Usina da Pedra SP, batch n° 67-08/2003 (MW 380000, with 99.9% PHB in the dry material. Polyethylene glycol (PEG – 300, MW 300) was supplied by Oxiteno. The films have been obtained by the casting method on Pyrex trays, using two distinct concentrations of the plasticizer. The polyalkanoate was dissolved in chloroform at 60°C in the presence of PEG. The solution was casted into a Pyrex glass mold and the solvent was evaporated to obtain a dry medium.

The thermal properties were evaluated by differential scanning calorimetry using a DSC 821 from Mettler Toledo. The mixtures were melted at 200 and quenched to 0°C. Analyses were performed with the samples (10 mg) under N2 atmosphere, using the following temperature program: heating from –50 to 200°C (10°C min⁻¹), cooling from 200 to –50°C (10°C min⁻¹), and a second heating from –50 to 200°C (10°C min⁻¹). The DSC apparatus was calibrated with In metal (m.p. 156.61°C; ΔH=28.54 J g⁻¹). TG tests were performed in SDTA-822 thermobalance (Mettler Toledo), using samples at about 30 mg in sapphire crucibles, under dynamic nitrogen atmosphere (50 mL min⁻¹), at a heating rate of 5 K min⁻¹. Water vapor permeability was
determined according to a method proposed by Gontard et al. [8] based on the ASTM E96-80 [9]. Solubility tests were carried out at 25°C for 24 h, with the samples stirred in a closed recipient. The films were dried in a ventilated oven at 90°C for 24 h. The dried films were weighted in a Mettler analytical balance. The results are expressed as percentage mass loss in water at room temperature.

Results and discussion

The films of PHB/PEG were transparent, homogeneous and flexible compared to the brittle pure thermopressed PHB film. The decomposition temperatures of PHB/2% PEG and PHB/5% PEG films started at 257 and 256°C, respectively. These temperatures are very close together indicating that the addition of plasticizer did not change the thermal stability of the final blends. Figures 1 and 2 show the TG curves of these films.

PHB is completely miscible with additives like PEG 300. The plasticizer weakens the intermolecular forces between adjacent polymer chains. Consequently, there is a change in free volume that causes reduction of the glass transition temperature in the system. The crystallinity of the samples was determined from the melting enthalpy ratios ($\Delta H_m$), assuming that the enthalpy of 100% crystalline PHB is 146 J g$^{-1}$ [10]. The results of DSC (Table 1) showed that rate of crystallization and crystallinity degree of the blends decrease with the increasing of additive concentration. Furthermore, the films exhibit lower melting and crystallization temperatures. The degree of crystallinity is 59% for powdered PHB that is in agreement with the literature data [11]. The value obtained for the pure PHB film is lower compared to the literature data. This is probably due to the favorable conditions of the casting process. Figures 3 and 4 show the DSC curves of the samples. The glass transition was calculated as the mid-point of the heat capacity change. The results show that $T_g$ decreases with increase concentration of additive in the blends.

The cold crystallization peak shifts to a lower re-crystallization temperature, when the content addi-

![Fig. 1 TG curve of PHB/2% PEG](image1)

![Fig. 2 TG curve of PHB/5% PEG](image2)

![Fig. 3 DSC curve of PHB/2% PEG at heating rate of 10°C min$^{-1}$](image3)

![Fig. 4 DSC curve of PHB/5% PEG at heating rate of 10°C min$^{-1}$](image4)
tive is increased. This can be explained that during the non-isothermal crystallization, the crystallization rate is decreased in the presence of a plasticizer. Consequently the nucleation is hindered and promotes the formation of small spherulites, increasing the flexibility of the blends as compared to the pure material. Permeability and solubility (Table 2) were affected by the presence of PEG due to its hygroscopic character. An increase in the PEG content increases the water permeability and solubility.

Conclusions

In conclusion, PHB is completely miscible with the PEG 300. The investigation of blends by DSC technique showed a decrease in crystallinity associated with an increase of PEG content; furthermore, the used process of casting contributed to decrease the crystallinity as it was compared to the processes cited in the current literature. In the studied blends, crystallization took longer time (temperature is shifted to lower values) than in pure PHB, probably due to a lower nucleation density. The presence of PEG, as in the case of any typical plasticizer, interferes with intramolecular interactions between polymer macrochains. The hygroscopic character of the PEG influences the permeability and solubility of the blends. As a consequence of the reduced crystallinity, the amorphous phase increases and can improve the permeability of water throughout this phase.

References