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Calorimetric and SEM studies of PHB–PET polymeric blends

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Abstract PHB [poly (3-hydroxybutyrate)], post-consumer soft-drink bottles poly (ethylene terephthalate) PET (herein named PET-R) and PHBPET-R (blends of PHB and PET-R in several compositions) samples were evaluated by differential scanning calorimetry (DSC) and scanning electronic microscopy (SEM) in order to verify their thermal properties and porosity according to amounts of PET-R added the blends. The DSC curve showed that the solvents used to solve the polymer mixture cause changes in the thermal behavior of PET-R films and in PHBPET-R blends. SEM studies of the PHBPET-R blends show that with a gradual mass increase of PET-R, there are gradual increases in the porosity of the films.

Keywords Polymer · Biodegradation · Polymeric blend · PHB · PET

Introduction

Conventional plastic materials present extremely low degradation rates which can cause serious environmental problems. Large amounts of plastic waste materials have been accumulated day by day. Alternatives to conventional polymers, for that ones more compatible with environmental preservation, have become increasingly necessary [1–3]. Ethylene poly-terephthalate (PET) is the polymer which accumulates bacause of its low degradation rate and originates mainly from post-consumer soft-drink bottles [4, 5]. However, poly(3-hydroxybutyrate) (PHB) originates from renewable sources is a biodegradable aliphatic polyester. It degrades completely by aerobic microorganisms to CO_2 and H_2O [6–9].

This work aims to the possibility of recirculation of PET from post-consumer soft-drink bottles forming blends with PHB. Pure PHB has some disadvantages, such as its high degree of crystallinity and its thermal instability. Thus, its mixture with conventional polymers with low degradability but good mechanical properties can be a solution to obtain environmentally more friendly biodegradable polymers. Blends of PET and PHB might show changes in the properties of the final products, e.g. in the increase of the mechanical properties of the PHB or the biodegradability of the PET [10]. PHB and PET blends were obtained in the form of a film solving both of them in the same solvents. From the DSC curves, some physico-chemical characteristics like crystallization and the melting temperatures of these films were evaluated. In addition, the porosity and physical properties of the films were also studied by using Scanning Electron Microscopy (SEM).

Experimental

Post-consumer soft-drink bottles were washed, dried at room temperature, cut into pieces of approximately 2 mm^2 and solved in phenol/tetrachloromethane solution ($\sim$1:1 v/v) at 80 °C. After dissolving of the PET-R, trichloromethane was used as the solution's stabilizing agent.

Samples of PHB were prepared by solving in trichloromethane at 60 °C. After stopping heating, the PET-R solution drop by drop was added into the PHB solution under intense stirring. Films of PHBPET-R were obtained by spilling the solution into Petri dishes and drying at room

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Table 1 PHB and PET mass ratios in samples 1–7

Sample	PHB/g	PET/g	PHB/PET (mass)
1	0.5006	0.0632	8/1
2	0.5002	0.1214	4/1
3	0.5003	0.2509	2/1
4	0.5002	0.5013	1/1
5	0.2502	0.5003	1/1
6	0.1251	0.5010	1/1
7	0.0625	0.5010	1/1

temperature for 48 h. The mass ratios of the PET and PHB solutions are presented in Table 1.

DSC curves were recorded by using a TA Instruments model 2910 DSC under dry nitrogen with 50 mL min^{-1} flow rate and at heating rate of 10 °C min^{-1}, aluminum pan and in the 30–300 °C temperature range.

The sample surfaces were examined using a JEOL JSM-T330A (JEOL, Akishima Ltd, Japan) microscope with a NORAN EDX (Energy Dispersive X-ray Analysis) (Thermo Electron Corporation Waltham, MA) Scanning Electron Microscope.

Results and discussions

Figure 1a and b show the DSC curves of the first and second heating for PET-R and PHB respectively. In Fig. 1a the melting temperature (Tm) of PET-R is 245 °C while the second heating curve presents the vitreous transition temperature (Tg), the crystallization temperature (Tc) and the melting temperature (Tm) at 65, 150 and 245 °C, respectively [11].

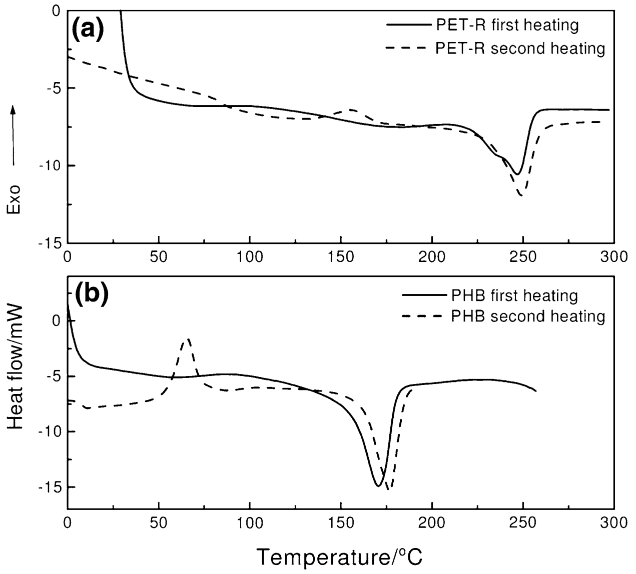

Fig. 1 DSC curves for PHB and PET-R under nitrogen atmosphere (50 mL min^{-1}) at a heating rate of 10 °C min^{-1}

The DSC curve in Fig. 1b, shows the melting upon first heating for the PHB at 170.4 °C and a second heating shows the Tg, Tc and Tm at 6.7, 65.8 and 177.1 °C, respectively [12].

Figure 2 illustrates the DSC curves for the first and second heating for PHB and PET-R films solved previously in trichloromethane solution and then dried at room temperature. It can be seen that in Fig. 2a in the first heating the physico-chemical properties of PET-R were affected by the solvents, where two thermal events appears at 70 and 147 °C, which are missing in the first heating of the raw PET-R (see Fig. 1a, first heating). The DSC curve for the second heating is similar to the second heating curve can bee seen in Fig. 1a. For PHB it seems the shape of the DSC curves were not influenced by the solvents (see Fig. 2), it is similar to the corresponding one in Fig. 1b.

Figure 3 shows the DSC curves of phenol (a) and PHB-PET-R films 1/20 obtained in solution and dried at room temperature (b). Phenol melts at 44.3 °C and two more endothermic events also appear at 127.6 °C and 149.3 °C while the PHBPET-R 1/20 films shows an endothermic peak at 69.3 °C which does not appear in case of raw PHB or PET-R. Comparing the endothermic effects in the DSC curves of the phenol [13] and the film, a 25 °C displacement can be seen which may indicate a possibile interaction between the PHBPET-R and the phenol.

The DSC curves in Fig. 4 show the PHBPET-R blend 1/4, sample 6. The curves in Fig. 4a were obtained by heating the samples from 30 to 300 °C. In the first heating, when the main thermal events were at 70, 158 and 205 °C. The DSC curve was obtained by heating sample 6 (see Table 1) from 0 to 90 °C at first heating (see Fig. 4b), then

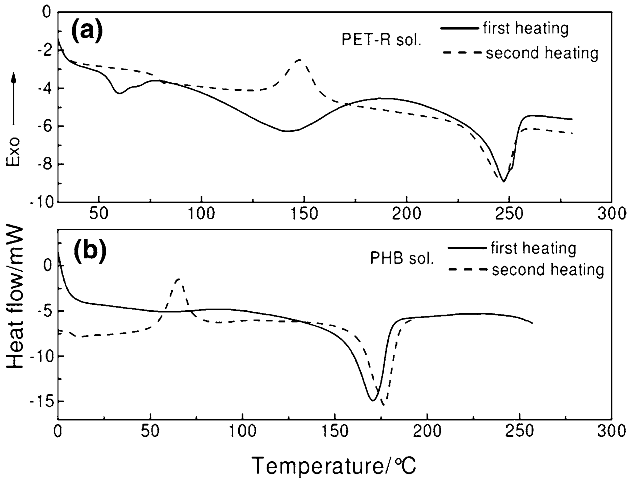

Fig. 2 DSC curves for the PHB and PET-R films obtained in solution for the first heating and second heating under nitrogen atmosphere (50 mL min^{-1}) and at a heating rate of 10 °C min^{-1}

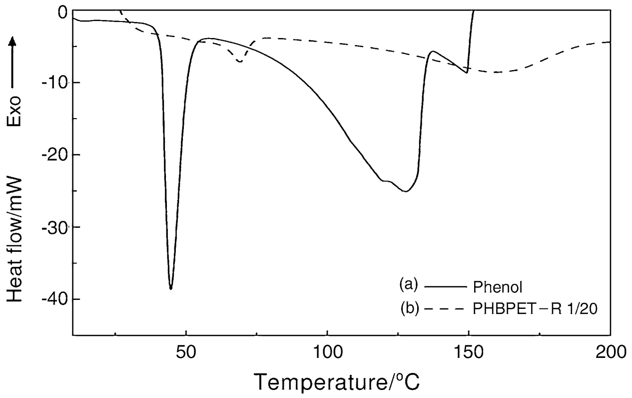

Fig. 3 The first DSC heating curves of the phenol and the PHBPET-R 1/20 film under nitrogen atmosphere (50 mL min^{-1}) at a heating rate of 10 °C min^{-1}

it was slowly cool down to 0 °C and again heated up to 200 °C (second heating, Fig. 4c). The same sample was then cooled down again to 0 °C and then heated up to 300 °C (third heating, Fig. 4d).

Comparing the DSC curves in Fig. 4b–d it can be seen that Fig. 4b presents an endothermic peak at 70 °C, which disappears in the second heating, Fig. 4c. Probably it can be due to the termination of the interaction between phenol and the blend. In Fig. 4c, an endothermic event at 158 °C can be seen, which disappears when the sample is cooled and heating again (see Fig. 4d). Now it can be seen only the corresponding PHB and PET-R melting point at 175 and 250 °C, respectively.

Figure 5a shows the DSC curves of the PHBPET-R blend films where the proportion of PET-R is larger than PHB (samples from 5 to 8). It can be observed that the interaction between PHBPET-R 1/2 blend and phenol (60–80 °C) did not appear. However, the melting point of the sample is detected between 160 and 180 °C. The PHBPET-R 1/4 and 1/20 are show the phenol interaction through the endothermic peak at 70 °C and a depression in the 100–200 °C temperature range. The DSC curves present an increase in the intensity of the peaks at 70 °C with a gradual increase of the PET-R mass within the samples indicating that interaction of phenol is due to presence of PET-R.

Figure 5b shows the curves of the PHBPET-R films previously dried on a hot plate at 80 °C. The endothermic event at 70 °C and the depression between 100 and 200 °C (Figs 2–4) cannot be observed. It can be seen that for the films obtained by drying the interaction between PET-R and phenol cessated.

The morphology analyses to the blend films were obtained by using Scanning Electronic Microscopy (SEM) with a source of field emission. Figure 6 presents the micrograph of the PHBPET-R 10/1, 1/1, 1/2 and 1/20 blends. An increase in the porosity of the samples can be seen when the ratio of PET-R is increased.

For the 1/2 and 1/20 sample, Fig. 6c–d formation of spheres can be observed, which are more visible in the second one, where a kind of coalescence occurred among the droplets leading to the formation of large empty spaces between them. It could be attributed to the interfacial repulsion between the PHB and the PET-R [14, 15].

PHBPET-R blends obtained by dry of the solvent can present increase in porous forms depending on the application interest modifying the proportion between PET-R and PHB in presence of phenol.

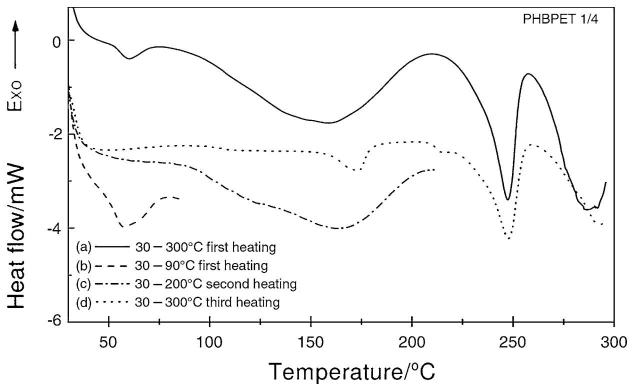

Fig. 4 DSC curves of the PHBPET-R 1/4 films (a–d) obtained in solution under nitrogen atmosphere at a heating rate of 10 °C min^{-1}

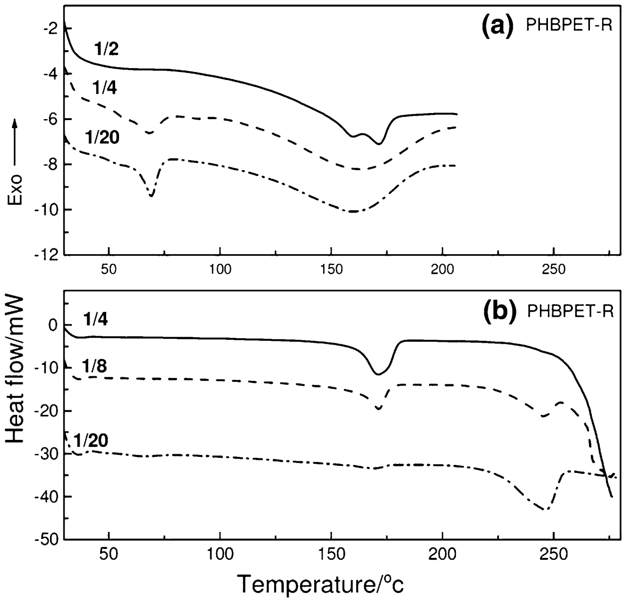

Fig. 5 DSC curves of the films PHBPET-R 1/2, 1/4, 1/8 and 1/20, obtained in solution under nitrogen atmosphere and at a heating rate of 10 °C min^{-1}

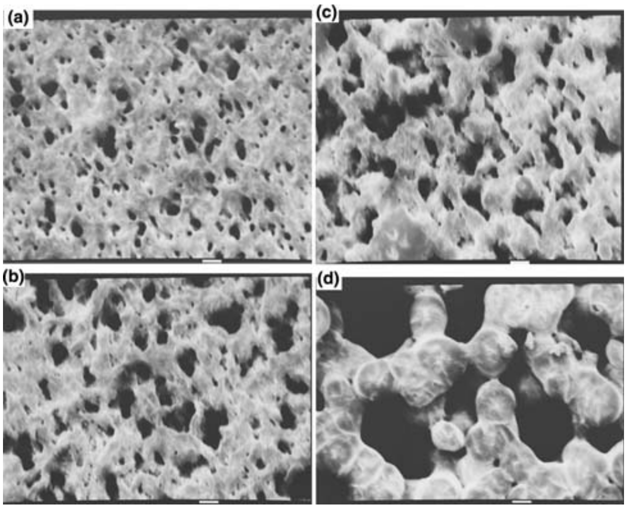

Fig. 6 SEM micrograph of the films (**a**) PHBPET-R 1/10; (**b**) 1/1; (**c**) 1/2 and (**d**) 1/20 obtained in solution

Conclusions

Similar melting temperatures were observed for PHBPET-R blends without any significant interaction between then.

An increase in the porosity of the films was also observed when the ratio of PET-R where the blends contained phenol was gradually increased.

Finally, for those samples where the proportion of the PHBPET-R was higher than two a formation of spheres and empty spaces occurred, which was in relation to the interfacial repulsion between the PHB and the PET.

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