STUDY OF CRYSTALLINE MORPHOLOGY OF PBT, PET AND PBT/PET BLENDS BY DMTA AND TIME-RESOLVED SYNCHROTRON SAXS/WAXS/DSC

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Abstract. *Isothermal melt crystallization of poly(butylene terephthalate) (PBT), poly(ethylene terephthalate) (PET) and PET/PBT blends with and without a transesterification catalyst was studied by time-resolved small-angle X-ray scattering (SAXS), differential scanning calorimety (DSC) and wide-angle X-ray scattering in order to investigate the effects of the catalyst and blending on the morphological parameters of the PBT and PET. For the neat polymers, it was found that the catalyst worked as a nucleant agent, increasing the crystallization rate. For the PET/PBT blends, WAXS analysis showed that PET and PBT crystallize separated, since all the peaks of both polymers appear in the WAXS difractogram of the blend. SAXS results showed that both amorphous and crystalline lamellas of blend are larger than that found in the neat polymers, suggesting a miscibility between the amorphous phases and the occurrence of transesterification reactions during the blend mixture, probably forming a amorphous copolymer. This speculation is coherent with the result of dynamic mechanical thermal analysis (DMTA), which shows the presence of only one glass transition in the blend, located between the glass transitions of the neat polymers.*

Keywords: *PET/PBT blends, crystalline morphology, small angle x-ray scattering.*

1. INTRODUCTION

Blends of PET/PBT are potentially attractive because can combine the fast crystallization rate of PBT with the low cost of the PET grade bottle. These blends present a good superficial appearance and the mechanical properties are reasonable (Utracki, 1995). These good properties are due to the compatibilization between the polymers promoted by the miscibility between the amorphous phases and the formation of block copolymers of PET-PBT by transesterification reactions during the melt processing of the blend.

The effect of melt mixing on the properties of these blends has been studied more extensively. Much less effort, however, has been directed towards understanding the reactions occurring during melt blending scattering in order to investigate the effects of the catalyst and blending on the morphological parameters of the PBT and PET. In the blend of PBT with PET, exchange reaction can take place between terephthalates groups and result in the formation of copolycondensates. The reaction may proceed according to three types of reaction mechanisms: alcoholysis by a hydroxyl end group, acidolysis by an acidic end group and midchain ester exchange (transesterification). In the blend of high molecular mass polymers, the direct ester exchange should be the first reaction because of low-end group concentrations. In addition, the progressive transesterification causes a transition from homopolymers via block copolymers to random copolymers. The products of transesterification act as compatibilizers between both blend components. Titanium alkoxides are the most eficient catalysts for exchange reactions in the case of poly(alkylene terephthalate) systems. The fast exchange reaction in the presence of these catalysts can make it dificult to control the chemical structure when a low extent of exchange is desired and affect the crystalline morphology, cinetic of the crystallization, important parameters for processing and mechanical properties of the this systems.

The motivation of this work is due to the fact that there are relatively few studies on PET/PBT blends in the literature (Avramova, Fakirov *et al.*, 1992; Avramova, 1995; Backsona, Richards *et al.*, 1999; Montaudo, 2008; Park, 2008; Wang, Meng *et al.*, 2008; Guerrica-Echevarria e Eguiazabal, 2009; Stocco, La Carrubba *et al.*, 2009) and the necessity for a better characterization of this system, due to its technologic importance. Isothermal melt crystallization of poly(butylene terephthalate) (PBT), poly(ethylene terephthalate) (PET) and PET/PBT blends with and without a transesterification catalyst was studied by time-resolved small-angle X-ray scattering (SAXS), differential scanning calorimety (DSC) and wide-angle X-ray scattering in order to investigate the effects of the catalyst and blending on the morphological parameters of the PBT and PET.

2. EXPERIMENTAL

2.1 Materials and processing of blends

The PET utilized (BMA-S80) was obtained from Rhodia-Ster, PBT (VALOX-315) was supplied by GE Plastics and the catalyst tetra-n-butyl titanate was supplied by Du-Pont Brazil. It was prepared PET, PBT and PET/PBT blends (composition : 50/50 wt/wt) with 0 and 250 ppm of catalyst. For the compounding, initially the polymers were dried overnight at 100 °C in a vacuum oven and subsequently melt-mixed at 275 °C in a 30 mm twin screw extruder (Werner-Pfleiderer model ZSK-30) at 100 rpm. The molding was carried out by injection in a Arburg Allrounder model 270V injection machine at 275ºC (Mantovani, Perez *et al.*, 2004; Barbosa Jr, 2006).

2.2 SAXS and DMTA experiments

SAXS measurements were performed at the small angle scattering workstation (D11A) at LNLS, using a linear position sensitive detector. The wavelength of the radiation used was 1.7433 Å and the sample to the detector distance was 1181.7 mm. It was also used a second linear position sensitive detector closer to the sample to perform the WAXS measurements (Mantovani, Pessan *et al.*, 2001a; Mantovani, Pessan *et al.*, 2001b; Mantovani, Mendes *et al.*, 2003). The apparatus for the time-resolved SAXS/WAXS/DSC is illustrated in Figure 1.

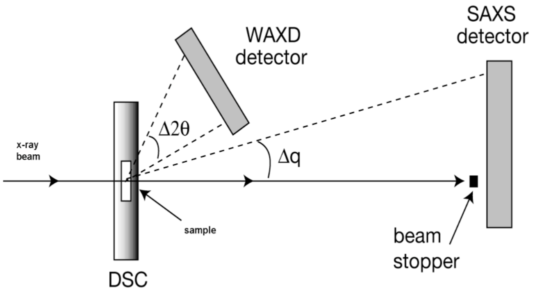

Figure 1. Illustration of the SAXS/WAXS/DSC apparatus in the x-ray beam line.

A Linkam DSC (model THM 600) of single-pan design was used for the samples temperature control for the isothermal crystallization experiments (Mantovani, Pessan *et al.*, 2001a). The samples were cut from the molded samples and encapsulated in d.s.c. pans fitted with mica windows. In the experiments, the samples were initially equilibrated at 270 °C (above the melt temperature of PET and PBT) for 5 minutes and after that the temperature was jumped in a high cooling rate to the crystallization temperature (210 °C). Each SAXS measurement during the crystallization consisted of a sequence of frames with acquisition times varying from 26 to 52 seconds for each frame. The procedures for the calculation of the crystalline parameters from the time-resolved SAXS data are well described in the literature (Hsiao e Verma, 1998; Hsiao, Wang *et al.*, 1999; Mantovani, 2002). These procedures consist on the calculation of the correlation function of each frame in order to calculate the lamellar crystalline thickness 'l_c', lamellar amorphous thickness 'l_a' and the relative invariant 'Q'. Dynamic mechanical thermal analysis (DMTA) of the injected samples were performed in a DMTA IV Rheometrics equipament, at a frequency of 1 Hz.

3. RESULTS AND DISCUSSION

3.1 Effect of catalysts on the crystallization kinetics of PBT and PET

Figure 2 show the evolution of the crystalline parameters of the PET with and without catalyst during the isothermal crystallization at 210 °C and Figure 3 show this evolution for the PBT with and without catalyst. In Figure 2a and 3a it can be observed that the crystalline lamellar thickness decrease during the crystallization, for the polymers with and without catalyst. This decrease can be attributed to the continuous formation of stacks of small crystalline lamellas between the primary stacks after the initial stage of the crystallization, i.e., after the primary crystallization (Hsiao, Wang *et al.*, 1999). These figures also show that catalyst promotes a decrease of the crystal lamellar thickness of PET, but the amorphous lamellar thickness (l_a) is not altered. The decrease of 'l_c' by the incorporation of catalyst can possibly be explained by the PET transesterefication promoted by this component. This process alter the PET chains structure and thus may alter the stacking order of the chains.

In figures 2b and 3b are shown the evolution of the relative invariant (*Q*) during the crystallization. This parameter is proportional to the crystallization degree and can be used as a qualitative analysis of the crystallization kinetics. The curves show a sigmoidal growth in the initial stage of crystallization, correspondent to primary crystallization, followed by a much slower growth, correspondent to secondary crystallization. From the figures 2b and 3b it can be inferred that the neat polymers take a longer time to complete the primary crystallization as compared with the polymers with catalyst. This indicates that the catalysts increase the crystallization kinetics, probably because the catalyst act like a nucleant agent.

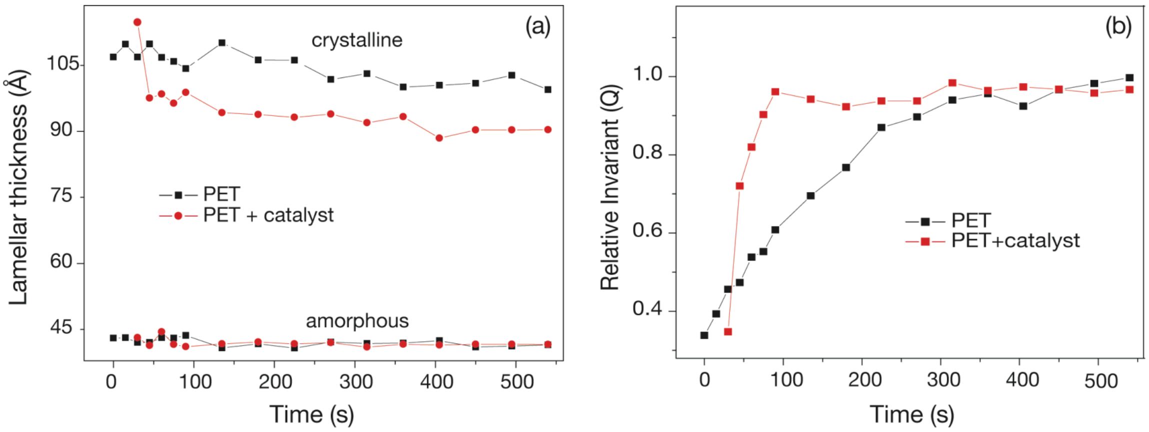

Figure 2. Time evolution of the crystalline parameters of the PET with and without catalyst during the crystallization at 210 °C.

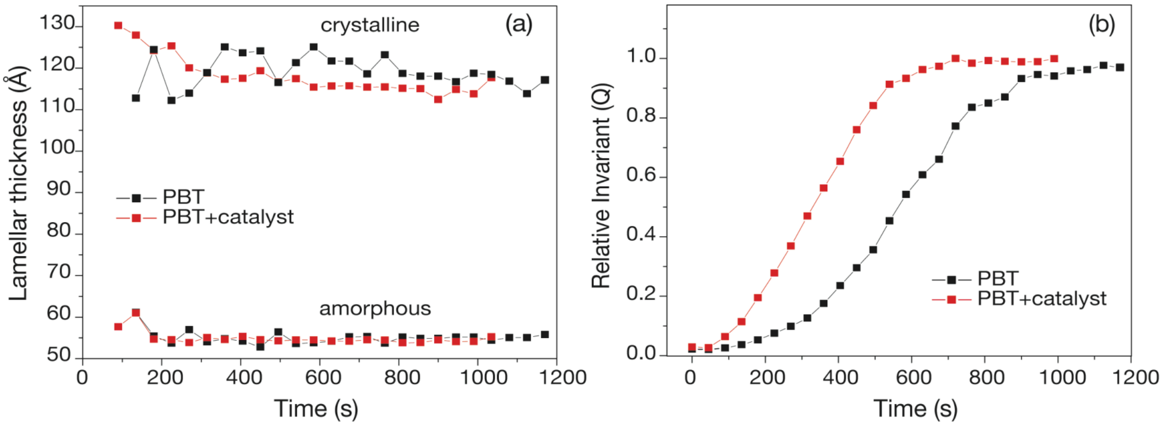

Figure 3. Time evolution of the crystalline parameters of the PBT with and without catalyst during the crystallization at 210 °C.

3.2. Structural analysis of PBT/PET blends

Figure 4 shows the WAXS diffractograms for the PET, PBT and the blend PET/PBT containing 250 ppm of the Ti catalyst. We can observe that the blend diffractogram present all the diffracted peaks of PET and PBT in the same diffracted angle, indicating that the PET and PBT do not co-crystallize during the isothermal crystallization.

Figure 5 presents the Lorentz-corrected SAXS one-dimensional scattering curves of PBT, PET and the blend PBT/PET, taken after the end of the isothermal crystallization at 210 °C. It should be noted that we could not applied a correlation function in the SAXS curve of PET/PBT because the electron scattering model which this function is based on could not be applied in this blend, since it contains two populations of crystallites, which can not be discerned from the correlation function. However, we can apply the Bragg's correlation in order to achieve a estimative of the long period , *L*, of the blend, which correspond to the sum of the amorphous and crystalline lamellas thickness. The *L* values found for the PBT, PET and PET/PBT blends were 14.6, 17.8 and 18.4 nm, respectively. The fact that the L value for the blend is higher than PBT and PET indicates that during the blending there are an increase of l_c and/or l_a of the PET and PBT. We speculate that is unlikely that the increase of L is due to an increase of l_c , because, as shown in Figure 4 the crystalline reflexions of the polymers remained unaltered after blending. In another hand, an increase of l_a is more likely, because it can occur if the amorphous regions of PBT and PET are miscible.

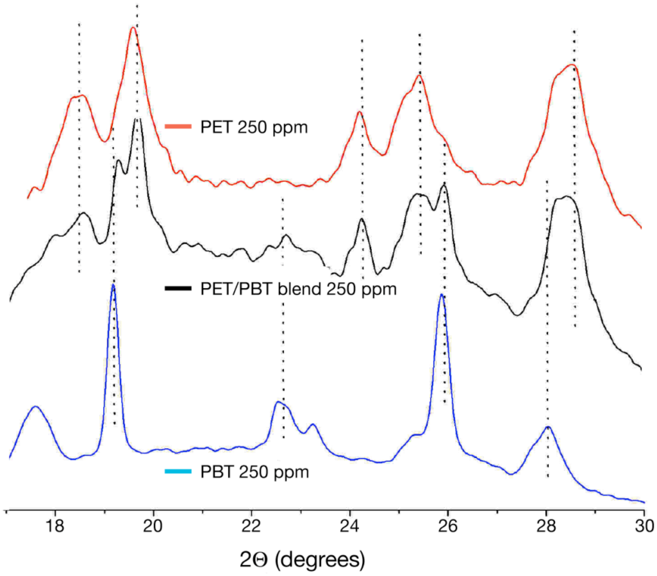

Figure 4. WAXS of PET, PBT and PET/PBT blend with 250ppm of catalyst.

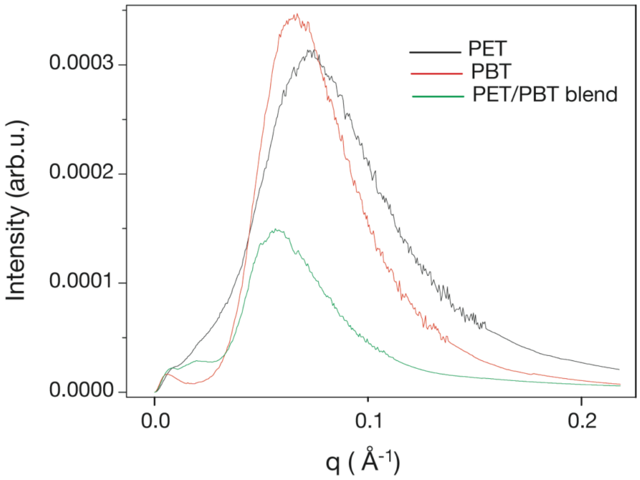

Figure 5. One-dimensional SAXS curves for the neat polymers and PET/PBT blend.

In order to investigate possible miscibility between the amorphous regions of PBT and PET in the PBT/PET blend, DMTA analysis were performed in the blend, and the results are shown in Figure 6. From this Figure, it can be seen the *tan δ* peaks associated to the glass transitions temperatures, which are 53.8, 87.0 and 59.8 °C for the PBT, PET and PET/PBT blend, respectively. The presence of a unique glass transition for the PET/PBT blend, located between the glass transitions of PET and PBT, is a clear indicative of miscibility between the amorphous phase of these polymers (Stocco, La Carrubba *et al.*, 2009). It is also possible that the amorphous phase is constituted by copolymers of PET/PBT, which could be formed by transesterefication reactions during the melt blending.

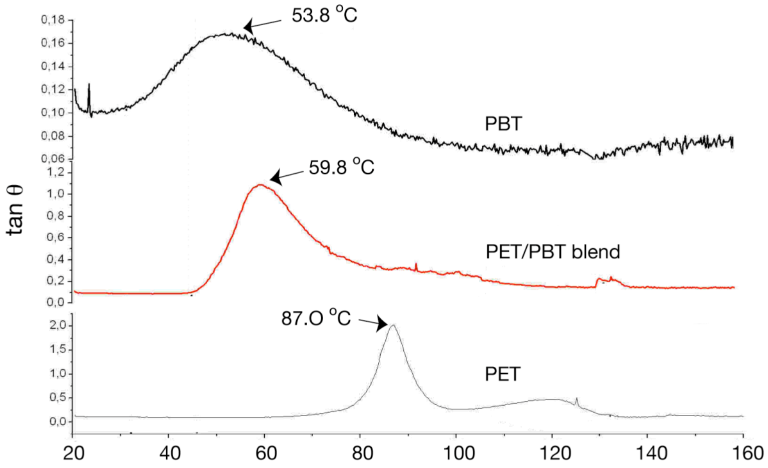

Figure 6. DMTA curves for the PBT, PET and PET/PBT blend.

4. CONCLUSION

Time-resolved SAXS analysis of the isothermal crystallization of PET and PBT showed that the incorporation of catalysts decrease the crystalline lamellar thickness and increase the crystallization rate of these polyesters. For the PET/PBT blend, DMTA results indicate that the amorphous phases of neat polymers are miscible in the blend, what leads to a increase of the amorphous lamellar thickness, as evidenced by the SAXS analysis of the blend.

5. ACKNOWLEDGEMENTS

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