**MICROSTRUCTURE AND MECHANICAL PROPERTIES OF PBT-PC_c BLOCK
COPOLYMERS: INFLUENCE OF COMPOSITION, STRUCTURE AND PHYSICAL AGING**

L.Giri, Z.Roslaniec*, T.A.Ezquerro and F.J.Baltá-Calleja.

Instituto de Estructura de la Materia, CSIC, Serrano 119, Madrid 28006, Spain.

*Institute of Materials Engineering. Technical University of Szczecin

Al. Piastow 17, 70-130 Szczecin, Poland.

Abstract

The microhardness of films of poly(butylene terephthalate) cyclo-aliphatic carbonate (PBT-PC_c) block copolymers was determined. The PBT-PC_c compositions investigated were 100/0, 95/5, 80/20, 70/30, 60/40, 50/50, and 40/60. The microhardness of the amorphous films is discussed in terms of a model given by the additivity values of the single components H_a^{PBT} and $H_a^{PC_c}$. Physical aging of the glassy samples leads to a rise in the microhardness for the various copolymer compositions. However, the hardness additivity of the aged samples is preserved. It is further shown that the deviation of hardness from the additivity law, for the semicrystalline copolymers, is mainly due to the depression of the crystal hardness values of the PBT crystals and partly due to a decrease in crystallinity of the PBT phase. Discussion of results permits to derive a value for the microhardness of infinitely thick PBT crystals which is not far off from that reported for poly(ethylene terephthalate).

Introduction

Thermoplastic elastomers are polymeric materials composed of amorphous "soft" segments, characterized by a low glass transition temperature, and "hard" segments having high strength and high melting temperatures [1]. The coexistence in the same polymeric chain of incompatible species comprising a block copolymer has a tremendous effect on both phase behaviour and morphology of the resulting polymer [1,2,3]. Depending upon the degree of microphase separation present in a block copolymer, thermal and mechanical properties different from those exhibited by the individual homopolymers are possible [1,4,5,6]. Block copolymers based on poly(butylene terephthalate) (PBT) and poly(tetramethylene oxide) (PO4) have received a lot of attention, especially on the relationship between microstructure and properties [7]. Recently, aliphatic poly(carbonate) (PC_a) has been used to prepare block copolymers and multiblock terpolymers based on (PBT) [8,9,10]. PBT-PC_a block copolymers have shown to exhibit higher melting point depressions [8,9], than PBT-PO4 block copolymers [11]. Moreover, the variation of the bulkiness of the carbonate block by using cyclo-aliphatic carbonate(PC_c), instead of PC_a, has important effects on the resulting thermal properties[8,9].

In the present paper we report new results relating to the surface mechanical properties, as revealed by microhardness, of new PBT-PC_c copolymers with varying amount of ether and carbonate segment content.

Experimental

Sample preparation

Dimethyl terephthalate, 1,4-butanediol and dihydroxy-polycarbonate (cyclo aliphatic carbonate (PC_c) Duracarb 140) were polymerised by a three-stage polycondensation method as described elsewhere [8,10]. Copolymers with a varying content of PC_c segments (between 0 to 60% in weight) and PBT segments between 40 to 100% in weight were prepared. The obtained polymers were extruded from the reactor and granulated. The granulated polymers were dried for 8 hours at 70°C under reduced pressure and injection moulded at ≈50 MPa. For X-ray, DSC and

microhardness characterization, 300 μ m thick films were prepared by compression moulding between thin Teflon plates at a temperature 20°C higher than the corresponding melting point of each polymer. Finally, the films were quenched at room temperature in the form of glassy films. The films were finally stored, at room temperature, for a period of 6 months.

Experimental techniques

Wide angle X-ray diffraction patterns (WAXS) were obtained at room temperature using a Rigaku goniometer with Ni-filtered CuK α radiation from a Rigaku rotating anode generator. The crystallinity α (referred to the sum of PBT and PC_c amorphous content) and the lattice parameters of PBT crystals were determined from the WAXS patterns after calibration with Si as a standard and performing absorption, thickness and planarity corrections [12].

The small angle X-ray scattering (SAXS) patterns were obtained with a point collimation Rigaku camera using a sample to film distance of 300mm. A rotating anode X-ray generator using Ni-filtered CuK α radiation with a fine focus working at 40KV and 70mA was used. Densitometer traces of the X-ray films were recorded using a Joyce & Loebel microdensitometer. The long period, L, was determined from the SAXS maxima using Bragg's law after subtraction of the background intensity and correcting for the Lorentz geometrical factor.

The calorimetric measurements were carried out in a Perkin Elmer - DSC4 differential scanning calorimeter. Scanning rates of 10°C/min and about 15 mg samples of the glassy films were used. Calibration was made by using standard indium samples. All the samples except pure PBT and the sample containing 5wt.%PC were amorphous when quenched from the melt. The samples were crystallized in a Linkam THM 600 hot stage at temperatures 10°C above the temperature corresponding to the crystallization exotherm peak observed in the DSC thermograms. The time of crystallization t_c was 30 minutes and the temperature of crystallization T_c was varied from 100°C to 130°C depending on the composition.

Microhardness (H) was measured at room temperature using a Leitz Tester adapted with a square based diamond indenter. The H value was derived from the residual projected area of indentation according to the expression $H = kP/d^2$ (MPa), where d is the length of the impression diagonal in meters, P the contact load applied in N and k is a geometrical factor equal to 1.854. A loading cycle of 0.1 min and loads of 0.5 and 1N were used.

Results and discussion

Wide angle X-ray diffraction

When quenched from the melt the PBT/PC_c copolymers containing more than 20 wt% PC_c are completely amorphous. After annealing at appropriate temperature the PBT segments crystallize. Fig.1. shows the amorphous halo of the PBT/PC_c copolymer containing 20wt% PC_c and the subsequent crystalline WAXS pattern of the same material crystallized at T_c = 100° C for t_c = 30min. The crystalline peaks correspond to the reflections of the α -polymorphic form of the PBT homopolymer. On the other hand, pure PBT and the PBT/PC_c sample containing 5wt% PC_c are not amorphous even after quenching. Fig.2. shows the WAXS patterns of all the investigated, annealed, semicrystalline copolymers. From the patterns it turns out that mainly the PBT structure retains its form in all the copolymers; i.e., the main reflections of PBT homopolymer like the (100) and (010) remain present in all the samples. Only a slight change in the 010 spacings corresponding to the lateral packing of the PBT molecules in the lattice, for compositions higher than 20wt% PC_c, is appreciable (Fig.3).

Small angle X-ray diffraction

The X-ray long period L was derived from the maxima of the small angle scattering profiles after direct application of Bragg's law for the homopolymer PBT, and for the copolymers with 20, 30 and 40wt% PC_c content. The rest of the samples did not show any discrete SAXS maxima. The crystal thickness l_c was calculated from the X-ray long period L, by using the relation $l_c = L \alpha$, where α is the crystallinity obtained from the WAXS patterns.

Calorimetric measurements

The DSC scans of the copolymer samples immediately after quenching show the presence of a typical step, in the range 40-50°C depending on composition corresponding to the glass transition temperature (T_g) (Fig.4). On the other hand, the T_g of the aged material is revealed by the presence of a small endothermic peak which corresponds to a relaxation of the glass toward equilibrium (not shown in Fig.4). As pointed out above, pure PBT and the sample containing 5wt% PC_c cannot be obtained in the amorphous form, which is evident from the absence of a crystallization exotherm in these two samples. For the amorphous samples there is a slight increasing tendency in T_g values with increasing PC_c concentration (see Table 1). Fig.4 also shows the melting endotherms in the higher temperature range. From the thermograms, one observes that the melting temperature decreases as we increase the PC_c content till 30wt%. For the copolymers with higher PC_c content, the melting endotherm is much less pronounced.

Microhardness measurements

Fig.5. illustrates the variation of microhardness (H) as a function of PC_c content for the quenched amorphous samples measured immediately after solidification (fresh samples, H_a^{fresh}) and after storage for 6 months at room temperature (aged samples, H_a^{aged}). The aged samples clearly show larger microhardness values than the freshly prepared samples. For all amorphous blends, the microhardness linearly increases with the increasing concentration of PC_c units according to:

$$H_a = H_0 + kw_{PCc} \quad (1)$$

where the intercept H_0 gives the H -value of purely amorphous PBT and w_{PCc} is the wt% of the PC_c component. For the fresh and the aged samples two different values of H_0 are obtained viz, 54MPa and 94MPa as the H_a -values of the fully amorphous fresh PBT and aged PBT samples.

From the thermograms we have observed that for the amorphous samples (PC_c content greater than 20wt%) T_g roughly increases with increasing PC_c content (see Table 1). The parallel variation of microhardness and T_g with PC_c content immediately suggests that the

microhardness increase is caused by the shift of T_g towards higher temperatures. The shift of T_g increases the $\Delta T = T_g - T$ values, ΔT being the difference between the temperature of measurement T and the T_g of the copolymer. Consequently microhardness increases due to the fact that hardness increases with increasing ΔT . Fig.6 illustrates the linear correlation found between the difference, $\Delta H = H_a^{\text{sample}} - H_a^{\text{PBT}}$ and ΔT with increasing PC_c content.

The microhardness of the crystallized samples (H) shows first a decrease with PC_c content till 20wt% and then a linear increase with $PC_c \geq 20\text{wt}\%$. (Fig.5). This decrease in microhardness value can be partly attributed to the corresponding decrease in crystallinity from the PBT homopolymer ($\alpha = 0.285$) to the PBT_{80}/PC_{c20} copolymer ($\alpha = 0.176$) as given in Table.1. The hardness of a semicrystalline polymer additionally depends on the hardness of the crystals (H_c) themselves. Assuming the crystals are randomly distributed and oriented, the value of H_c can be calculated from the additivity relation [13]

$$H = H_c \alpha + H_a (1 - \alpha) \quad (2)$$

From Fig.5. it is also observed that H_c for the PBT crystals decreases with increasing PC_c concentration till $w_{PC_c} \approx 20\text{wt}\%$. The long period L , crystallinity α , crystal thickness l_c and H_c values are given in Table.1. It is clearly seen from Fig.7 (plot of $1/H_c$ vs $1/l_c$) that the decrease in H_c can be correlated with the decrease in crystal thickness of the PBT domains. The dependence of H_c on l_c is given by:[14,15]

$$H_c = H_c^\infty / (1 + b/l_c) \quad (3)$$

where H_c^∞ is the hardness value for infinitely large PBT crystals and b is a parameter which is related to the surface free energy σ_e of the crystalline lamellae and to the energy δh required for plastic destruction of the crystals, according to $b = 2\sigma_e/\delta h$.

From the intercept of the straight line of Fig.7 one can get a value for the microhardness of infinitely thick PBT crystals as $H_c^\infty = 369\text{MPa}$, and from the slope the value of $b = 15\text{\AA}$. At this point we must mention that for infinitely thick PET crystals, the reported microhardness value is 380MPa , which is not far off from the obtained value above for PBT. In addition, we have to consider that the values of l_c used in this evaluation represent only a lower bound. The upper

bound is obtained if one puts $l_c=L$, assuming that all amorphous material lies outside of the crystal lamellar stacks. With this assumption, and performing the same extrapolation, we obtain microhardness value of infinitely large crystals as $H_c^\infty \approx 511\text{MPa}$ and $b=153\text{\AA}$.

We used in Fig.7. only the l_c value for the copolymers with a PC_c content less than 50%. The samples with higher PC_c concentration do not show any discrete long spacing. Hence, the occurrence in these samples of wide angle X-ray diffraction maxima could be explained by the absence of crystal stacks of minimum size as to give coherently diffracting domains.

Conclusions

The microhardness of amorphous PBT/ PC_c block copolymers can be explained in terms of a simple additive parallel model of two independent components. Physical aging, after several months, induces a significant hardening of the samples. Upon annealing, the hardness of the random copolymers increases owing to the reinforcing contribution of the developing crystalline regions. Composition, crystal thickness and surface free energy play an important role in determining the final hardness value and can be quantitatively accounted for.

Acknowledgements

The authors acknowledge DGICYT (Grant PB94-0049), Spain, for the generous support of this investigation. One of us (L.Giri) thanks the Ministerio de Educación y Ciencia, Spain, for the tenure of a grant. The authors wish also to thank Prof. Phillip H. Geil for his valuable comments and suggestions.

References

- [1] N.R. Lesse, G. Holden and H.E. Schroeder, eds. *Thermoplastic Elastomers, A Comprehensive Review*, Hanser Publishers, Munich, 1987.
- [2] F.S. Bates and G.H. Fredrickson, *Annu. Rev. Phys. Chem.* **41**, 525 (1990).
- [3] S. Fakirov, A. Apostolov, P. Boeseke and H.G. Zachmann, *J. Macromol. Sci.-Phys.*, **B29(4)**, 379 (1990).
- [4] Z. Roslaniec, *Polymer*, **33**, 1717 (1992).
- [5] Z. Roslaniec, *Polymer*, **34**, 1249 (1993).
- [6] Z. Roslaniec, *Polymer*, **34**, 359 (1993).
- [7] G. Wegner, *Thermoplastic Elastomers, A Comprehensive Review*, N.R. Lesse, G. Holden, and H.E. Schroeder, eds., Hanser Publishers, Munich, 1987, p.405.
- [8] Z. Roslaniec and H. Wojcikiewicz, *Polimery*, **33**, 360 (1988).
- [9] Z. Roslaniec, *Polimery*, **37**, 328 (1992).
- [10] Z. Roslaniec, T.A. Ezquerra and F.J. Baltá-Calleja, *Colloid & Polym. Sci.*, **273**, 58 (1995).
- [11] J.L. Castles, M.A. Vallance, J.M. McKenna and S.L. Cooper, *J. Polym. Sci., Polym. Phys.*, **23**, 2119 (1985).
- [12] F.J. Baltá-Calleja and C.G. Vonk, *X-ray Scattering of Synthetic Polymers*, A.D. Jenkins, ed., Elsevier, Amsterdam, 1989, p.89.
- [13] F.J. Baltá-Calleja, *Trends in Polymer Science*, **2(12)**, 419 (1994).
- [14] F.J. Baltá-Calleja and H.G. Kilian, *Colloid Polym. Sci.*, **263**, 697 (1985).
- [15] F.J. Baltá-Calleja and H.G. Kilian, *Integration of Fundamental Polymer Science and Technology*, L.A. Kleintjens and P.J. Lemstra, eds., Elsevier Applied, London, 1986, p.517.

Figure Captions

- Fig.1. WAXS patterns of the PBT/PC_c (80/20) copolymer:
after quenching (bottom) and after annealing at 100°C for 30 minutes (top).
- Fig.2. WAXS patterns of the investigated copolymers after annealing in the temperature range 100-130°C for 30 minutes.
- Fig.3. Plot of the (010) and (100) spacings of the PBT α -form as a function of PC_c concentration.
- Fig.4. DSC (2ndrun) scans for the copolymers investigated.
- Fig.5. Plot of microhardness vs composition for freshly prepared amorphous (H_a^{fresh}) physically aged (H_a^{aged}) semicrystalline (H) and fully crystalline (H_c) PBT/PC_c copolymers.
- Fig.6. Plot of $\Delta H = H_a^{\text{sample}} - H_a^{\text{PBT}}$ vs $\Delta T = T_g - T$.
- Fig.7. Plot of $1/H_c$ vs $1/l_c$.

TABLE 1

PBT/PC _c	T _g (°C)	Crystallinity* α	Long period L (Å)	Crystal thickness l _c (Å)	H (MPa)	H _c (MPa)
100/0	48	0.28 ₅	150	43	149	287
95/5	45	0.23 ₀	--	--	125	226
80/20	37	0.17 ₇	85	15	112	178
70/30	44	0.18 ₅	98	18	119	204
60/40	56	0.16 ₈	170	29	125	241
50/50	47	0.17 ₉	--	--	123	212
40/60	52	0.16 ₀	--	--	134	284

* This value is referred to the total PBT and PC amorphous content.

Fig. 4

Fig. 2.

Fig. 3

Fig 6