JOURNAL OF MATERIALS SCIENCE 27 (1992) 2161–2164

Mechanical properties and structure of glassy and semicrystalline random copolymers of poly(ethylene terephthalate) and poly(ethylene naphthalene-2,6-dicarboxilate)

C. SANTA CRUZ, F. J. BALTÁ CALLEJA
Instituto de Estructura de la Materia CSIC Serrano 119, 28006 Madrid, Spain
H. G. ZACHMANN, D. CHEN
Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstraße 45, 2000 Hamburg 13, Germany

The microhardness, H, of random copolymers of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene-2,6-dicarboxilate) (PEN) was determined over a wide range of compositions. It is shown that microhardness of the materials is strongly affected by the composition. The mechanical property, H, of the quenched amorphous copolyester films is discussed in terms of a simple model given by the additivity values of the single components H_a^{PET} and H_a^{PEN}. In materials containing up to 30% PEN, crystals of PET are found after annealing at temperatures 10 °C below their melting points. In materials containing $\sim$ 80% PEN, after annealing at about 20 °C below the melting point, crystals of PEN are formed. The observed deviation of H for the crystallized films from the additive behaviour of the single components can be quantitatively related to two factors: the changes occurring in the crystallinity value and in the thickness of PET and PEN crystals.

1. Introduction

Random copolymers of poly(ethylene terephthalate), p-hydroxybenzoic acid (PET/PHB) and poly(ethylene naphthalene-2,6-dicarboxilate) p-hydroxybenzoic acid (PEN/PHB) form thermotropic liquid crystalline melts if their content of PHB exceeds 30% [1]. In the PEN/PHB copolyesters containing up to 50% PHB, crystals of PEN are formed, whereas in systems containing 80%–90% PHB, crystals of PHB are found. The mechanical properties of these materials have been investigated as a function of composition using the microhardness, H, technique [2]. It is well known that hardness is directly related to the macroscopic mechanical properties of the materials [3–5]. The mechanical behaviour has been interpreted in the light of several microstructural parameters, including the thickness of the crystals, polymorphic crystal forms and the fraction of crystalline content [2]. In the case of quenched glassy copolyesters containing PHB, we postulated the additivity of microhardness for the two single components. PHB and its copolymers containing more than 50% PHB could not, however, be solidified in the fully amorphous form [1]. For the crystallized samples of PET/PHB and PEN/PHB it was shown that the microhardness of the PET and PEN crystals was an increasing function of the crystal thickness [2]. On the other hand, for high concentrations of rigid PHB units, the samples always crystallize and the material shows a hardness increase which is proportional to the PHB content.

In the present paper a mechanical study of copolyesters of PET/PEN, both copolymer units having flexible chain segments and lacking a liquid-crystalline behaviour, is described. All the range of PET/PEN copolymers could, therefore, be prepared in the amorphous state. Results of a study of the influence of composition and molecular structure on the microhardness value will be presented.

2. Experimental procedure

Samples of random PET/PEN having 10%, 20%, 30%, 50%, 80% and 100% PEN mole composition were synthesized in our laboratory [6]. Amorphous films were obtained by melt pressing above the melting point and quenching in ice–water. The samples were crystallized by annealing the glassy materials at the temperatures shown in Table I. The degree of crystallinity was calculated from the amorphous density measured on quenched samples and from the crystal density derived from the crystal unit cell. Small-angle X-ray scattering (SAXS) patterns were obtained with a Kratky compact camera. Scattering was measured in overlapping angular regions of $0.013\ \text{nm}^{-1} < s < 0.1\ \text{nm}^{-1}$ and $0.08\ \text{nm}^{-1} < s$ with slit heights of 60 and 130 μm, respectively. The

0022–2461

TABLE I Experimental values for the density of quenched and crystallized materials, temperatures at which the materials were crystallized and crystallinity derived from density

PET/PEN	ρ_{quench} (g cm^{-3})	ρ_{cryst} (g cm^{-3})	T_c (°C)	α
100/0	1.3373	1.4081	240	0.49
90/10	1.3351	1.3747	230	0.25
80/20	1.3343	1.3614	210	0.17
70/30	1.3320	1.3389	210	0.05
50/50	1.3310	–	200	–
40/60	1.3305	–	200	–
20/80	1.3279	1.3525	220	0.31
0/100	1.3281	1.3565	220	0.39

scattering curves for the homopolymers, PET and PEN, and for the copolymers with 90/10 and 20/80 PET/PEN compositions are shown in Fig. 1. The rest of the samples did not show any discrete SAXS maxima. Fig. 1 also shows, as an example, the scattering curve for the material with 40/60 PET/PEN composition. The correlation function method [7] was used to determine the long period, L, the crystal thickness, l_c, and the linear crystallinity, $\alpha_L = l_c/L$. Fig. 2 shows the corresponding correlation functions for the samples of Fig. 1. From the depth of the correlation function in the first minimum, the product $\alpha_L(1 - \alpha_L)$ can be determined where α_L represents the crystallinity within the regions in which crystallites are alternated by amorphous layers. This value is larger than the crystallinity, α, determined from macroscopic density because in addition to the amorphous layers between the crystals, larger amorphous regions outside of the crystallite-amorphous layers may be present. The value of $L/2$ is derived from the position of the first minimum in the correlation curve.

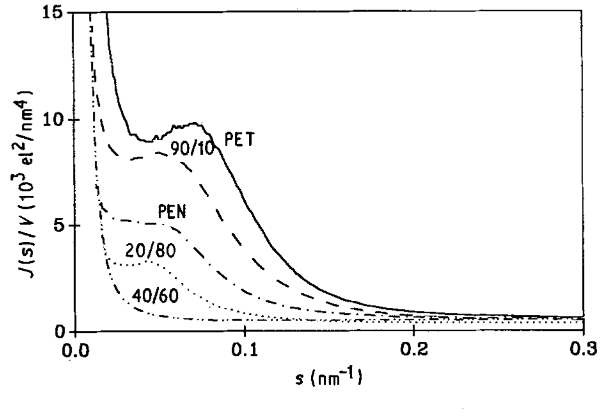

Figure 1 X-ray small-angle scattering intensity as a function of the scattering vector for different investigated copolyesters.

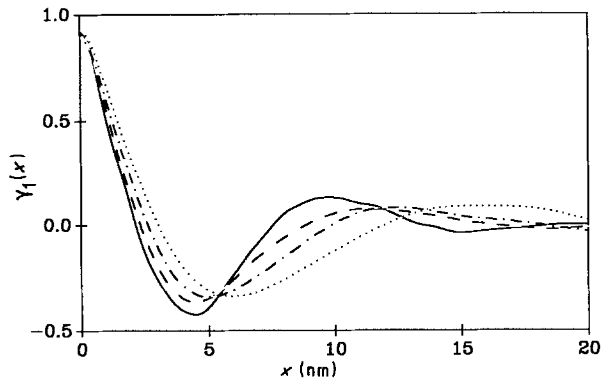

Figure 2 Correlation functions for the crystalline samples of Fig. 1. (——) PET, (– – –) 90/10, (···) 20/80, (—·—) PEN.

Microhardness was determined using a Vickers tester. The hardness (Pa) is given by

$$H = kP/d^2 \tag{1}$$

where P is the force (N), d the diagonal length of the indentation (m) and k a geometrical factor equal to 1.854. Loads of 0.15, 0.25, 0.5 and 1 N were used to correct for instant elastic recovery. To minimize the creep of the material surface under the indentor, a loading cycle of 0.1 min was chosen.

3. Results and discussion

The whole series of PET/PEN copolyesters is completely amorphous when quenched from the melt as revealed by the WAXS patterns. However, when annealed at high temperature, some of the samples are capable of crystallizing. Fig. 3 illustrates the wide-angle X-ray diffraction patterns of the annealed copolyester series as a function of composition. For the samples containing from 0–30 mol % PEN, the PET sequences crystallize while the PEN segments remain in the amorphous regions. On the contrary, in the samples containing 80% and 100% PEN, the PEN sequences crystallize in the α-polymorphic form [1]. The PET segments are excluded here in the non-crystalline regions. Only the samples containing 50% and 60% PEN (the latter is not shown in Fig. 3), annealed at high temperature, do not crystallize.

Table I collects the experimental values for the density of quenched and crystallized materials, the temperature at which the samples were crystallized, and the crystallinity values derived from density.

Fig. 4 shows the variation of the microhardness of the quenched amorphous samples, H_a, and that of the

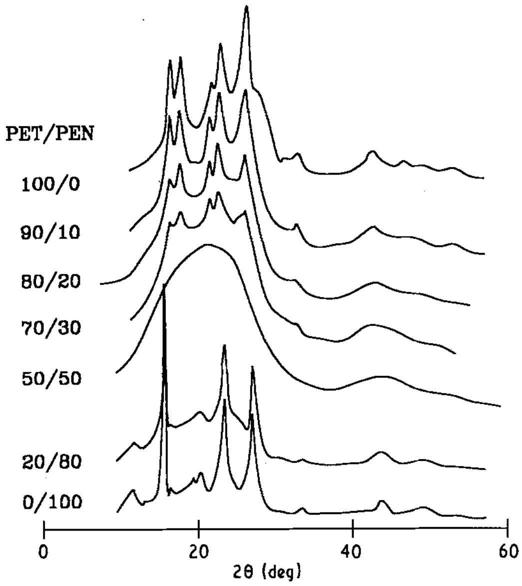

Figure 3 Wide-angle X-ray diffraction patterns as a function of scattering angle for some of the investigated samples.

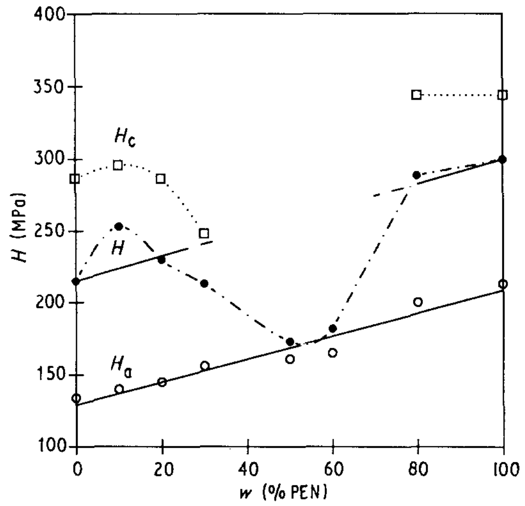

Figure 4 Experimental microhardness values as a function of PEN mole content for the quenched materials, H_a, annealed samples, H. The crystal hardness value, H_c, was derived using Equation 3.

TABLE II Experimental values for the long period, crystal thickness, linear crystallinity and crystal hardness for the copolymers as a function of composition

PET/PEN	L (nm)	l_c (nm)	α_L	H_c(MPa)
100/0	9.0	5.0	0.60	287
90/10	9.0	6.5	0.72	296
80/20	–	(5.0)[a]	–	(287)[b]
70/30	–	(3.6)[a]	–	(248)[b]
20/80	12.0	7.4	0.62	344
0/100	10.5	7.3	0.69	341

[a] Values derived from the breadth of the $(0\bar{1}1)$ and (0 1 0) WAXS reflections.

[b] Values calculated using Equation 4.

crystallized samples, H, as a function of PEN content. It is seen that H_a linearly increases with the increasing concentration of PET units, w_{PET}, according to the predictions of a mechanical parallel model

$$H_a = H_a^{\mathrm{PET}} w_{\mathrm{PET}} + H_a^{\mathrm{PEN}} w_{\mathrm{PEN}} \qquad (2)$$

where w_{PEN} is the total concentration of PEN units within the copolymer. The larger values of H shown in Fig. 4 for the crystallized samples are related either to the presence of PET (left) or PEN (right) crystals. When the concentration of PET units prevails, the probability for bundles of PET sequences to agglomerate forming crystallites also increases. On the other hand, if the concentration of PEN segments is larger, then, the probability of these sequences to pack in the form of crystalline aggregates is also larger. Larger crystallinity and crystal thickness values consequently give rise to larger H values.

In addition, the hardness of the crystals, H_c, was calculated using the additivity relation of crystalline and amorphous hardness values [8, 9] for the PET/PEN compositions 100/0, 90/10, 20/80 and 0/100

$$H = H_c \alpha_L + H_a(1 - \alpha_L) \qquad (3)$$

where $\alpha_L = l_c/L$ represents the so-called linear crystallinity. Equation 3 has been shown to apply for PET samples crystallized at different temperatures and times of crystallization [10].

The values of H_c obtained are collected in Table II. It is noteworthy that the materials with the 80/20 and 70/30 PET/PEN compositions do not show any SAXS maxima. However, these copolyesters present a well-defined semicrystalline WAXS pattern (see Fig. 3). These results suggest the presence of a very small proportion (0.17 and 0.05 volume fraction) of crystallites which do not form diffracting units and which are embedded in a predominantly amorphous matrix. Hence, for these compositions we have derived the crystal thickness values, l_c, of these coherently diffracting domains along the [0 0 1] direction, from the analysis of the integral width of the $(0\bar{1}1)$ and (0 1 0) wide-angle reflections. The l_c values obtained are collected in Table II. For the 20/80 and 0/100 PET/PEN compositions, the H_c values are nearly the same, because the PEN crystal thicknesses and crystallinities, α_L, in both cases are very similar. On the other hand, the H_c value for the copolyester with the 90/10 PET/PEN composition is slightly larger than that for the 100/0 PET/PEN composition, due to the smaller PET crystal thickness of the latter.

In order to calculate H_c values for the materials with the 80/20 and 70/30 PET/PEN compositions it is necessary to use the dependence of H_c on l_c which has been derived in previous studies [8]

$$H_c = H_c^{\infty}/(1 + b/l_c) \qquad (4)$$

where $H_c^{\infty} = 380$ MPa is the hardness value for the infinitely large PET crystals and $b = 1.9$ nm is a parameter which characterizes the hardness depression from H_c^{∞} due to the finite thickness of the crystals [2]. We have recently shown that b is related to the ratio of the surface free energy to the enthalpy for plastic deformation of the crystals [11]. The use of Equation 4 yields the H_c values quoted in Table II. It is worth noting that all the H_c and l_c values obtained for PET and PEN crystals contained within these copolyesters fit the predictions of Equation 4 found for PET and PEN crystallites the PET/PHB and PEN/PHB copolyesters [2] using the above-mentioned H_c^{∞} and b values for PET and $H_c^{\infty} = 820$ MPa and $b = 6.0$ nm values for PEN.

In conclusion, while in the case of PHB copolymers, samples with a high concentration of PHB units could not be quenched into the amorphous state, in the present flexible copolyesters, glassy amorphous materials can be produced over the whole range of compositions. In the case of the amorphous PET/PEN copolymers the microhardness for the whole range of compositions follows a simple additive behaviour. Similarly to the results obtained in PET/PHB and PEN/PHB systems, the annealed samples show the lowest microhardness values for concentrations near 50%. This finding is consistent with the fact that, even after annealing, the samples are always amorphous at these compositions. If, however, one increases either the PEN or the PET content, microhardness will always increase due to the hardening contribution of the developing crystalline regions. The influence of crystal thickness, crystallinity and the hardness of the crystals can be quantitatively accounted for.

Acknowledgements

The authors thank the internationales Büro, Kernforschunganlage, Karlsruhe, and CSIC, Madrid, for the generous support of this Cooperation Project. Grateful acknowledgement is also due to CICYT, Spain, for the support of this investigation (grant MAT88-0159). One of us (HGZ) thanks the Secretaria de Estado de Universidades e Investigación, Spain, for the tenure of the Humboldt-Mutis Price during part of this work.

References

1. S. BUCHNER, D. CHEN, R. GEHRKE and H. G. ZACHMANN *Molec. Cryst. Liq. Cryst.* **155** (1988) 357.
2. F. J. BALTÁ CALLEJA, C. SANTA CRUZ, D. CHEN and H. G. ZACHMANN *Polymer*, in press.
3. F. J. BALTÁ CALLEJA, *Adv. Polym. Sci.* **66** (1985) 117
4. B. DARLIX, B. MONASSE and P. MONTMITONNET, *Polym. Test.* **6** (1986) 107.
5. B. MARTÍN, J. M. PEREÑA, J. M. PASTOR and J. A. de SAJA, *J. Mater. Sci. Lett.* **5** (1986) 1027.
6. D. CHEN, PhD thesis, University of Hamburg (1990).
7. G. R. STROBL and M. J. SCHNEIDER, *J. Polym. Sci.* **18** (1980) 1343.
8. F. J. BALTÁ CALLEJA and H. G. KILIAN, *Colloid Polym. Sci.* **266** (1988) 29.
9. *Idem, ibid.* **263** (1985) 697.
10. C. SANTA CRUZ, F. J. BALTÁ CALLEJA, H. G. ZACHMANN, N. STRIBECK and T. ASANO, *J. Polym. Sci., Polym. Phys.* **29** (1991) 819
11. F. J. BALTÁ CALLEJA, C. SANTA CRUZ, R. K. BAYER and H. G. KILIAN *Colloid Polym. Sci.* **268** (1990) 440.

Received 7 January
and accepted 13 May 1991