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New aspects of the microstructure of glassy PET/PEN blends as revealed by microhardness

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The microhardness of films of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) blends prepared by co-precipitation from solution followed by melt-pressing and quenching was determined. The miscibility, transesterification and crystallization properties of these blended films were reported previously [1]. The PET/PEN compositions chosen were 10/90, 30/70, 44/56, 60/40, 70/30 and 90/10. The microhardness of films was notably affected by the composition. It is shown that the deviation of microhardness from the additivity law of the single components depends on the time for which the blend was melt-pressed before quenching in ice water. The results are discussed in light of changes occurring from the initial two-phase structure of the single components through the one-phase structure up to the PET-co-PEN obtained by transesterification of the two components.

1. Introduction

The crystallization behaviour and the physical ageing of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) has been extensively investigated by means of microhardness studies [2, 3, 4, 5]. Microindentation involving a mechanical deformation on a small scale is one of the simplest methods of determining the microhardness of a material [6, 7]. Microhardness, H, is, in addition, a technique which offers a direct information on microstructural changes in polymers [8, 9, 10]. This technique has also been shown to be a promising method for the microstructure investigation of polymer blends and can provide information on the degree of interpenetration of the blend components [11].

We have previously studied the microhardness–structure correlation of glassy random copolymers of PET and PEN [12]. It was shown that the micromechanical properties of these materials are strongly affected by the composition and by the crystallization conditions of the single components [12]. The crystallization behaviour of both materials is well known [13, 14, 15, 16]. The microhardness of the quenched amorphous copolyesters was discussed in terms of the additivity law of the single components. After cold crystallization the deviation of the microhardness of the aged material from the additive behaviour of the single components could be described by the changes occurring in the crystallinity and the crystal thickness of the PET and PEN crystals [12].

Previous studies on blends of PET and PEN indicate that the thermal behaviour of the blends strongly depends on the time during compression moulding (t_m) before quenching the films in ice water [1]. For t_m values between 0.2 and 0.5 min two glass transition (T_g) values were observed by means of dynamic mechanical analysis, indicating the presence of two phases, an amorphous PEN-rich phase and an amorphous PET-rich phase. For t_m in the range of 2 to 45 min only a single value of T_g and, consequently, a single phase is found to exist. Within this time range transesterification of the two compounds also takes place resulting in a copolyester of PET and PEN.

The aim of the present work is to examine the variation of the mechanical properties (microhardness) of these PET/PEN blends as a function of, both composition and melt pressing time t_m. In particular it is interesting to compare these results with those obtained in the case of random copolyesters of PET and PEN [12].

2. Experimental procedure

PET and PEN were synthesized from ethylene glycol together with dimethyl terephthalate and dimethyl-2,6-naphthalene dicarboxylate, respectively, as described elsewhere [17, 18]. Blends of these starting materials were obtained by coprecipitation from the solution in hexafluoroisopropanol. Amorphous films were, then, obtained from the precipited powder, by melt pressing *in vacuo* for different times t_m, varying from 0.2 min to 45 min followed by quenching in ice water. PET/PEN blends with weight compositions 90/10, 70/30, 60/40, 44/56, 30/70, and 10/90 were prepared.

Microhardness was determined at room temperature using a based square diamond tester. The test uses a squared pyramidal diamond with included angles $\tau = 136°$ between the non-adjacent faces of the pyramid. The H value was derived from the residual projected area of indentation according to the expression $H = 2\sin(\tau/2)P/d^2 = 1.854P/d^2$, where d is the diagonal length of the impression in metres and P the force applied in N. The force is applied at a controlled rate, held for 0.1 min and removed. The length of the impression is measured to ± 1 μm with a microscope equipped with a filar eyepiece. A loading cycle of 0.1 min and loads of 0.5 and 1 N were used.

3. Results and discussion

The PET and PEN blends are completely amorphous after quenching from the melt as revealed by the DSC experiments [1]. Fig. 1 illustrates in detail the variation of the microhardness (H) with melt pressing time t_m for the PET/PEN composition 44/56. Fig. 2 shows the results obtained for the rest of the series of blends. In all cases, H shows first a rapid initial increase with t_m exhibiting a maximum just before $t_m = 10$ min and, then, for longer times, a gradual decrease down to values which can be even lower than the starting ones.

In order to explain the variation of H versus t_m it is convenient to analyse the results of hardness as a function of composition. Fig. 3 shows the experimental values of H as a function of composition, taking t_m as a parameter. It is seen that for $t_m \sim 0.2$ min, H linearly increases with increasing concentration of PEN content according to the prediction of the mechanical parallel model given by

$$H = H_a^{\mathrm{PET}} w_{\mathrm{PET}} + H_a^{\mathrm{PEN}} w_{\mathrm{PEN}} \tag{1}$$

where H_a^{PET} and H_a^{PEN} are the hardness of amorphous PET and PEN and w_{PET} and w_{PEN} are the weight fractions of PET and PEN, respectively. These results indicate that the microhardness of the PET/PEN blends shows similar values as those obtained for PET/PEN amorphous random copolyesters [12]. With increasing t_m up to 10 min one observes a shift of the straight line towards higher values. Finally for $t_m = 45$ min one observes the lowest values of H.

Let us recall that when the melt-pressing time is about 0.2–0.5 min two T_g values are observed, indicating that there are two phases present [1]. In case of $t_m \geqslant 2$ min a single T_g value and, thus, a single phase is found. For $t_m \sim 10$–45 min no crystallization and melting during heating in the differential scanning calorimeter (DSC) at 10 °C min^{-1} is observed, indicating that an amorphous copolyester has been obtained by transesterification of PET and PEN during melt pressing. The first initial increase in hardness up to $t_m = 0.5$ min could be attributed to the corresponding shift of T_g towards higher temperatures. It is known that in the case of amorphous blends temperature is the dominant parameter in determining the yield behaviour of the glassy material [19]. The further increase in H up to $t_m = 2$ min could be associated to the change from a two-phase system into one single amorphous phase composed of interpenetrating molecules of both polymers. Such an homogeneous system should offer a higher mechanical resistance to yield and to plastic deformation. Finally, H increases further up to $t_m \sim 10$ min where the copolyesters of PET and PEN have been formed by transesterification. Fig. 4 illustrates the variation of the viscosity as a function of t_m for the 44/56 blend, showing that no detectable changes in this property are observed.

One may ask at this stage: why does H gradually decrease with increasing t_m if the molecular weight and the viscosity remain practically constant? One possible explanation could be that at the beginning of the transesterification process the copolyester has a rather block-like character. Only after longer times

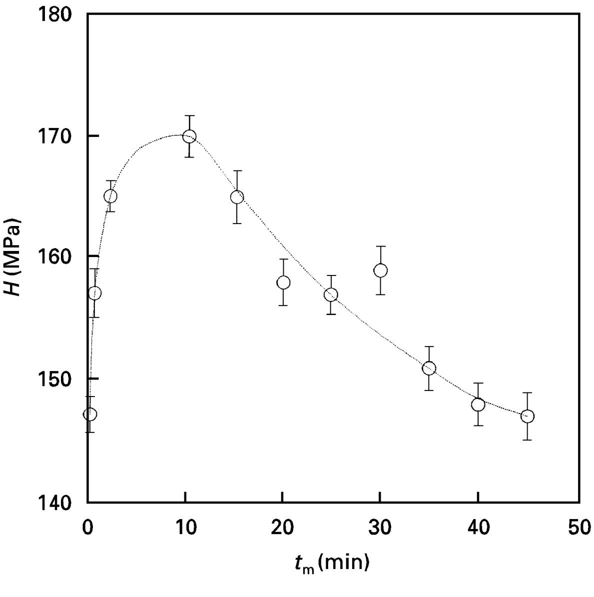

Figure 1 Variation of the microhardness of a PET/PEN (44/56) blend as a function of melt-pressing time.

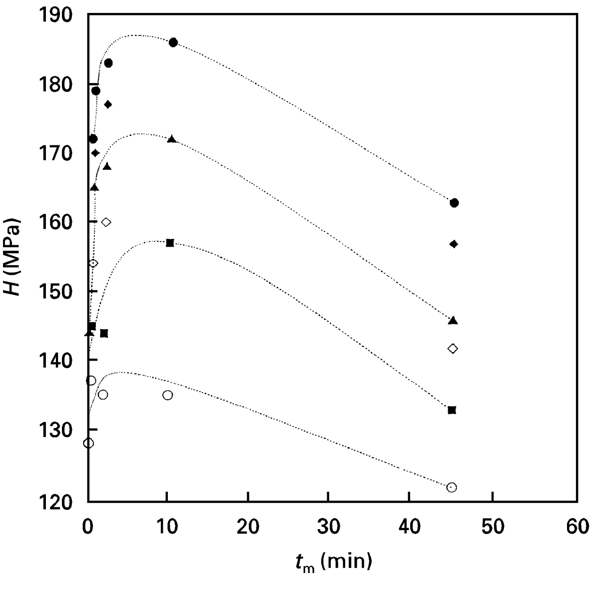

Figure 2 Plot of H versus t_m for different PET/PEN blend compositions. ●, 10/90; ◆, 30/70; ▲, 44/56; ◇, 60/40; ■, 70/30; ○, 90/10.

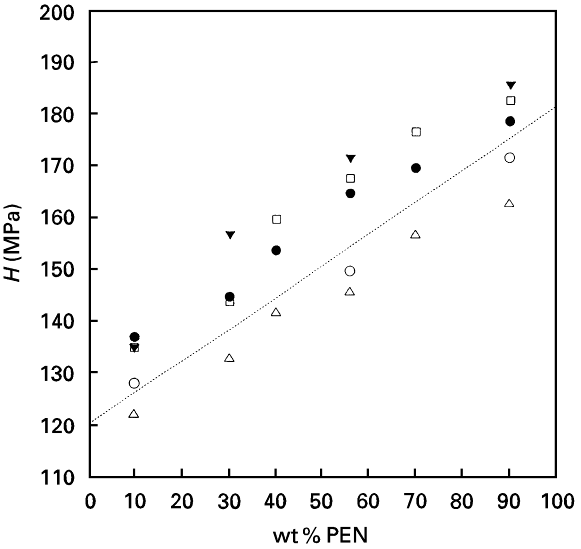

Figure 3 Variation of microhardness as a function of wt % PEN for different melt pressing times (t_m). The dotted straight line follows the additivity predictions of the single components (Equation 1). ○, 0.2 min; ●, 0.5 min; □, 2 min; ▼, 10 min; △, 45 min.

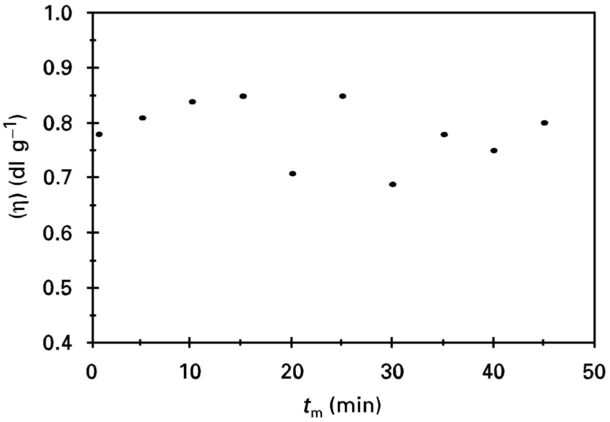

Figure 4 Plot of the viscosity η (dl g^{-1}) of the PET/PEN (44/56) blends as a function of melt-pressing time.

does it become a statistical copolymer. Our results, therefore, indicate that the microhardness of the block copolyester is larger than that of the statistical copolymer. The existence of blocks may lead to a microphase separation between PEN and PET blocks. It seems, then, reasonable to assume that parallely packed sequences of blocks with the same chemical compositions would yield less easily than parallel copolymer sequences of statistical composition.

In conclusion, in order to obtain the optimum mechanical properties of these blends, one should use melt pressing times in the range of 5–10 min. Otherwise, the mechanical properties represented by microhardness can be reduced by 10–15%.

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