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**NEW ASPECTS OF THE MICROSTRUCTURE OF GLASSY PET/PEN BLENDS
AS REVEALED BY MICROHARDNESS**

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Abstract

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 composition 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 2-phase structure of the single components through the one-phase structure up to the PET-co-PEN obtained by transesterification of the two components.

Introduction

The crystallization behaviour and the physical aging 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 with a point indenter involving a mechanical deformation on small scale is one of the simplest methods of determining the microhardness of a material [6,7]. Microhardness, H , is 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 already previously studied the mechanical properties and structure of glassy random copolymers of PET and PEN [12]. It was shown that the mechanical properties of these materials are strongly affected by the composition and by the crystallization of the single components [12]. The crystallization behaviour of both materials is well known [13, 14]. The microhardness of the quenched amorphous copolyesters was discussed in terms of the additivity law of the single components. In semicrystalline copolyesters the deviation of aged material from the additive behaviour was 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 [8]. For t_m values between 0.2 and 0.5 minutes two glass transition (T_g) values were observed by means of dynamical 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 and 45 minutes 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].

Experimental

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 precipitated powder, by melt pressing in vacuo for different times t_m , varying from 0.2min to 45minutes 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 hardness is given by $H=kP/d^2$, where P is the force in Newton, d is the diagonal length of the indentation in meters and $k=1.854$ is a geometrical factor. Loads of 0.5 and 1N and a loading cycle of 6 seconds were used to correct for the elastic recovery.

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 14/56. 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 H-values.

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

$$H = H_a^{PET} w_{PET} + H_a^{PEN} w_{PEN} \quad (1)$$

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 [5]. With increasing t_m up to $t_m \sim 10$ 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 $t_m \geq 2$ 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 DSC instrument at $10^\circ\text{C}/\text{min}$ 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 a 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 deformation. Finally, H increases further up to $t_m \sim 10$ min where the copolyesters of PET and PEN has 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 is the

following one: at the beginning of transesterification the copolyester has a rather block-like character. Only after larger times it becomes a statistical copolymer. Our results, thus, 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 reasonable to assume that parallel sequences of blocks will yield less easily than parallel 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 minutes. Otherwise, the mechanical properties represented by microhardness can be reduced by 10-15%.

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FIGURE CAPTIONS

- Fig. 1 Variation of the microhardness of a PET/PEN (44/56) blend as a function of melt pressing time.
- Fig. 2 Plot of H versus t_m for different PET/PEN blend compositions.
- Fig. 3 Variation of microhardness as a function of weight per cent of PEN for different melt pressing times (t_m). The dotted straight line follows according to equation (1) the additivity predictions of the single components.
- Fig. 4 Plot of the viscosity of the PET/PEN (44/56) blends as a function of melt pressing time.

Fig 1

Fig. 2