

# Cold crystallization studies on PET/PEN blends as revealed by microhardness

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The cold crystallization of amorphous films of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) blends, with different composition, prepared by co-precipitation from solution followed by melt-pressing for 2 min at 280 °C and quenching in ice–water, was followed by measuring the microhardness,  $H$ , in real time as a function of crystallization temperature and time. An analytical model was derived, relating properties of the individual components to the blend microhardness based on an Avrami-type equation to account for the crystallization of the components upon heating. Fitting of the model to the experimental results revealed a two-step hardening process of the blends. The degree of transesterification of the blends, can be estimated with this model. Finally, a removal of the physical ageing, inducing a decrease in  $H$  of PET in the blend, was observed upon heating above its glass transition temperature.

## 1. Introduction

The microhardness of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) relating to the development of crystallinity during crystallization, has been previously investigated [1–4]. A linear relationship was empirically found between the degree of crystallinity of these polyesters and their microhardness,  $H$ . Because the time-dependence of the relative crystallinity of a polymer can often be described by an Avrami equation [5–7], a similar approach was proposed to characterize the microhardness evolution with time of a polymer film [1, 8]

$$H_i = H_{a,i} + (H_i^{\max} - H_{a,i}) [1 - \exp(-Gt_c^n)] \quad (1)$$

where  $H_i^{\max}$  and  $H_{a,i}$  are the microhardness of the fully crystallized and fully amorphous polymer, respectively,  $t_c$  is the crystallization time, and  $G$  and  $n$  are the modified Avrami parameters for microhardness. The parameter,  $G$  is proportional to the number of nuclei per unit volume and the rate of nucleus formation [5].  $G$  is strongly temperature-dependent. The Avrami exponent,  $n$ , is characteristic of the nucleation type and the crystal growth geometry, and may show values ranging from below 1 to above 6. A list of the correspondence between crystallization type and Avrami exponent can be found elsewhere [6]. This correspondence is, however, not uniquely fixed for one single set of conditions. Additional information on nucleation, morphology, and mechanism is needed fully to

interpret the exponent,  $n$ . Furthermore, the value of the Avrami parameters obtained from microhardness data may differ slightly from that obtained from crystal growth analysis, if the relation between the two is not perfectly linear.

Blends of crystallizable aromatic polyesters such as PET and PEN are of high interest because they offer a large range of advanced properties which can be accurately controlled provided the blending mechanisms are well understood. Andresen and Zachmann [9] studied the miscibility, transesterification, and crystallization in blends of PET and PEN. They showed that, depending on the processing conditions, a single phase, consisting of a solution of the two constituents, was first obtained followed by a reaction of transesterification between PET and PEN leading to the formation of a copolyester.

We studied previously the variation of the microhardness measured at room temperature of amorphous PET/PEN copolymers [10] and blends [11] as a function of both composition and melt-pressing time,  $t_m$ . It was observed that, for a given  $t_m$  value, the microhardness measured at room temperature first increased with increasing blending time, then reached a maximum value for processing time ranging between 2 and 10 min, and finally decreased for longer melt-pressing times. These variations of the microhardness were discussed in terms of the variation in microstructure studied by Andresen and Zachmann [9].

At temperatures higher than  $T_g$  of the individual components, these will crystallize with time, thus

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leading to an increase of the microhardness of the blend. The aims of this work were (1) to report the time crystallization dependence of the microhardness of PET/PEN blends, processed in the melt (at 280 °C) for a time  $t_m = 2$  min, as a function of composition and crystallization temperature,  $T_c$ ; (2) to relate the properties of the individual constituents with the microhardness of the blend; and (3) to discuss the influence of the microstructure of the blend on its micro-mechanical properties on the basis of the value of the model parameters used to best fit the experimental results.

## 2. Experimental procedure

### 2.1. Materials

PET and PEN were synthesized in the laboratory of Professor Zachmann, Hamburg, from ethylene glycol, together with dimethyl terephthalate and dimethyl-2,6-naphthalene dicarboxylate, respectively, as described elsewhere [12, 13]. Blends containing different concentrations,  $x_{0,PET}$  and  $x_{0,PEN}$ , of these starting materials were obtained by coprecipitation from the solution in hexafluoroisopropanol. Thin amorphous films of PET/PEN blends were then obtained from the precipitated powder by melt pressing in vacuum at a temperature  $T_m = 280$  °C, during a time  $t_m = 2$  min, followed by quenching in ice–water.

### 2.2. Techniques

Microhardness of the blend films was determined as a function of crystallization time,  $t_c$ , at various temperatures,  $T_c$ . Each film was placed under rotary pump vacuum for 24 h prior to testing, in order to eliminate moisture which considerably affects the microhardness measurements at high temperature [14]. Then, the samples were placed on a hot stage (Mettler FP52) mounted under a microindenter with a square diamond tester (Leitz Durimet) at the testing temperature,  $T_c$ , ranging between 95 and 125 °C for the samples with excess of PET and from 145–175 °C for the films with excess of PEN, as indicated in Table I. The temperature of the film was continuously controlled with a thermocouple placed in a cavity close to the heated surface. The hardness is given by  $H = kF/d^2$ , where  $F$  is the force applied by the indenter,  $d$  is the diagonal length of the indentation, and  $k = 1.854$  in SI units, is a geometrical factor [8]. The microhardness of the heated films was measured as a function of crystallization time,  $t_c$ , until it reached a maximum value,  $H^{max}$ , at which it stabilized.

TABLE I Thermal treatment of the films as a function of PET content

$T_c$ (°C)	$x_{0,PET}$			$T_c$ (°C)	$x_{0,PET}$			
	0.0	0.1	0.3		0.6	0.7	0.9	1.0
145	×	×	×	95			×	
155		×		105	×	×	×	×
165		×		115			×	
175		×		125			×	

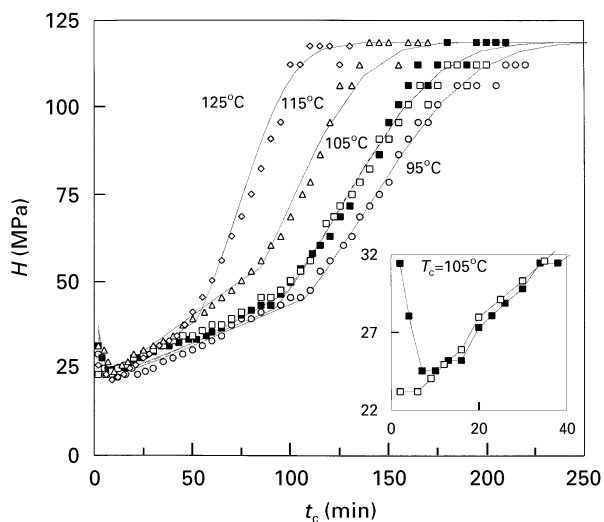


Figure 1 Microhardness,  $H$ , of the blend PET/PEN (90/10) as a function of crystallization time,  $t_c$  for different annealing temperatures,  $T_c$ . Inset: initial stage of the hardening process of (□) a fresh and (■) an aged film measured at  $T_c = 105$  °C.

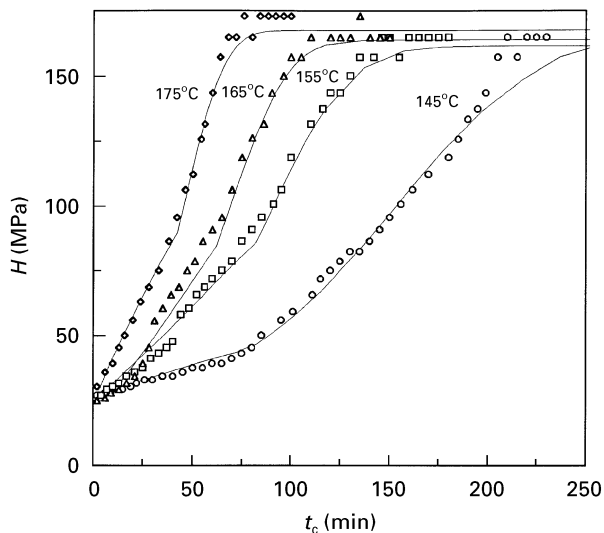


Figure 2 Plot of  $H$  versus  $t_c$  for different  $T_c$  values for the blend PET/PEN (10/90).

## 3. Results

### 3.1. Crystallization kinetics of the single components

The microhardness of a blend with a concentration  $x_{0,PET} = 0.9$  was measured as a function of time,  $t_c$ , at the crystallization temperature  $T_c = 95, 105, 115,$  and  $125$  °C, respectively. Films with concentrations,  $x_{0,PET} = 0.1$ , were measured at temperatures,  $T_c = 145, 155, 165,$  and  $175$  °C, respectively. The results are plotted in Fig. 1 for  $x_{0,PET} = 0.9$  and in Fig. 2 for  $x_{0,PET} = 0.1$ .

In Fig. 1, it is seen that the microhardness of the blends with excess of PET first shows a slight decrease and then it increases continuously until it stabilizes at a maximum value,  $H^{max}$ . The magnitude of the initial drop decreases when the amount of PET present in the blend is low and becomes negligible when the

concentration of PEN exceeds the amount of PET (see Fig. 2). This effect can, therefore, be assigned mainly to PET. We suggest that it results from the physical ageing effect of PET leading to an increase of microhardness, which disappears upon thermal treatment above the  $T_g$  of PET. In order to determine whether these initial high  $H$  values are due to the effect of ageing, a film was heated for 4 min above  $T_g$  (at  $T = 100^\circ\text{C}$ ) and then cooled rapidly. The microhardness of this film measured at room temperature drops from 133.5 MPa to 106.2 MPa before and after the heat treatment. The microhardness measured at the temperature  $T_c = 105^\circ\text{C}$  of the fresh film ( $\square$ ) is compared to an aged sample ( $\blacksquare$ ) in the inset of Fig. 1. It can be seen, indeed, that the initial drop in hardness disappears in the freshly prepared sample.

The subsequent rise in microhardness of the blends in Figs 1 and 2 is due to the crystallization of the pure PET and PEN components, respectively, and follows an Avrami-type Equation 1. For temperatures lower than  $125^\circ\text{C}$  (cf. Fig. 1), i.e. lower or equal to  $T_g$  of PEN, only PET crystallizes, while for temperatures higher than  $145^\circ\text{C}$  (cf. Fig. 2), both PET and PEN crystallize. The hardening rate increases with increasing temperature, as expected in crystallization kinetics-related phenomena. The maximum hardness plateau,  $H^{\max} \cong 118$  MPa, is quasi-independent of  $T_c$  in the range  $95\text{--}125^\circ\text{C}$  (cf. Fig. 1), suggesting that in all cases PET has reached its maximum degree of crystallinity. Similarly, the maximum hardness plateau  $H^{\max} = 165$  MPa for the  $x_{0,\text{PET}} = 0.1$ -blend, is also independent of  $T_c$  in the range  $145\text{--}175^\circ\text{C}$  (cf. Fig. 2). Consequently, we can conclude that the end of each test, both PET and PEN have reached their maximum degree of crystallinity.

### 3.2. Influence of blend composition

The time evolution of the microhardness of polymer films at a crystallization temperature  $T_c = 105^\circ\text{C}$  is shown in Fig. 3 for different PET concentrations:  $x_{0,\text{PET}} = 1.0$  (pure PET), 0.9, and 0.6. It is interesting to note that maximum hardness is obtained for the blend containing 10% PEN (118 MPa), and that the blend containing 40% PEN shows the lowest hardness value (45 MPa), in spite of the fact that pure PEN is harder than PET. This effect can be attributed to the transformation of part of the PEN and PET components initially present into an amorphous transesterified copolyester of lower hardness than PEN [9].

The hardening rate of the films decreases with increasing concentration of the PEN component. This effect is in agreement with the results reported by Andresen and Zachmann [9] that the half-time of crystallization of PET and PEN in the blend is lower than in the pure material. They suggest that this effect could be due to the dilution of PEN by PET which would decrease the rate of formation of the nuclei. In terms of the Avrami Equation 1, which describes the crystallinity-related hardening effect of a single component, this statement can be interpreted as follows: the value of  $G$  should be lower for the blends than for the pure materials, while the Avrami exponent,  $n$ ,

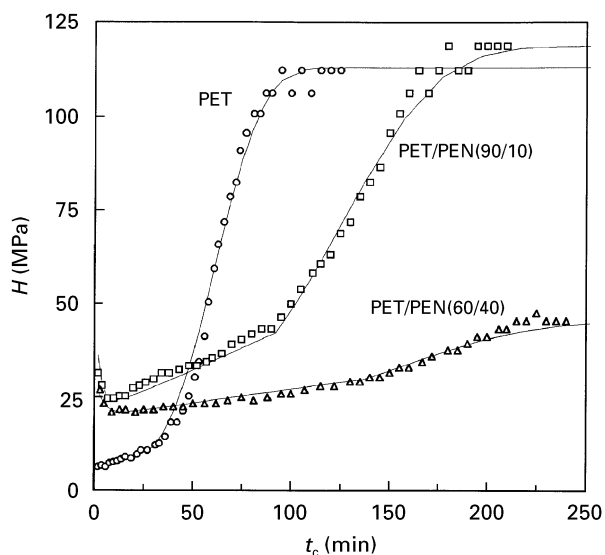


Figure 3 Time-dependence of the microhardness of polymer films at a crystallization temperature  $T_c = 105^\circ\text{C}$  for various PET concentrations.

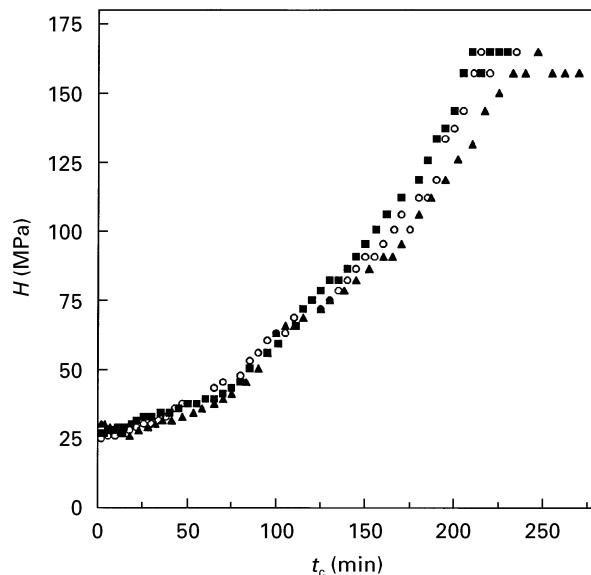


Figure 4 Time-dependence of the microhardness of polymer films at a crystallization temperature  $T_c = 145^\circ\text{C}$  for PEN concentrations: (○) PEN, (■) PET/PEN (10/90), (▲) PET/PEN (30/70).

should remain constant. We will see in the discussion below that our results are partly in agreement with this assumption.

Fig. 4 shows the microhardness of blends with excess of PEN ( $x_{0,\text{PET}} = 0.3, 0.1,$  and  $0.0$  (pure PEN)), at the temperature,  $T_c = 145^\circ\text{C}$ . It can be seen that microhardness is fairly insensitive to PET concentration in the range investigated. At  $T_c = 145^\circ\text{C}$ , both PET and PEN crystallize and the microhardness of the blend is mainly controlled by the PEN component.

### 4. Modelling of the microhardness

In order better to understand the mechanisms involved in the hardening process of the PET/PEN

blends, an analytical model is proposed, putting in relation parameters of the individual components. The assumptions made in the model are as follows.

1. Microhardness is an additive function of the hardness of the individual components present in the blend [10]

$$H = \sum_i x_i H_i \quad (2)$$

where  $x_i$  is the concentration of component  $i$  in the blend with  $i = \text{PET}, \text{PEN}$ . In addition a third component, NT, referring to the transesterified copolyester, has to be introduced.

2. A fraction,  $v$ , of the component of minor nominal concentration,  $x_{0,m}$ , will react with an equal quantity of the other component to form  $2vx_{0,m}$  volume fraction of transesterified polyester. The actual volume fraction of copolyester,  $x_{\text{NT}}$ , and of polyester,  $x_i$  with  $i = \text{PET}, \text{PEN}$  can, thus, be expressed as a function of nominal concentration,  $x_{0,i}$ , as,

$$x_{\text{NT}} = 2vx_{0,m} \quad (3a)$$

$$x_i = x_{0,i} - \frac{1}{2}x_{\text{NT}} \quad (3b)$$

3. The microhardness of a material is related to its degree of crystallinity through an Avrami-type Equation 1 [3].

4. PET and PEN are allowed to crystallize above their respective  $T_g$  (70 °C for PET and 120 °C for PEN) while the transesterified NT copolyester does not crystallize upon heat treatment. Consequently, its microhardness is assumed to be constant throughout the test.

5. Molecular reorganization built up upon heat treatment above  $T_g$  (ageing of PET disappears).

Microhardness of the films can be described by Equation 2. The volume fraction,  $x_i$ , of the different components is defined by Equation 3. The fraction,  $v$ , of the component of minor concentration,  $x_{0,m}$ , which transesterifies with an equal amount of the other com-

ponent  $x_{0,M}$  can be determined by introducing Equation 3 into Equation 2 and rearranging to yield

$$v = \frac{x_{0,m}H_m + x_{0,M}H_M - H}{x_{0,m}(H_M + H_m - 2H_{\text{NT}})} \quad (4)$$

with  $x_{0,M} > x_{0,m}$  and  $H_M$  and  $H_m$  being their respective hardness values. At the end of each test, the degree of crystallinity of each component is known, and the corresponding value of their microhardness, together with the maximum value of the sample hardness, can be introduced into Equation 4 to determine  $v$ .

The value of the hardness parameters in Equation 1,  $H_i^{\text{max}}$  and  $H_{a,i}$  can be determined experimentally on pure PET and PEN (cf. Figs 1 and 2). However, the initial drop of the microhardness of the amorphous PET,  $H_{a,\text{PET}}$  (see Fig. 1), attributed to a molecular reorganization as a result of the removal of the physical ageing, needs to be characterized. We can describe it by an exponential decay

$$H_{a,\text{PET}} = (H_{a,\text{PET}}^{\text{max}} - H_{a,\text{PET}}^{\text{min}}) \exp\left(-\frac{t_c}{\tau}\right) \quad (5)$$

where  $\tau$  is the temperature-dependent reorganization time associated with a molecular redistribution.

In order to determine the values of the Avrami exponent,  $n$ , and the prefactor,  $G$ , of the component  $i$ , Equation 1 can be expressed in the form

$$n \log t_c + \log G = \log \left[ -\ln \left( 1 - \frac{H_i - H_{a,i}}{H_i^{\text{max}} - H_{a,i}} \right) \right] \quad (6)$$

This equation is represented graphically in Fig. 5a for the PET component in a blend of PET concentration 0.9, crystallized at the temperature  $T_c = 105$  °C. The microhardness evolution with time of an individual component  $i$  in the blend can be extracted from the experimental film hardness data by expressing Equation 2 as

$$H_i = \frac{1}{x_i} \left( H - \sum_{j \neq i} x_j H_j \right) \quad (7)$$

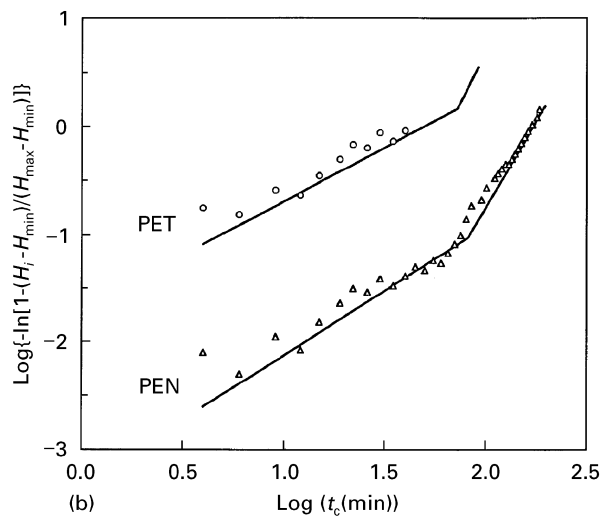
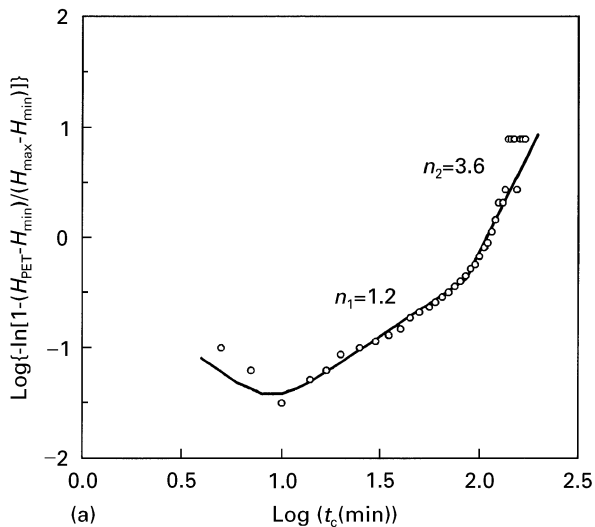


Figure 5 Variation of  $\log [-\ln[1 - (H_i - H_{\text{min}})/(H_{\text{max}} - H_{\text{min}})]]$  versus  $\log t_c$ : (a) for PET in a PET/PEN (90/10) blend crystallized at  $T_c = 115$  °C; and (b) for (○) PET and (△) PEN in a PET/PEN (10/90) blend crystallized at  $T_c = 145$  °C. (—) The model.

At  $T_c = 105^\circ\text{C}$ , PEN remains amorphous and the summation of the right-hand side of Equation 7 is constant during the whole duration of the test. In Fig. 5b, both PET ( $\circ$ ) and PEN ( $\triangle$ ) data, are represented for a  $x_{0,\text{PET}} = 0.1$  for the blend crystallized at  $T_c = 145^\circ\text{C}$  in the same plot. Note that the determination of the Avrami parameters for PET in Fig. 5b is quite difficult, because hardness of the compound is mainly controlled by PEN.

In Fig. 5 one clearly sees that, after the first exponential drop due to the molecular reorganization in PET, the material hardens following two different regimes, with two distinct slopes,  $n_1$  and  $n_2$ . In view of this result, which can be generalized to all the samples tested in this work, Equation 1 should be written as

$$H_i = H_{a,i} + (H_i^{\max} - H_{a,i})[1 - \exp(-G_k t_c^{n_k})] \quad (8)$$

with  $k = 1, 2$  and  $G_1 = G_2 t_{c1 \rightarrow 2}^{(n_2 - n_1)}$

where  $t_{c1 \rightarrow 2}$  is the time at which the change in hardening kinetics takes place. Similarly,  $G$  and  $n$  should be replaced by  $G_k$  and  $n_k$ , respectively, in Equation 6.

## 5. Discussion

The predictions of the model (—) are compared to the experimental hardness data in Figs 1–3 and 5. In all cases, the model is in good agreement with the measured data. The microhardness value of the various components needed for the computation (Equations 2, 5, and 8) were determined from experimental data of pure PET and PEN (cf. Figs 1 and 2) and are listed in Table II. These values were kept constant for all the experimental conditions ( $x_{0,i}$ ,  $T_c$ ) tested.

The concentration,  $x_i$ , of the various components was determined by introducing the value of  $v$  calculated from Equation 4 into Equation 3; the result is shown in Table III. The fraction of transesterified copolyester depends only on the blending conditions,  $T_m$  and  $t_m$ , and the concentration,  $x_{0,i}$  of the various components, and is independent of the crystallization temperature,  $T_c$ . It increases with increasing degree of blending from  $v = 0.01$ – $0.04$  for  $x_{0,i} = 0.1$  to  $v = 0.93$  for  $x_{0,\text{PET}} = 0.6$ . For a given blend composition,

TABLE II Microhardness value of the individual components

Parameter	PET	PEN	NT
$H_{a,i}^{\min}$ (MPa)	6	25 (180 <sup>a</sup> )	22
$H_{a,i}^{\max}$ (MPa)	60	–	–
$H_i^{\max}$ (MPa)	113	170 (177 <sup>b</sup> )	–

<sup>a</sup>For  $T_c \leq T_g$  (PEN).

<sup>b</sup>For  $T_c = 175^\circ\text{C}$ .

TABLE III Concentration of the various components in the blend

$x_{0,\text{PET}}$	0.0	0.1	0.3	0.6	0.7	0.9	1.0
$v$	–	0.013	0.040	0.927	0.363	0.040	–
$x_{\text{PET}}$	–	0.099	0.288	0.229	0.591	0.896	1.000
$x_{\text{PEN}}$	1.000	0.889	0.688	0.029	0.191	0.096	–
$x_{\text{NT}}$	–	0.002	0.024	0.742	0.218	0.008	–

a higher degree of transesterification was calculated for the films with excess of PET (i.e.  $x_{0,\text{PET}} > x_{0,\text{PEN}}$ ).

Andresen and Zachmann [9] suggest that after transesterification, a single phase is formed. These authors showed that after  $t_m = 2$  min at  $T_m = 280^\circ\text{C}$ , dilution of PEN and PET components was completed and that a single-phase copolyester is formed. They concluded that a certain degree of transesterification was expected after 2 min processing but were not able to quantify it. Their DSC results showed that after  $t_m = 2$  min, the melting peak of PEN had disappeared in blend of  $x_{0,\text{PET}} = 0.6$  and  $0.7$ , suggesting that most PEN had transesterified (i.e. high  $v$ ), while the blends containing  $x_{0,\text{PET}} = 0.3$  clearly showed the melting peak of both PET and PEN indicating a lower value of  $v$ , in good quantitative agreement with our results.

The exponential decay (Equation 5) used to characterize the initial drop of the amorphous PET microhardness allows the relaxation time,  $\tau$ , to be determined as a function of temperature. It can be determined with most accuracy in the  $x_{0,\text{PET}} = 0.9$  blend, decreasing, as expected, with increasing temperature, from  $\tau = 3$  min at  $95^\circ\text{C}$  to  $2.2$  min at  $125^\circ\text{C}$ .

Table IV lists the Avrami parameters used to fit the experimental microhardness data. Two hardening regimes can clearly be identified in Fig. 5, characterized by two distinct slopes  $n_1$  and  $n_2$ . The blends crystallized between  $95$  and  $125^\circ\text{C}$  (i.e.  $x_{0,\text{PET}} > x_{0,\text{PEN}}$ ) show a value of the Avrami exponent for the hardening of PET,  $n_1 = 1.2$  and  $n_2 = 3.6$  independent of  $T_c$  and PET content. The values of  $G_1$  and  $G_2$  increase with  $T_c$  as expected from the conclusions of Andresen and Zachmann [9] discussed above.

At crystallization temperatures above  $125^\circ\text{C}$ , both PET and PEN crystallize. The determination of the Avrami parameters for PET is shown to be less accurate – and in some cases could not be determined – than at lower temperatures because the blend microhardness was mainly controlled by PEN for two reasons: (i) the blends tested between  $145$  and  $175^\circ\text{C}$  contained more PEN than PET, i.e.  $x_{0,\text{PEN}} > x_{0,\text{PET}}$  (cf. Table I), and (ii) PEN is harder than PET. The exponents,  $n_1 = 1.2$  and  $n_2 = 3.6$ , were obtained for PET, and a two-stage hardening process of PEN could be characterized by the Avrami exponents,  $n_1 = 1.5$  and  $n_2 = 3.2$  for  $x_{0,\text{PET}} = 0.1$ , and  $n_2 = 5.2$  for pure PEN and for  $x_{0,\text{PET}} = 0.3$ . Again,  $G_1$  and  $G_2$  increase with crystallization temperature.

If the hardening rate of the blends is linearly related to the crystallization kinetics, then the value of the Avrami exponents can be related to the crystal-growth geometry. The low value of  $n_1 = 1.2$ – $1.5$  followed by an increase of the exponent,  $n_2 = 3.2$ – $5.2$  for both

TABLE IV Avrami parameters for microhardness

$T$ (°C)	$X_{0,PET}$	0.0		0.1			0.3		0.6		0.7		0.9		1.0	
		145	145	155	165	175	145	105	105	95	105	115	125	105		
PET	$G_1 \times 10^3$	–	11.5	40.6	<sup>a</sup>	<sup>a</sup>	3.14	0.1	0.6	1.0	1.0	2.0	1.8	0.9		
	$n_1$	–	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2		
	$G_2 \times 10^8$	–	40.0	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	8.0	0.8	3.5	1.4	2.0	4.7	14	26.0		
	$n_2$	–	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6		
PEN	$G_1 \times 10^2$	0.12	0.4	0.7	1.1	2.0	0.2	–	–	–	–	–	–	–		
	$n_1$	1.5	1.5	1.5	1.5	1.5	1.5	–	–	–	–	–	–	–		
	$G_2 \times 10^8$	$2 \times 10^{-4}$	7.0	40.0	90.0	400	$2 \times 10^{-4}$	–	–	–	–	–	–	–		
	$n_2$	5.2	3.2	3.2	3.2	3.2	5.2	–	–	–	–	–	–	–		

<sup>a</sup>Cannot be determined with enough accuracy.

PET and PEN, suggests that the crystals present a branching fibrillar geometry [6]. In such geometry, the once-nucleated fibrillar crystals branch into other fibres after having grown to a given length. This branching process leads to a sheaf-like structure and eventually a spherulite is formed. In agreement with these views, the appearance of sheaf-like bundles of lamellae in the first states of cold crystallization of PEN and the final development of dendritic structures, has been recently observed using electron microscopy [15].

## 6. Conclusions

1. The variation of microhardness of glassy PET/PEN blends has been characterized as a function of composition and cold crystallization temperature in the 95–175 °C range.

2. For PET rich samples,  $H$  shows first a decrease after a few minutes of annealing (molecular reorganization as a result of removal of physical ageing) and then it rises sharply (crystallization of PET for  $T_c < T_{g,PEN}$ ) for longer annealing times.

3. For PEN-rich samples,  $H$  shows a gradual increase with annealing time (crystallization of PEN component).

4. Two different slopes can be distinguished for the component in excess in the Avrami plots, which is evidence of the occurrence of two distinct hardening kinetics mechanisms.

5. A model has been developed which allows the degree of transesterification within the blend to be estimated.

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