Elastic properties of oriented polymers, blends and reinforced composites using the microindentation technique

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Abstract The elastic behaviour of poly(ethylene terephthalate) (PET) and nylon 6 (PA6), their blends (1:1 by weight) and microfibrillar-reinforced composites (MFC) of the above mentioned homopolymers has been investigated by means of load-displacement analysis from indentation experiments. The dependence of the elastic modulus of the homopolymers upon the degree of crystallinity and the crystal size, as derived from indentation experiments, is discussed. A linear correlation between the elastic modulus anisotropy and the microindentation hardness anisotropy values is found to sustain for the oriented materials. Results reveal that the indentation modulus values of the PET/PA6 blends follow the parallel additivity model of the individual components. The use of the additivity law is also shown to furnish a value, otherwise not accessible from direct measurements, of the modulus of the microfibrils within the microfibrillar-reinforced composites.

Key words PET, PA6, blends, microfibrillar-reinforced composites, microindentation hardness, elastic modulus, additivity law

Column title: Elastic properties of oriented PET/PA6 blends

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Introduction

In the last years a number of studies concerning the elastic properties of several materials using indentation techniques has been reported [1-8]. The use of modern ultramicrohardness devices enables a continuous load-displacement monitoring as the indenter is driven into and out of the investigated surface of the samples [1, 2]. The slope of the unloading curves is regarded as a measure of the elastic properties of the studied materials. Several methods have been proposed for the calculation of Young's modulus values from indentation depth-sensing curves [1-3]. The majority of the above cited studies deal with the elastic modulus of inorganic materials: metals, ceramics or oxide films. Studies on organic materials are exclusively devoted to neat polymers [3, 4, 7, 8]. The influence of polymer microstructure (crystallinity, crystal size, etc) on the elastic modulus of poly(ethylene terephthalate) (PET), as derived from indentation experiments, has been the object of a recent report [9]. The aim of the present study is to extend the above investigations to other oriented polymers, polymer blends and composites.

A new type of polymer composites, namely microfibrillar-reinforced composites (MFC's), has been lately developed [10-12]. The processing of MFC's is substantially different from conventional macrocomposites. In MFC's, both components are initially blended and subsequently drawn. During the drawing process, microfibrils are created, which act as a reinforcement to the polymer matrix [10]. Additional annealing of the composite above the melting temperature of the lower melting component produces the isotropization of the polymer matrix while the oriented microfibrillar structure is preserved. Furthermore, during the annealing

treatment, a copolymer phase is formed at the microfibrils' interfaces, thus, ensuring a good adhesion between the microfibrils and the surrounding matrix [13].

The structure development during the different processing stages of PET/PA6 MFC's has been followed by X-ray scattering and microhardness techniques [13]. The PET microfibrils are shown to notably enhance the mechanical properties of the PA6 matrix. The above study highlights the capability of the microindentation hardness technique to reveal the micromechanical properties of the microfibrils which are, otherwise, not accessible from direct measurements.

In the present study we wish : i) to examine the correlations between polymer microstructure and the elastic modulus derived from microindentation, E , in oriented polymer systems (PET, nylon 6); ii) to ascertain whether an additivity relation holds for the indentation E -modulus of polymer blends (PET/nylon 6) and iii) to investigate the elastic properties of the microfibrils in the microfibrillar reinforced composites.

Experimental

Materials

The polymers used were poly(ethylene terephthalate) (PET) (Goodyear Merge 1934F, $M_n = 23.400$ g/mol) and polyamide 6 (PA6) (Allied Signal Capron 8200, $M_n = 20.600$ g/mol). These polymers were ground to a particle size of less than 0.4 mm (after cooling in liquid nitrogen) and subsequently mixed in the solid state (1:1 wt/wt). Quenched films of the blend and of the respective homopolymers, of thickness 0.10–0.13 mm and width 4–5 mm, were prepared according to the procedure

described in reference 13. X-ray scattering and DSC measurements of all the quenched samples revealed an amorphous isotropic structure for PET while the PA6 and PET/PA6 samples were shown to develop partial crystallinity.

Quenched samples of both, homopolymers and blends, were subjected to a drawing process as described in reference 13, followed by an annealing treatment in vacuum with fixed ends at 220°C or 240°C for 5 h or 25 h. The sample preparation conditions are given in Table 1. The structure and morphology of the samples were characterized by means of X-ray diffraction, DSC and SEM measurements [13]. The blends subjected to the highest annealing temperature (B-D-3 and B-D-4) present a microfibrillar reinforced composite (MFC) structure [13].

Technique and Calculation Procedure

For the indentation experiments with continuous load-displacement monitoring during loading and unloading an ultramicrohardness tester, type Shimadzu DUH-202, was used. The measurements were performed at room temperature with a Vickers indenter, i.e. a square-based diamond pyramid.

A peak load of 147mN was reached at a loading rate of 13.2 mN/s. After a holding time of 6 seconds, the load was released at the same constant velocity as in the loading cycle. For each E -value 5-10 measurements were averaged.

As an example, figure 1 shows a typical load-displacement curve for an oriented PET sample. The reduced modulus E^* , also known as indentation modulus [14], was derived by the procedure proposed in reference 2, according to the equation:

$$E^* = \left(\frac{\pi}{A} \right)^{1/2} \frac{S}{2} \quad (1)$$

where $S = \partial P / \partial h$ is the initial unloading stiffness (see figure 1) and $A = 24.5 h_c^2$ is the projected area of contact at maximum load between the indenter and the sample.

The elastic modulus E is related to the reduced modulus E^* through the equation:

$$E = E^* (1 - \nu^2) \quad (2)$$

where ν is the Poisson's ratio for the material tested. We have assumed $\nu = 0.3$ for the amorphous samples and $\nu = 0.35$ for the semicrystalline ones [15].

The contact depth h_c is derived using the following equation:

$$h_c = h_p + (1 - \varepsilon)(h_{max} - h_p) \quad (3)$$

where h_p is calculated from the intercept of the initial unloading slope with the displacement axis (as shown in figure 1), h_{max} is the maximum displacement reached by the indenter and ε is a constant dependent on the indenter geometry. In our case an ε value of 0.72 was chosen, which corresponds to a conical geometry. Furthermore, the method uses a power law relationship to describe the unloading curves:

$$P = \alpha (h - h_f)^n \quad (4)$$

where P is the load at a given penetration depth h , and the α , h_f and n constants are determined by a least-squares fitting procedure. The initial unloading stiffness S was found by analytically differentiating equation 4 and evaluating the derivative at the maximum load and displacement.

To minimize the error on the determination of the true zero of indentation depth, the experimental loading curve was fitted to a power law function of the type:

$$P = m(h - h_o)^{n'} \quad (5)$$

where m is a material constant, n' is the index of the deformation and h_0 is the true zero point.

Results and discussion

Table 2 summarizes the reduced E^* modulus values obtained according to equation 1, the elastic modulus values calculated using equation 2 and the Young's modulus values E_T derived from the stress-strain curves of previous tensile measurements [13]. Figure 2 illustrates the evolution of E^* for blend samples prepared at various stages of the MFC processing (see Table 1). Values for the homopolymers are also included for comparison. In all cases, there is a tendency for the E^* values to increase after the various processing stages, i. e., orientation and increase of temperature and annealing time. This result is a consequence of the specific structure developed at each processing stage. An attempt is made below to independently evaluate the influence of some of the morphological parameters upon E^* .

Influence of microstructure on the elastic modulus

Degree of crystallinity

In addition to the elastic modulus, the degree of crystallinity w_c , from DSC and the crystal size of PA6 D_{200} , from WAXS, as taken from reference 13 are collected in table 2.

Figure 3 presents the variation of E^* as a function of w_c^{PET} , for the oriented homopolymer PET. The E^* values measured on other oriented PET samples with the same draw ratio are also included [9]. From the extrapolation of the linear dependence, an E^* -value for the amorphous oriented PET (drawn at $\lambda = 4$) of 2.3 GPa can be estimated. This value is within the range of E^* recently measured on other amorphous oriented PET samples with a similar draw ratio [9].

Crystal size

In contrast to PET, the w_c values of PA6 remain practically constant (around 30%) irrespective of the preparation conditions. However, PA6 shows a clear increase in the crystal size (table 2) both, upon drawing and further thermal treatment (see table 1). This finding opens up the possibility to evaluate the influence of the crystal size on the indentation modulus. Figure 4 illustrates the clear dependence of E^* upon $1/D_{200}$ for PA6. The extrapolation of the straight line for $1/D_{200} = 0$ yields an E^* value of 3.8 GPa. This value would correspond to a 30% crystallinity system consisting of infinitely large crystals. Hence, an ideal fully crystalline PA6 made of infinite large crystals should have a maximum E^* value of about $E^{*\infty} = 12$ GPa. This value is analogous to the ideal microhardness value of infinitely thick crystals [16].

E – H correlation

Table 2 also includes the microhardness, H , and the indentation anisotropy values, ΔH , obtained in a preceding study [13]. Microindentation hardness measurements

were performed using a square-based diamond. H and ΔH values were derived from the diagonal of the residual impression after load release. Due to sample orientation, two different diagonal values, $d_{\parallel}$ and $d_{\perp}$, the impression diagonals parallel and perpendicular to the draw axis respectively emerged. Indentation anisotropy is defined as [16]:

$$\Delta H = 1 - (d_{\parallel} / d_{\perp})^2 \quad (6)$$

Figure 5 depicts the relation between the E -values, evaluated from microindentation measurements, and the H values taken from table 2. It is known that the E/H ratio offers a convenient measure of the plastic to elastic contribution to the total indentation depth [17]. A first order regression fit to the $E-H$ values gives different slopes for the homopolymers, the blends and the composites. The slope for the oriented blends ($E/H = 17$) lies between the slopes of the PET ($E/H = 16$) and PA6 ($E/H = 19$) homopolymers. In other words, PA6 exhibits a markedly plastic character, as compared to PET. It is noteworthy that the microfibrillar composites (open squares) present, for a similar microhardness value as that of the blends, the highest E values (largest E/H ratio).

Anisotropy of elastic behaviour

The E values for oriented samples, as derived from indentation measurements, appear to be significantly lower than the E_T values obtained from tensile tests (see table 2). This result is a consequence of the different loading directions during both kind of testing. While in the tensile tests the load was applied along the draw direction, in the indentation tests the load is perpendicular to this direction. It is well known that

oriented polymers exhibit a mechanical anisotropy due to the different cohesive forces along and across the chain direction [18].

On the other hand, results show that the E values for the quenched isotropic homopolymers are larger than the corresponding E_T values (see table 2). This is a well known observation, which has been explained in terms of the hydrostatic component of stress which enhances the E compressive values in isotropic polymers [19].

As E and E_T reflect the elastic properties perpendicular and parallel to the draw direction respectively, we have attempted to examine the possible correlation between the E_T/E ratio and the microhardness anisotropy ΔH . Indeed, figure 6 shows an apparent linear dependence for the PET homopolymer (continuous line), as well as for the blends and composites (dotted line). It seems that oriented PA6 (solid triangles) follows the trend of PET (solid circles) (the deviation of the data point for $E_T/E = 1$ is probably due to an uncertainty in the E_T value measurement). The plot of figure 6 could be relevant from a practical point of view, as it may allow a rapid evaluation of the elastic behaviour anisotropy in oriented polymers using the microhardness technique. However, one may expect that the $E_T/E - \Delta H$ slope in figure 6 could change with the strain rate used in the tensile experiment [20].

Additivity law for the elastic modulus derived from microindentation

Mechanical properties of complex polymer systems frequently follow additive relationships with respect to the constituting components. Several theoretical approximations have been developed to predict the modulus of two-phase blends [18].

The parallel and the series models present the two simplest lines of approach. The former case assumes that each component undergoes the same strain, with the stresses being summed up:

$$E = \varphi_1 E_1 + \varphi_2 E_2 \quad (7)$$

The latter case assumes a summation of strains for each component subjected to the same stress:

$$\frac{1}{E} = \frac{\varphi_1}{E_1} + \frac{\varphi_2}{E_2} \quad (8)$$

In addition, there are other models which take into account the influence of the adhesion and the morphology of the components on the elastic properties of the blends and composites [18, 21]. Scanning electron micrographs of MFC and drawn blends reveal a nearly perfect alignment of the microfibrils in the draw direction [13] and a good adhesion between the microfibrils and the matrix in the former. We have attempted to apply one of the commonly used models to the above oriented systems: the Halpin-Tsai equations, for which the transverse modulus of the blend is described in terms of the constituents through [21]:

$$E = E_m \frac{1 + \xi \eta V_f}{1 - \eta V_f} \quad (9)$$

$$\eta = \frac{E_f/E_m - 1}{E_f/E_m + \xi} \quad (10)$$

where E_m and E_f are the elastic moduli of the matrix and the reinforcing fibres (PA6 and PET respectively); V_f is the volume fraction of the fibre, being equal to φ_1 in equations 7 and 8 and ξ is a measure of the degree of interfacial adhesion between fibre and matrix and of other morphological details.

Blends

Table 3 summarizes the experimental and calculated E^* values, according to the above models, for the studied blends ($\varphi_1 = \varphi_2 = 0.5$). To derive the calculated data, the E^* values of the components of the blend were approximated to those of the respective homopolymer samples (see table 2). In addition, we assumed a perfect interfacial adhesion in equations 9 and 10 ($\xi = 2$). To take into account the differences in w_c and D_{200} between the blend components and the homopolymers, we have derived E^* from the plots of figures 3 and 4 when appropriate. The results obtained are collected in figure 7. Except for the first sample (B-Q), the three models fit reasonably well to the experimental values. This result could be a consequence of the similar mechanical properties of the matrix and the fibres, in contrast to other common composites (glass-fibre reinforced epoxy resins, etc) where the difference in the mechanical properties of the constituents is large.

For the isotropic blend B-Q, the calculated values are shown to be smaller than the measured ones. This deviation is a result of the different degree of crystallinity of the PET component within the blend (about 17%) with respect to the w_c^{PET} value of the corresponding unoriented homopolymer (4%). In this case, the above correction could not be performed, because the E - w_c^{PET} relationship of figure 3 refers to oriented systems.

The small difference between the parallel and the series model could be related to the specific morphology of the microfibrils which have been shown to form an interpenetrating mesh along the orientation direction [13]. During an indentation cycle, the randomly interpenetrated microfibrillar mesh is plastically deformed under

the influence of a compressive force, presumably yielding a complex series-parallel mechanical response.

Microfibrillar reinforced Composites

Reinforcing microfibrils in the MFC's samples (B-D-3 and B-D-4) are formed during the drawing process of the PET/PA6 blends [11, 12]. Since a direct evaluation of the elastic modulus of the microfibrils is not feasible, as they are not available as separate entities, the microindentation technique offers a possible route for the evaluation of their elastic properties.

In the preceding section, we have shown that the E^* modulus of the blends can be calculated by means of various additive models of the elastic moduli of the individual components. In what follows, let us use the simplest model, i. e., the parallel model. This behaviour is analogous to the microhardness additivity law for polymer blends [13, 16, 22]. Hence, equation 7 would describe the E^* values for the different components of the MFC sample, treated at the highest annealing temperature for the longest time (sample B-D-4). Due to the chemical transreactions taking place between the PET and the PA6 molecular segments [23], the morphology of the microfibrillar composite can be approximated to a three-phase system consisting of an amorphous PA6 matrix, an amorphous PET/PA6 copolymer matrix and almost fully crystalline microfibrils. Thus, we can rewrite equation 7 as follows:

$$E_{MFC}^* = 0.5(E_a^{*PA} + (1 - w_c^{PET})E_a^{*PET} + w_c^{PET}E_f^{*PET}) \quad (11)$$

where $w_c^{PET} = 0.75$ (see table 2), E_{MFC}^* denotes the experimental reduced elastic modulus of the composite ($E_{MFC}^* = 4.2$ GPa), E_a^{*PA} refers to the reduced modulus of the PA6 amorphous matrix, E_a^{*PET} corresponds to the modulus of amorphous PET ($E_a^{*PET} = 2.3$ GPa) (see figure 3) and E_f^{*PET} is the elastic modulus of the microfibrils. Equation 11 assumes an additivity law for the microhardness of the PET/PA6 copolymer amorphous domains. Let us now estimate the E_a^{*PA} value from the $E-H$ dependence shown in figure 5. It has been shown that the hardness of an amorphous PA6 sample is of $H_a^{PA} \approx 50$ MPa [13]. This hardness value would yield a corresponding modulus value of approximately $E_a^{*PA} = 1.08$ MPa (see figure 5). Using equation 11, with $E_a^{*PA} = 1.08$ MPa together with the above mentioned modulus values for the different components of the microfibrillar composite, a value of $E_f^{*PET} = 8.9$ GPa is derived. This result is in good agreement with the high H -values and reflects the high degree of crystallinity of the microfibrils reported in our preceding study [13].

Conclusions

1. The microindentation technique has been successfully applied for the evaluation of the elastic properties of PET and PA6 neat polymers, their blends and composite-like structures of these materials.

2. E^* modulus values of oriented PET samples are shown to be largely influenced by the degree of crystallinity within the samples.
3. A clear dependence of the E^* modulus on the crystal size D_{200} for PA6 samples with similar degree of crystallinity has been found.
4. A correlation between modulus anisotropy and microhardness anisotropy in the above PET and PA6-based oriented polymers has been derived.
5. The indentation elastic modulus of PET/PA6 blends is shown, for the first time, to follow an additive relationship of the individual components.
6. The use of the E^* -additivity law in microfibrillar-reinforced composites permits the evaluation of the modulus of the microfibrils, otherwise not accessible from direct measurements.

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Figure captions

Fig. 1 Load versus displacement recorded during an indentation cycle on oriented PET.

Fig. 2 E^* values after the various stages for the MFC processing (see table 1). 1st column: neat PET, 2nd column: neat PA6, 3rd column: blend.

Fig. 3 Plot of E^* versus the degree of crystallinity for oriented PET. Solid squares are taken from ref. 9.

Fig. 4 Plot of E^* versus reciprocal crystal size $1/D_{200}$ for PA6.

Fig. 5 Plot of E versus H for oriented: ● PET; ▲ PA6; ■ blends and □ composites

Fig. 6 Correlation between E_T/E and microindentation anisotropy ΔH in oriented: ● PET; ▲ PA6; □ blends and composites

Fig. 7 Experimental E^* values for the PET/PA6 blends (first column) and calculated E^* values according to: the parallel model (second column); the series model (third column) and the Halpin-Tsai equations (fourth column).

Table 1 Sample preparation conditions

Sample designation	Composition PET/PA6 (wt/wt)	Zone drawing		Annealing in vacuum with fixed ends	
		Temperature °C	Draw ratio (λ)	T _a (°C)	t _a (h)
PET-Q	100/0	-	-	-	-
PET-D	100/0	85	4.0	-	-
PET-D-1	100/0	85	4.0	220	5
PET-D-2	100/0	85	4.0	220	25
PET-D-4	100/0	85	4.0	240	25
PA-Q	0/100	-	-	-	-
PA-D	0/100	180	3.8	-	-
PA-D-1	0/100	180	3.8	220	5
PA-D-2	0/100	180	3.8	220	25
B-Q	50/50	-	-	-	-
B-D	50/50	180	4.2	-	-
B-D-1	50/50	180	4.2	220	5
B-D-2	50/50	180	4.2	220	25
B-D-3	50/50	180	4.2	240	5
B-D-4	50/50	180	4.2	240	25

Table 2 Reduced modulus, E^* , derived from microindentation measurements; elastic modulus, $E=E^*(1-\nu^2)$; Young's modulus, E_T , from tensile testing; degree of crystallinity, w_c ; crystal size of PA6, D_{200} ; microhardness, H ; and microindentation anisotropy, ΔH .

Sample	E^* [GPa]	E [GPa]	E_T [GPa]	w_c (DSC)	D_{200} [nm]	H [MPa]	ΔH [%]
PET-Q	3.35 ± 0.07	3.05 ± 0.06	1.1	0.04		134	0
PET-D	2.6 ± 0.1	2.30 ± 0.07	9.4	0.10		147	34.0
PET-D-1	3.43 ± 0.08	3.01 ± 0.06	10.6	0.44		194	25.3
PET-D-2	4.04 ± 0.08	3.54 ± 0.06	11.4	0.49		216	22.4
PET-D-4	4.4 ± 0.1	3.8 ± 0.1	9.5	0.48		240	15.1
PA-Q	1.76 ± 0.04	1.54 ± 0.03	0.2	0.28	3.3	117	0
PA-D	2.5 ± 0.1	2.2 ± 0.1	4.5	0.32	4.1	126	10.8
PA-D-1	3.2 ± 0.1	2.8 ± 0.1	4.8	0.35	9.7	133	7.3
PA-D-2	2.87 ± 0.04	2.73 ± 0.03	2.7	0.31	10.6	150	5.0
				PET			
B-Q	2.8 ± 0.1	2.47 ± 0.08	-	0.17	-	131	0
B-D	3.1 ± 0.1	2.73 ± 0.08	8.8	0.39	3.7	152	27.0
B-D-1	3.32 ± 0.05	2.91 ± 0.01	9.3	0.46	8.3	170	19.0
B-D-2	3.4 ± 0.1	3.0 ± 0.1	9.8	0.48	8.6	172	20.7
B-D-3	4.1 ± 0.1	3.6 ± 0.1	7.8	0.53	12.2	175	6.5
B-D-4	4.2 ± 0.1	3.6 ± 0.1	8.6	0.75	0	177	4.3
				PA6			

Table 3 Measured and calculated E^* values, according to equations 7, 8 and 9.

Sample	E^*_{meas} [GPa]	E^*_{parallel} [GPa]	E^*_{series} [GPa]	$E^*_{\text{Halpin-Tsai}}$ [GPa]
B-Q	2.81 ± 0.15	2.56	2.31	2.45
B-D	3.12 ± 0.11	3.09	2.98	3.05
B-D-1	3.32 ± 0.05	3.32	3.31	3.32
B-D-2	3.44 ± 0.13	3.45	3.35	3.42

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig. 6

Fig. 7