JOURNAL OF MATERIALS SCIENCE 19 (1984) 2615–2621

Anisotropy of ultra-high modulus polymers drawn through a die

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The influence of processing conditions on the microhardness of ultra-oriented linear polyethylene (LPE) and polyoxymethylene (POM) produced by drawing the material through a heated conical die has been examined. After indentation with a square-based diamond the die-drawn rods exhibit an anisotropic impression which can be related primarily to a local elastic recovery of the material surface parallel to the fibre axis. It is found that the microindentation anisotropy ΔMH is a unique function of the actual draw ratio achieved, which depends on the drawing speed. A correlation between ΔMH and elastic modulus has also been found. These results confirm that the changes in structure with increasing draw ratio increase the elastic stiffness and improve the recovery behaviour. These changes in structure involve an increase in the number of taut tie molecules or intercrystalline bridges which leads to the increased modulus, and also produce a more effective oriented molecular network which gives rise to improved recovery behaviour. The $MH_{\perp}/E$ ratio shows for these die drawn materials values $\leqslant 10^{-2}$ which are in the vicinity of those obtained for steel. The fibril orientation is partially destroyed at the die walls through friction effects giving rise to an anisotropy value at the surface which is smaller than that within the core of the die-drawn fibres. Finally the present data also emphasize the influence of the die dimensions on the anisotropy value.

1. Introduction

Indentation hardness of oriented polymers is a useful method for obtaining a direct measure of the anisotropy developed within the fibrous material [1]. Indentation anisotropy, ΔMH, arises as a consequence of high molecular orientation within highly parallel fibrils and microfibrils coupled with preferential local elastic recovery of these rigid structures during unloading. In the oriented polymer, resistance to local deformation emerges from the combination of intrinsic fibril stiffness and efficient longitudinal packing of elastic fibrils and microfibrils which are sheared and bent under the stress field of the indenter. Several materials have been studied to date. These include cold-drawn [2], high pressure oriented chain-extended [3], solid state extruded [4] (ultra-oriented), flow crystallized [5] and injection moulded [6] polymers. In these systems ΔMH, which offers a measure of preferential chain axis orientation, has been shown to be an increasing function of draw ratio R_A [1]. The concurrent increase of longitudinal elastic modulus with R_A in drawn polymers [7], on the other hand, has been attributed to an increasing number of taut tie molecules or intercrystalline bridges connecting crystal blocks and adjacent microfibrils which are the main contributor to the longitudinal mechanical stiffness of fibres [8].

In the present study we extend the above studies and report recent microhardness experiments performed on oriented linear polyethylene (PE) and polyoxymethylene (POM) by drawing them through a conical die. This has been shown to be a successful technique for the production of highly oriented thermoplastic polymer rods [9].

0022–2461/84 $03.00 + .12

TABLE I Polymer grade, melt flow index (MFI) and number and average molecular weight of the materials investigated

Polymer grade	MFI	$Mn \times 10^{-4}$	$M_w \times 10^{-4}$
PE 002/47	0.17	2.17	16.65
PE 002/55	0.15	1.69	15.5
PE 006/60	0.6	2.55	13.5
POM (D500)	2.5–5	4.5	9.0

A linear correlation between ΔMH and the longitudinal elastic modulus is derived for the first time. In addition, the influence of the processing method and the polymer used on the correlation obtained with the anisotropy illuminates the value of the microhardness technique.

2. Experimental details

2.1. Materials and preparation

The melt flow index and average molecular weights of the POM and the grades of PE investigated are given in Table I. Series of rods with a different actual drawn ratio, R_A, for each grade of polymer were prepared by die-drawing [10, 11]. In this technique a billet of chosen diameter, d_0, to give a nominal draw ratio, R_N, is pulled out through a conical die by means of a coaxial force at a given temperature, T_d, and at a drawing speed, v_f. A conical die with a semi-angle of 15° and an exit diameter d_1, of 4 mm was used. In the case of PE 006/60 the exit diameter was 15.5 mm. For a given $R_N = (d_0/d_1)^2$ and temperature T_d the actual draw ratio achieved $R_A = (d_0/d_f)^2$ is a function of v_f. The die-drawing conditions and the values of R_A obtained for the rods are collected in Table II. The isochronous (10 sec) Young's modulus was measured at 20° C using a dead-loading three-point bend test. The maximum strain in the test was kept to less that 10^{-3} and precautions were taken to obviate end effects due to anisotropy of the rods [12]. Thus samples with a length/diameter ratio $\geqslant 25$ were tested. E values for POM and PE are also included in Table II.

2.2. Microhardness measurements

Microhardness measurements were carried out

TABLE II Processing conditions (die temperature T_d, die-drawing speed v_f nominal [R_N] and actual [R_A] draw ratios) and mechanical properties (longitudinal elastic modulus E; and microindentation anistotropy ΔMH at the surface) for the rods investigated

Material	T_d (° C)	R_N	v_f(mm min^{-1})	R_A	E(GPa)	ΔMH(%)
POM (D500)				1		0.0
	150	4		2.6		
	150	4	10	4.9	7.8	11.7
	150	4	20	5.2	7.9	15.6
	150	4	40	5.9	8.4	16.3
	150	4	60	6.6	10.6	19.5
	150	4	120	8.7	14.0	17.6
	150	4	200	10.7	18.8	26.0
	150	4	250	11.3	20.4	23.0
PE 002/47				1		0.0
	100	5	50	5.6	5.3	23.4
	100	6.5	140	7.7	7.6	25.0
	100	8	160	9.5	10.5	31.3
	100	6.5	–	12.5	–	29.9
PE 002/55				1		0.0
	100	5	20	5.7	4.9	17.7
	100	5	220	9.8	10.0	30.9
	100	8	69	10.1	8.2	22.7
	100	10	10	10.5	13.0	30.8
	115	5	220	10.8	11.2	26.3
	100	8	100	11.5	15.2	36.1
PE 006/60				1		0.0
	100	4	10	4.7	9.7	22.1
	100	6	20	7.8	14.6	27.7
	100	8	20	10.7	22.1	32.1
	100	8	30	14.2	32.9	34.4
	100	10	22	19.5	42.5	36.0

at room temperature ($T \sim 22^\circ$ C) with a Leitz hardness tester using a 100 μm height square pyramid diamond. The measurement of the indentation diagonals was made to within $\pm$ 0.5 μm using a micrometer in conjunction with a microscope. Loads of 0.05 and 0.1 kg and a loading time of 20 sec were used. A series of 6 to 10 indentations were made for each sample. Long delayed recovery was minimized by measuring the final permanent deformation immediately after load release. The hardness value (in GPa) was calculated by dividing the peak contact load of impression (in kg), P, by the square of the values of the indentation diagonals (in μm) parallel, $l_\parallel$, and normal, $l_\perp$, to the fibre axis. A proportionality constant of 18 180 was used. The die-drawn rods were aligned on the microscope to obtain indentations with diagonals parallel, $l_\parallel$, and perpendicular, $l_\perp$, to the rod axis. Special care was taken to locate the indentation just on the upper surface of the rod. A geometrical correction taking into account the cylindrical curvature of the rods [13] was applied in order to obtain the $MH_\perp$ value from:

$$l_\perp^c = l_\perp + \tfrac{7}{2}\,[d_f - (d_f^2 - l_\perp^2)^2].$$

The real microindentation anisotropy is defined as $\Delta MH = 1 - (l_\parallel / l_\perp^c)^2$. MH measurements were also carried out on the inner section of the rods after longitudinal cleavage, particularly for the three PE grades. The smoothness of the inner cleaved surface of the rods allowed the derivation of even more accurate and easily obtained MH and ΔMH data than those obtained on the outer surface. In these experiments ΔMH is calculated directly using the uncorrected $l_\perp$ value. ΔMH values at the surface are given in Table II.

3. Results

The hardness for the isotropic POM sample ($MH \sim$ 0.17 GPa) is nearly three times larger than that for PE ($MH \sim$ 0.06 GPa). Die-drawing of the samples results in a clear hardening of the material. Perhaps the main feature of the die-drawn samples is the anisotropy exhibited by the indentation pattern. The apparent derived hardness value is highest when the indentation diagonal is parallel to the fibre direction and lowest when normal to it. Previous work shows that the former value is not a real measure of hardness but corresponds to an elastic recovery of the material in the draw direction. The latter value on the other hand, defines the plastic component of the hardness value. Fig 1 illustrates the clear increase in $MH_\parallel$ and $MH_\perp$ for PE 002/55 and POM as a function of the actual draw ratio. The plastic component ($MH_\perp$) increases at the same rate with R_A for both polymers whereas the elastic component shows a faster increase with R_A for POM than for PE. The anisotropy for a given R_A is, however, larger for PE than for POM. Lamellar orientation has fully developed for $R_A \simeq 5$, as revealed by small-angle X-ray diffraction (SAXD) [14]. Thus POM with $R_A = 2.6$ exhibits MH values lying in between the isotropic and the uniaxial oriented POM.

In order to investigate a possible differences between the outer surface and the core, MH measurements were carried out on the inner surface of the rods after cleaving them longitudinally. The smooth flat surfaces obtained allowed reliable data of MH and ΔMH to be collected. Fig. 2 shows MH data obtained from the core (open symbols) for PE 002/47 and PE 006/60. In this case the draw ratio range was expanded up to values of $R_A \sim 20$. MH data from the outer surface are also given for comparison. A good linearity of $MH_\parallel$ from the core through the R_A range investigated is observed while a levelling off tendency for high R_A values is observed for $MH_\parallel$ from the outer surface. It is noted that $MH_\parallel$ at the core is slightly higher than $MH_\parallel$ at the outer surface. This difference is particularly noticeable for PE 002/47, and also occurs for PE 002/55.

Most revealing is the clear linear increase of ΔMH measured at the core with elastic modulus E for two PE samples (Fig. 3). For POM the ΔMH data which are more scattered were measured at the surface due to the inherent inhomogeneity of the cleaved samples. A lower increase of ΔMH with E is observed here.

In Fig. 4, ΔMH values obtained from the core against R_A are drawn. Straight lines with slopes 1.7% and 2.9% can be drawn for PE 006/60 and PE 002/47, respectively. The dotted line corresponds to previously data obtained for hydrostatically extruded PE [1, 13].

Fig. 5 represents the $MH_\perp$ values obtained for the three PE grades against R_A. Here there is a segregation of data according to the polymer grade. For a given R_A value the highest $MH_\perp$ value corresponds to PE 006/60 and the lowest one to PE 002/47. As regards the $MH_\perp$ values, for $R_A = 1$ they obviously depend on the billet

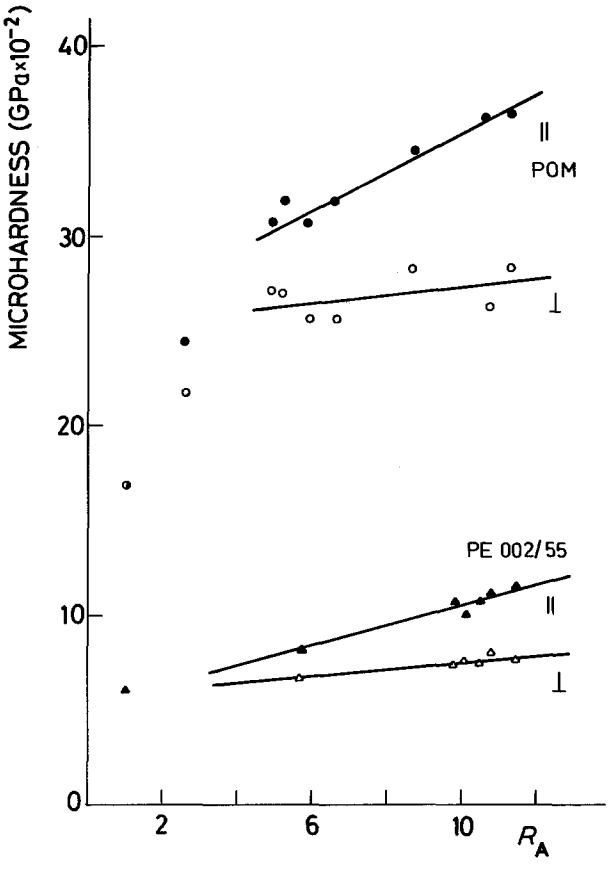

Figure 1 Surface microhardness data parallel and perpendicular to the long rod axis of die-drawn samples of POM and PE as a function of draw ratio. Loading time: 20 sec. Load: 0.1 kg (POM) and 0.05 kg (PE).

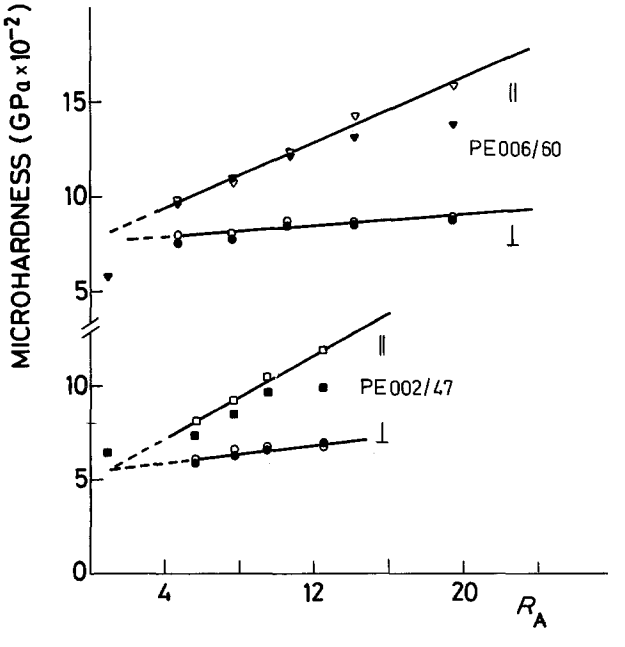

Figure 2 Microhardness as a function of draw ratio of die-drawn polyethylenes parallel and perpendicular to the draw direction. Solid data are taken at the surface. Open data are measured in the fibre core after cleavage. Loading time and load as in Fig. 1.

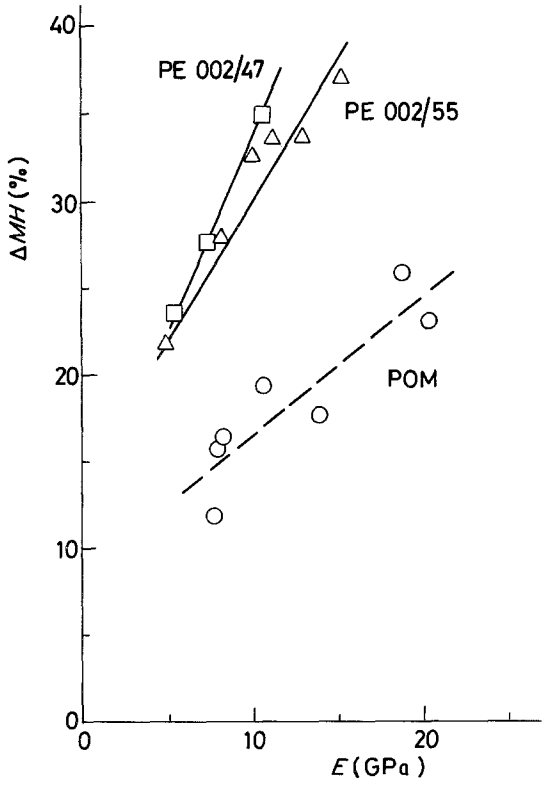

Figure 3 Correlation of microindentation anisotropy and longitudinal elastic modulus for die-drawn samples of PE at the core and POM at the surface.

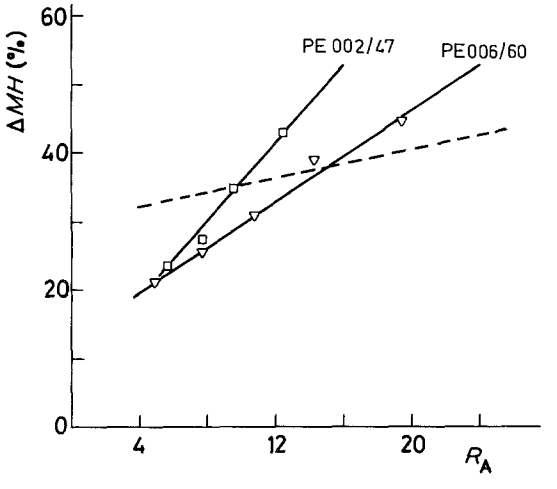

Figure 4 Linear correlation between microindentation anistropy and draw ratio for die-drawn PE with different die diameters: 4 mm (□) and 15.5 mm (▽). The dotted straight line illustrates the correlation obtained for PE extruded in an Instron capillary rheometer at high pressure [1].

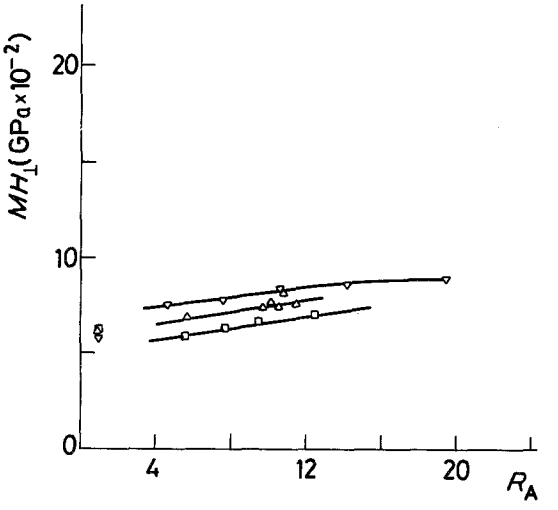

Figure 5 Plastic component of microhardness, $MH_\perp$, against R_A for various die-drawn polyethylenes with varying initial density: grade 006/60, 0.960 g cm^{-3} (▽); grade 002/55, 0.955 g cm^{-3} (△); and grade 002/47, 0.947 g cm^{-3} (□).

preparation conditions which were not identical for the three grades.

4. Discussion

The above results indicate that the *MH* value depends, as expected, on the chemical nature of the polymer (Fig. 1). Thus the *MH* for POM is more than three times larger than that for PE. This is due to the higher cohesion energy of the POM crystallites, consistent with a higher melting point for the polymer. It has previously been shown that for a given material, microhardness is very sensitive to the microstructure (crystal thickness, long period, perfection of crystal) and consequently to the packing density of the molecules within the material [15]. A remarkable hardening of the die-drawn materials with increasing draw ratio substantiates the abrupt transformation from the isotropic lamellar into the fibre structure.

The fibrous texture of the die-drawn rods consists of highly aligned strands of fibrils and microfibrils, in which crystal blocks oriented perpendicular to the fibre direction (rod axis, *c*-axis) act as cross-links for the tie molecules bridging adjacent crystals. Fig. 5 shows that resistance to plastic deformation ($MH_\perp$) of the fibrous structure is greater the higher is the density value. This measurement makes it possible to distinguish between the three polymer grades

according to their densities. The density increase implies the presence of thicker crystals, which are evidenced by a larger SAXD period [14]. The square-based indenter induces a nearly spherically symmetrical strain on the sample surface. The strain field developed beneath is asymmetrical, however, because of the inherent anisotropy of the fibrous material. Since the indentation is symmetrical while the load is applied (square-based diamond) the anisotropy of the plastic impression arising after unloading is due to an instant elastic recovery of strands in fibre direction. This result is consistent with the known improvements in recovery of drawn polyethylene with increasing draw ratio [16]. The increase in elastic modulus E with R_A in drawn PE, on the other hand, has been attributed to the concept that taut tie molecules or intercrystalline bridges connecting the crystal blocks within the fibrils increase with draw ratio and are the main contributor to the elastic properties of fibres [17]. The microindentation anisotropy measured increases with R_A for both polymers though PE shows higher ΔMH values than POM for a given R_A (Table II). Significant differences between the hardness measured in the outer surface and the inner core are detected. Such differences in microchemical behaviour on the fibre surface have been previously detected in other ultra-drawn PE strands [1] and are caused by the friction of the material against the die walls. Due to a shearing effect the parallel fibril orientation is partially destroyed and the number of taut tie molecules or intercrystalline bridges in the outer surface is reduced with respect to the core, with the result that $MH_{\parallel}$ (core) $> MH_{\parallel}$ (outer surface). This difference is particularly noticeable for PE 002/47 (Fig. 2) and PE 002/55 and for the higher R_A values.

The plot of Fig. 3 supports, in addition, the expected relative increase in ΔMH against E for two PE specimens. This means that here the increasing number of bridges contributes both to the elastic recovery in the drawing direction and to the elastic modulus of the fibres. Fig. 3 also indicates that the ΔMH increase depends slightly on the polymer grade, probably due to a different recovery behaviour which has been shown to be related to the branch content [18]. In contrast, the POM curve shows an even lower capacity of this material to recover elastically than PE. Morphological details concerning the distribution and connectedness of taut tie molecules and intercrystalline bridges can play an important role here.

Another relevant aspect to comment on is that the residual impression parameter, $(1 - \Delta MH)4/49$, and the $MH_{\perp}/E$ ratio (an indicator of a material's incapacity to absorb impact energy) show for the die-drawn material values of 5 to 7×10^{-2} and $\leqslant 10^{-2}$, respectively, which are in the vicinity of the values obtained for steel. This means that these materials occupy a position near to a perfect plastic solid according to the criteria given by Lawn and Howes [19].

The present results also point to the influence of the die dimensions on the microindentation anisotropy and, hence, on the concentration of taut tie molecules or intercrystalline bridges. Fig. 4 clearly shows a difference of slopes in the plots of ΔMH against R_A between the small-scale (2.9%) and the large-scale (1.7%) die-drawing machine. The great difference of cross-section in both cases could be responsible for the differences in the slope calculated for a given die temperature, T_d, during production. The higher the cross-section of the rod, the lower is the heat exchange rate from the core. The core consequently quenches more quickly for thin rods than for thicker ones and retains a greater extension of the longitudinal microtensions imposed during the drawing process. Finally, it is interesting to observe that the die-drawing method, for drawing ratios $R_A > 12$, furnishes products with superior elastic properties – i.e. a larger number of taut tie molecules or intercrystalline bridges – than the solid state ram extrusion process [1] (dotted straight line in Fig. 4).

5. Conclusions

From the above results we can conclude:

1. The hardening of isotropic PE and POM by drawing through a die reaches values up to 30% and 50% respectively.

2. The microindentation anisotropy developed in oriented PE is strongly influenced by the orientation process during die-drawing.

3. Microindentation measurements reveal differences in anisotropy between the core and the surface of the rods.

4. The microindentation anisotropy is an increasing function of the elastic modulus. The relationship depends on the polymer type.

Acknowledgements

Thanks are due to CAICYT, Madrid, for supporting this investigation.

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Received 20 October
and accepted 3 November 1983