A Microindentation Study of Polyethylene Composites Produced by Hot Compaction

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ABSTRACT: Microindentation measurements are reported on a range of single polymer polyethylene (PE) composites, which are produced by hot compaction of high modulus PE fibers. It is possible to measure two hardness values, parallel and perpendicular to the fiber direction respectively, from which the microindentation anisotropy is defined. The hardness values relate to the instantaneous elastic recovery of the fibers, and the results show that the microindentation measurement is deforming a material volume below the surface of the sheets comparable to the dimensions of the fibers. It appears that the microindentation anisotropy approaches a limiting value with increasing fiber orientation, i.e., as the Young's modulus of the fibers increases. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1659–1663, 2006

Key words: microhardness; microindentation anisotropy; hot compaction; high modulus PE fibers

INTRODUCTION

Single polymer composites, in which the reinforcing oriented fibers or tapes are combined with a polymer matrix of identical or very similar polymer composition, are the subject of extensive study, and a number of different routes have been developed for their manufacture.[1–4] In the Leeds hot-compaction technique, the polymer matrix is produced by melting and recrystallizing a thin skin on the surface of the original fibers or tapes.[1] Our initial studies were performed on high modulus melt-spun polyethylene (PE) fibers,[5] aiming at producing structures with high-energy absorbing characteristics. Electron microscopy of permanganate-etched samples has contributed very significantly to the elucidation of the structure of the hot-compacted materials.[6]

The purpose of the present study is to examine the effect of fiber anisotropy on the micromechanical properties of the hot-compacted composites; in particular, the microhardness. In addition to the fundamental nature of these studies, this is also an important measure, which can relate to the scratch resistance of these new materials. Previous microhardness studies have shown that microindentation is a promising technique for the nanostructural characterization of semicrystalline polymers and multicomponent systems.[7–9] Microindentation anisotropy has been shown to be related to molecular orientation.[10,11] In this article, the behavior of a range of high-modulus PE composites produced by the Leeds hot-compaction process is discussed. The results are of interest in terms of an understanding of the surface structure of these new materials, in addition to their relevance for practical applications. As expected, the results reveal that, in these woven materials, improved hardness relates primarily to increased instantaneous elastic recovery after load removal.

EXPERIMENTAL

Materials

Hot-compacted sheets produced from four types of high-modulus PE were studied, either as fibers or tapes (Table I). These were Tensylon melt-extruded tapes, Spectra gel-spun fibers, Dyneema gel-spun fibers, and Certran melt-spun fibers. Further details of the origin of these materials are given in a previous publication.[12] Because of the different processing routes, there are significant differences in their morphology, which have also been discussed previously.[12,13]

The tensile modulus of the PE fibers and tapes was measured using an RDP servo mechanical tensile tester. The sample strain was measured by a Messphysik video extensometer, and the tests were

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TABLE I
The High Modulus Polyethylenes Investigated

Trade name	Process	Geometry	Tensile modulus at a strain rate $10^{-3}s^{-1}$ (GPa)
Tensylon	Melt extrusion	Tape	88
Spectra	Gel spun	Fiber	70
Dyneema	Gel spun	Fiber	70
Certran	Melt spun	Fiber	42

TABLE II
Details of the Polyethylene Woven Fabrics

Trade name	Reinforcement details	Areal density (g/m^2)
Tensylon	Tape dimensions ~ 1800 × 45 μm^2	83
Spectra	Filament diameter ~ 30 μm	113
Dyneema	Filament dimensions ~ 20 × 7 μm^2	191
Certran	Filament diameter ~ 17 μm	175

carried out at a strain rate of 10^{-3} s^{-1}, with a gauge length of 5 cm.

Production of hot-compacted sheets

Hot-compacted sheets were produced from plain weave-woven fabrics: Figure 1 shows pictures of the weave styles of the four PE materials (the scale at the top of each picture shows divisions in millimeters), and the details of these clothes are given in Table II.

Samples were also produced from unidirectional arrays of Tensylon tapes and Certran fibers. In all cases, the materials for hot compaction were stacked in a matched metal mold, which in turn was placed in a hot press, set at the required compaction temperature and an applied pressure of 2.8 MPa (400 psi). The compaction temperature was monitored by a thermocouple, and once the assembly had reached the compaction temperature, it was left for 10 min, before cooling to 90°C, prior to removal from the mold.

As described in the previous publication,[1] the optimum compaction temperature was determined for each material, which requires a compromise between the loss of the oriented phase due to the melting and

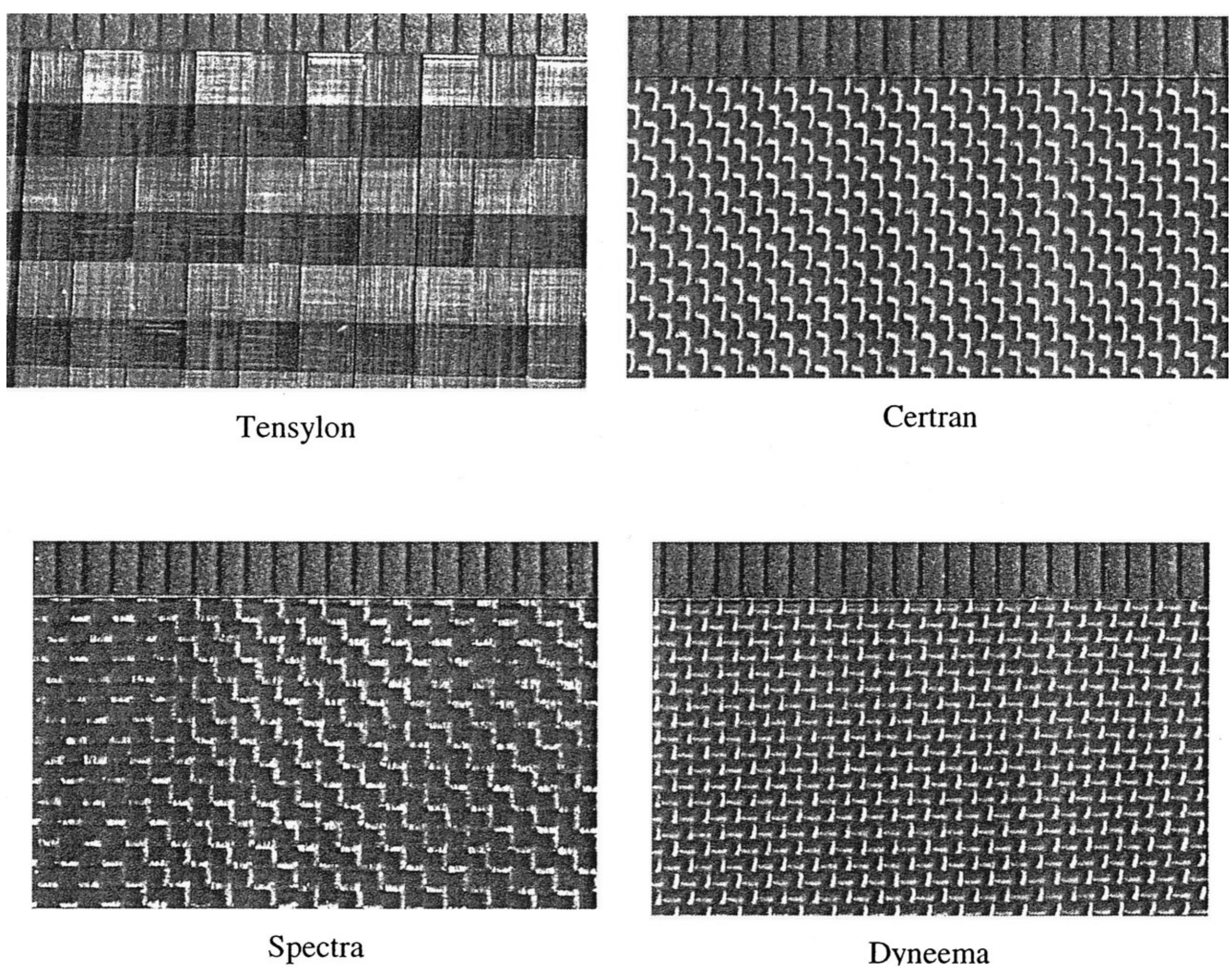

Figure 1 Details of the weave styles for the four materials (the scale bar shows divisions in millimeters).

TABLE III
Properties of Optimum-Compacted Woven Sheets

	Tensylon	Spectra	Dyneema	Certran
Initial fiber/tape modulus (GPa)	88	70	70	42
Sheet tensile modulus (GPa)	30	21	7	10
Peel strength (N/10 mm)	9	7.4	5.2	8
Predicted sheet tensile modulus (GPa)	31	25	25	15

recrystallization of the reinforcement surfaces and the requirement for adequate bonding in the self-reinforced structure. DSC measurements on the hot-compacted samples showed that for these materials the percentage of remaining oriented phase was in all cases very close to 70%.

Properties of hot-compacted sheets

The properties of the optimum compacted woven sheets are shown in Table III, and for the two unidirectional samples in Table IV.

To a first approximation, the tensile modulus of an ideal hot-compacted sheet, E_{comp}, can be predicted by a simple composite model, assuming the parallel rule of mixtures and taking into account the plain weave structure of the fabrics[14]:

$$E_{comp} = \frac{V_f}{2}E_f + \frac{(2 - V_f)}{2}E_m \tag{1}$$

where E_f is the fiber or tape modulus, E_m the matrix modulus, and V_f the fiber or tape-volume fraction after hot compaction.

On the assumption that $V_f = 0.7$ in all cases, the predicted sheet moduli are also shown in Tables III and IV. It can be seen that the measured tensile moduli of the woven sheets produced from Tensylon, Spectra, and Certran are in reasonable agreement with the predicted values, but the results for Dyneema are anomalously low. The previous study[3] showed that this is due to poor interfiber and interlayer bonding. The results for the unidirectional Tensylon and Certran sheets are consistent with those for the woven sheets.

TABLE IV
Properties of Optimum-Compacted Unidirectional Sheets

	Tensylon	Certran
Initial fiber/tape modulus (GPa)	88	42
Sheet longitudinal tensile modulus (GPa)	58	31
Sheet transverse modulus (GPa)	2.4	3.1
Sheet transverse strength (MPa)	26	10
Predicted sheet longitudinal modulus (GPa)	62	30

Microhardness measurements

In this study, the imaging method was used to measure the microhardness of the six hot-compacted sheets, whose properties are described in Tables III and IV. The method consists in the optical measurement of the residual impression produced by a Vickers square-faced pyramid diamond, with included angles of 136° between nonadjacent faces, which penetrates the surface of the material under a given load.[7] The microhardness, H, was derived by dividing the peak load by the contact area of impression[7]:

$$H = K\frac{P}{d^2} \tag{2}$$

where P is the load applied, d the length of the diagonal of the indentation, and K is the geometrical factor, which has a value of 1.854 in SI units.

As discussed in detail elsewhere (Ref. 7, line 15), an important aspect of the surface-indentation mechanism is the creep effect shown by polymers, which for tensile creep in oriented PE has been extensively discussed by one of the present authors.[15,16] The role of creep in microhardness tests has also been described in previous publications by another of the present authors.[17,18]

The samples were glued onto a metal holder to fix them and to avoid air gaps. The loads applied ranged between 100 and 500 mN, and were held constant for 6 s to minimize creep effects. The residual impressions were measured immediately after load release, to minimize long delayed viscoelastic recovery. The microhardness value was derived from an average of at least 10 indentations. The indentations were made along the preferred orientation of the fibers or tapes (see Fig. 2). Because of the anisotropy of the fibers/tapes in which the hot-compacted sheets were composed, the indentations had an anisotropic shape.

As a result of the anisotropic indentation, two different values of H could be measured: parallel and perpendicular to the preferred fibers orientation direction. The microhardness is larger (i.e., the length of the diagonal is shorter) when the indentation diagonal lies parallel to the fiber orientation direction than when normal to it.

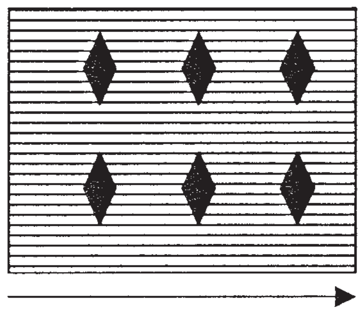

Figure 2 Pattern of indentations on the surface of the hot-compacted PE sheets.

RESULTS AND DISCUSSION

Figure 3 shows a plot of the force applied against the squared diagonal of the indentation for the woven Tensylon hot-compacted sheet. One can see that there is a linear relationship between the load and the squared diagonal of the indentation, both in the fiber direction (‖) and normal (⊥) to it, consistent with eq. (2). The data of Figure 3 show the anisotropy of the sample. The key fact is that the observed anisotropy is due to a greater instantaneous elastic recovery of the material along the main orientation direction.

As the microhardness values, parallel and normal to the fiber orientation, are independent of the load applied, from here onward, only the microhardness values derived from the load of 500 mN (50 g) will be discussed. For this force, the typical penetration depth for these materials is of the order of 10 μm. Because of the average length of the cross-section of the fibers (larger than 10 μm[13]), we are practically indenting only the first layer of the hot-compacted fibers at the surface of the sheets.

Table V shows the calculated microhardness values from the two diagonal lengths, along the orientation direction, $H_{\parallel}$, and normal to it, $H_{\perp}$, respectively. As discussed earlier, the values of $H_{\parallel}$ are larger than those for $H_{\perp}$, primarily due to greater elastic recovery along the fiber direction.

From the $H_{\parallel}$ results, it can be seen that with the exception of the Dyneema sample, the values of $H_{\parallel}$ are very similar. Previous studies, on the mechanical properties of these woven compacted sheets, indicated that the Dyneema sheet was poorly bonded compared with the other three woven materials.[12] One possibility is that the Dyneema sheet is debonding during indentation, leading to a lower recovery, and hence to lower microhardness values. It is well known that a high level of preferred molecular orientation can give reduced plastic deformation,[15,16] which could be a contributory factor as to why $H_{\parallel}$ shows greater recovery than $H_{\perp}$, leading to a larger hardness value in this direction. Indentation anisotropy, ΔH, can be calculated through the following equation[7]:

$$\Delta H = \frac{H_{\parallel} - H_{\perp}}{H_{\parallel}} \quad (3)$$

and the results for the woven compacted sheets are shown in Figure 4.

Table V also shows the values of the microindentation anisotropy, ΔH, for the unidirectional compacted sheets of two of the materials, Tensylon and Certran. Here, it is seen that, within experimental error, the results for $H_{\parallel}$ and $H_{\perp}$ and ΔH are identical with those measured from the woven samples. Because of the small size of the indentation, the penetration depth is of the order of 10 μm and the indentation diagonals of about 80–100 μm. The measured microindentation anisotropy is therefore related to the mechanical anisotropy on the scale of the fiber or tape dimensions and is not directly affected by the weave style or fabric construction.

Previous studies have suggested that there is a correlation between microhardness anisotropy and the elastic modulus.[19] This correlation can be attributed to the fact that high values of Young's modulus in oriented polymers correspond with high degrees of molecular orientation, which lead to lower creep and higher recovery.[15,16] The results in Table V suggest that the origin of changes in the microindentation anisotropy ΔH arise primarily from changes in $H_{\perp}$ and higher fiber modulus i.e., higher orientation implies poorer recovery in the transverse direction.

CONCLUSIONS

1. The microhardness values for the hot-compacted woven and unidirectional Tensylon and Certran sheets are identical within experimental error.

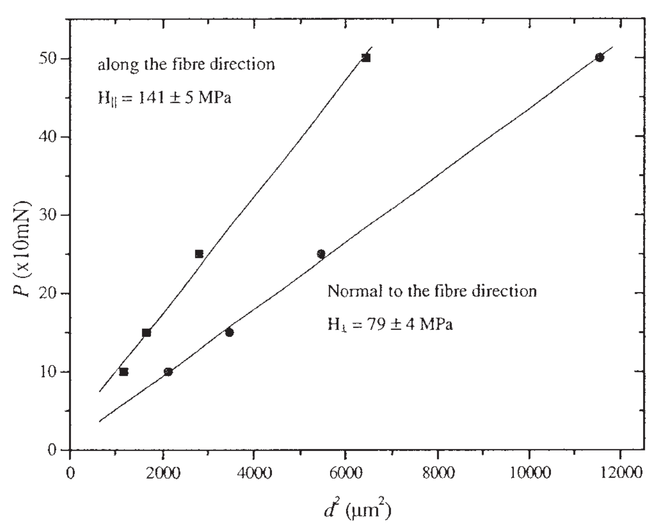

Figure 3 Plot of load, P, as a function of the squared diagonal of indentation, d^2, along the fiber's direction, ‖, and normal to it, ⊥, for the woven Tensylon tape.

TABLE V
Microhardness Values, Parallel and Perpendicular to the Fibre Direction, and Indentation Anisotropy of Woven and Unidirectional Hot Compacted Sheets

Material	$H_{\parallel}$ (MPa)	$H_{\perp}$ (MPa)	ΔH (%)	Fibre modulus (GPa)
Woven Tensylon	141 ± 5	79 ± 4	44 ± 5	88
Woven Spectra	140 ± 4	85 ± 2	39 ± 3	70
Woven Certran	141 ± 5	88 ± 2	38 ± 4	42
Woven Dyneema	126 ± 15	86 ± 10	32 ± 4	70
Unidirectional Tensylon	141.5 ± 4	74.7 ± 3	47 ± 4	88
Unidirectional Certran	142 ± 3	87.6 ± 2	38 ± 3	42

This confirms that the microhardness measurement is deforming elastoplastically the material below the surface of the sheets to a depth which is comparable to the dimensions of the fibers or tapes.

2. With the exception of the very poorly bonded Dyneema, the microindentation anisotropy values reflect the instantaneous elastic recovery behavior of the fibers. If the fiber modulus is higher, the immediate transverse recovery is lower, leading to a higher microindentation anisotropy. The compacted Dyneema sheet has poorer mechanical properties than the other materials, and the present data reveal that it also has the lowest microindentation anisotropy. This is probably due to debonding and failure during indentation, which would lead to a lower instantaneous recovery.

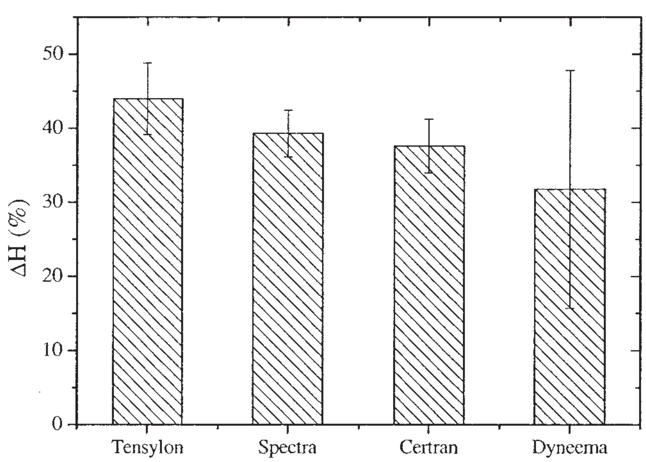

Figure 4 Microindentation anisotropy of the woven samples investigated.

3. The indentation anisotropy seems to approach a limiting value with increasing molecular orientation i.e., high Young's modulus of the fibers.

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