A microindentation study of polyethylene composites produced by hot compaction

I.Puente Orench, F.J. Balta Calleja
Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006, Madrid, Spain

P. J. Hine, I. M. Ward
IRC in Polymer Science & Technology, School of Physics and Astronomy, University of Leeds, Leeds LS 2 9JT, UK

Abstract

The micromechanical properties of polyethylene (PE) composites produced by hot compaction of high modulus fibres are reported. The microhardness of the composites has been explored using the microindentation test. Analysis of results permits to distinguish hardness values, parallel and perpendicular to the fibre direction. The values are related to the elastic recovery of the fibres and their yield stress. Measurements of the mechanical anisotropy are of special interest. Results show that the microindentation measurement is deforming a material volume below the surface of the sheets comparable to the dimensions of the fibres. Our findings indicate that the microindentation anisotropy approaches a limiting value for high molecular orientation i.e. high Young's modulus of the fibres.

Keywords: microhardness, indentation-anisotropy, hot-compaction, high modulus PE fibres.

1. Introduction

The recent development of single polymer composites, where the reinforcing oriented fibres or tapes are combined with a polymer matrix produced from a melted and recrystallised skin of the original fibres or tapes, provides a new class of materials of special interest [1]. Initial studies of hot compacted composites were performed on high modulus melt spun PE fibres, having high stiffness and strength [2], aiming at structures having very high energy absorbing characteristics. Electron microscopy studies have contributed to elucidate the influence of processing conditions on the physical properties of hot compacted polymer fibres [3].

The purpose of the present study is to examine the effect of fibre 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. Preceding microhardness studies have shown that microindentation is a promising technique for the nanostructural characterization of semicrystalline polymers and multicomponent systems [4,5,6]. The present paper attempts to correlate the indentation anisotropy measurements with the elastic properties of the hot compacted materials. Indentation anisotropy has also shown to provide valuable information about molecular orientation [7,8]. In this paper the behaviour of a range of high modulus polyethylene 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 elastic recovery after indentation.

2. Experimental

2.1. Materials

Hot compacted sheets produced from four types of high modulus PE were studied, either as fibres or tapes (Table 1). These were Tensylon melt extruded tapes, Spectra gel spun fibres, Dyneena gel spun fibres and Certan melt spun fibres. Further details of the origin of these materials is given in a previous publication [3]. Due to the different processing routes there are significant differences in their morphology which have also been discussed previously [3,9].

Insert Table 1

2.2 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 polyethylene materials (the scale of the top of each picture shows divisions in millimetres), while the details of these cloths are given in Table 2.

Insert Figure 1

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

Insert Table 2

As described in the previous publication [3], 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 recrystallisation 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%.

2.3 Properties of Hot Compacted Sheets

The properties of the optimum compacted woven sheets are shown in Table 3 and for the two unidirectional samples in Table 4.

Insert Table 3 and Table 4

The results show that the tensile moduli of the woven sheets produced from Tensylon, Spectra and Certran are in the same order as the initial moduli but that the sheet results for Dyneema are anomalously low. The previous study [3] showed that this is due to poor interfibre and interlayer bonding. The results for the unidirectional Tensylon and Certran sheets are consistent with those for the woven sample sheets.

2.4 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 3 and 4. 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 non-adjacent faces, which penetrates the surface of the material under a given load [4]. The microhardness, H, was derived by dividing the peak load by the contact area of impression [4]:

$$H = K \frac{P}{d^2} \tag{1}$$

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

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

Insert Figure 2

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

3. 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 fibre direction (||) and normal (⊥) to it, according to equation 1. The data of Figure 3 2 clearly show the anisotropy of the sample. The key fact is that the observed anisotropy is due to a greater elastic recovery of the material along the main orientation direction. The high hardness values can, therefore, be related to the increased elastic recovery.

Insert Figure 3

As the microhardness values, parallel and normal to the fibre orientation, are independent of the load applied, from here onwards, only the microhardness values derived from the load of 500mN (50g) will be discussed. For this force, the typical penetration depth for these materials is of the order of 10μm. Due to the average length of the cross section of the fibres (larger than 10μm [9]), we are practically indenting only the first layer of the hot compacted fibres at the surface of the sheets.

Figure 4 shows the calculated microhardness values from the two diagonal lengths, along the orientation direction, $H_{||}$, and normal to it, $H_{\perp}$, respectively. As discussed above, the values of $H_{||}$ are larger than those for $H_{\perp}$, primarily due to greater elastic recovery along the fibre direction.

Insert Figure 4 around here

From the $H_{||}$ results, it can be seen that with the exception of the Dyneema sample, the values of $H_{||}$ are very similar (Table 5). Previous studies on the mechanical properties of these woven compacted sheets, indicated that the Dyneema sheet was poorly bonded compared to the other three woven materials [3]. One possibility is that the Dyneema sheet is debonding during indentation, leading to a lower recovery and, hence to lower microhardness values. For the longer diagonals ($H_\perp$), there is a clear trend of increasing hardness (or increased recovery) with the level of preferred molecular orientation in the parallel direction. It is well known that a high level of preferred molecular orientation can give reduced plastic deformation [10] which could be a contributory factor as to why $H_{||}$ shows greater recovery (i.e more elastic deformation) than $H_\perp$, leading to a larger hardness value in this direction. Indentation anisotropy, ΔH, can be calculated through the following equation [4]:

$$\Delta H = \frac{H_{||} - H_{\perp}}{H_{||}} \tag{2}$$

A summary of the $H_\perp$, $H_{||}$ and ΔH results for the woven polyethylene samples is shown in Table 5.

Insert Table 5.

Figure 5 shows the values of the indentation anisotropy, for the four woven samples. As expected, the constant value of $H_{||}$ and the decreasing $H_\perp$ with increasing fibre modulus i.e. increasing molecular orientation, leads to an increase in ΔH with increasing fibre modulus.

Hardness measurements were also carried out on unidirectional compacted sheets for two of the materials, Tensylon and Certran and these results are also shown in Table 5. Here, it is seen that, within experimental error, the results for $H_\perp$ and $H_{||}$ and ΔH are identical to those measured from the woven samples. Because of the small size of the indentation, the penetration depth is of the order of 10 microns and the indentation diagonals of about of 80-100 microns. The measured microindentation anisotropy is therefore related to the mechanical anisotropy on the scale of the fibre or tape dimensions and is not directly affected by the weave style or fabric construction

Insert figure 5 around here

Previous studies have shown that there is a correlation between ΔH and the elastic modulus E [11]. Following the observation that the results from the unidirectional and woven compacted plates are very similar, the most appropriate E value would appear to be $E_{||}$ for the unidirectional sheet. The results in Figure 4 and Table 5 suggest that the origin of the change in ΔH is the decrease in $H_{\perp}$ ($H_{||}$ is the same for the different materials excluding Dyneema on the grounds of the poor bonding). For the woven sheets, we have also found a relationship between the microindentation anisotropy and the elastic modulus (see Figure 6).

Insert Figure 6

Examining again the results shown in Table 4, for the elastic properties of unidirectional compacted Tensylon and Certran samples, it can be seen that the higher the value of the longitudinal modulus (for Tensylon) the lower is the transverse modulus. Comparing the transverse modulus and transverse hardness values of these two compacted sheets, we can see that the higher the transverse modulus, the higher the apparent hardness $H_{\perp}$.(i.e. the higher is the recovery or the more elastic is the deformation behaviour). This may explain the ΔH increase with increasing fibre tensile modulus.

4. CONCLUSIONS

1) The microhardness values for the hot compacted woven and unidirectional Tensylon and Certran sheets are identical within experimental error. This confirms that the microhardness measurement is deforming elasto-plastically the material below the surface of the sheets to a depth, which is comparable to the dimensions of the fibres or tapes.
2) With exception of the very poorly bonded Dyneema, the microindentation values reflect the elastic recovery behaviour of the fibres because this determines the recovery behaviour of the composite; i.e. if the modulus is higher, then the material is more elastic and, hence the recovery is greater, leading to a higher apparent hardness. This is consistent with previous

investigations [4] and with the mechanical properties of these compacted sheets. 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 recovery and apparent hardness.

3) The indentation anisotropy approaches a limiting value with increasing molecular orientation i.e. high Young's modulus of the fibres.

Acknowledgments

The authors acknowledge the MEC, Spain (grant FIS2004-01331), for the generous support of this work. One of us I.P.O. also acknowledges the support of the FPI programme of MEC, Spain (grant BFM 2000-1474).

References

1. I.M.Ward and P.J. Hine, *Polymer*, **45**, (2004),1413.
2. G. Capaccio, I.M. Ward, *Nat. Phys. Sci.*, **243**, (1973),143.
3. P.J. Hine, I.M.Ward, N.D. Jordan, R.H. Olley and D.C. Bassett, *J. Macromol. Sci. Physics*, **B40**, (2001), 959.
4. F.J. Balta Calleja and S. Fakirov, in "Microhardness of Polymers", (Cambridge University Press, Cambridge 2000), p.11.
5. F.J. Baltá Calleja, A. Flores, "Hardness" in Encyclopedia of Polymer Science and Technology, (John Wiley & Sohns, Inc., New York, 3rd Ed. Vol 2, 2003),p 678.
6. I. Puente Orench, F. Ania, E. Baer, A. Hiltner, T. Bernal, F.J. Baltá Calleja, *Phil. Mag.*, **84, 18**, (2004), 1841.
7. D.R. Rueda, L. Kubera, F.J. Baltá-Calleja, *J. Mater. Sci. Letters*, **12**, (1993), 1140.
8. S. Henning, G.H. Michler, F. Ania, F.J. Baltá Calleja, *Colloid Polym. Sci.*, **283**, (2005), 486.
9. M.I. Abo El Maaty, R.H. Olley, D.C. Bassett, *J. Mater. Sci.*, **34**, (1999), 1975.
10. M.A. Wilding and I.M.Ward, Polymer, **19**, (1978) 969
11. D.R. Rueda, F.J. Balta-Calleja, J. Garcia Pena, A. Richardson and I.M.Ward, *J. Mater. Science*, **19**, (1984), 2615.

TABLE 1: The High Modulus Polyethylenes investigated.

Trade Name	Process	Geometry	Tensile Modulus, GPa (strain rate $10^{-3}s^{-1}$)
Tensylon	Melt extrusion	Tape	88
Spectra	Gel spun	Fibre	70
Dyneema	Gel spun	Fibre	70
Certran	Melt spun	Fibre	42

TABLE 2: Details of the polyethylene woven fabrics

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

TABLE 3: Properties of Optimum Compacted Woven Sheets

	Tensylon	Spectra	Dyneema	Certran
Initial fibre/tape modulus, GPa	88	70	70	42
Sheet tensile modulus, GPa	30±2	21	7	10±0.3
Peel strength N/10mm	9±1.2	7.4±1.5	5.2±1.5	8±1.2

TABLE 4: Properties of Optimum Compacted Unidirectional Sheets

	Tensylon	Certran
Initial fibre/tape modulus, GPa	88	42
Sheet longitudinal tensile modulus, GPa	58±3	31±1
Sheet transverse modulus GPa	2.4±0.2	3.1±0.2
Sheet transverse strength, MPa	26	10

TABLE 5: Microhardness values, parallel and perpendicular to the fibre direction, and indentation anisotropy of woven and unidirectional hot compacted sheets.

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

Figure Captions:

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

Figure 2: Pattern of indentations on the surface of the hot compacted polyethylene sheets.

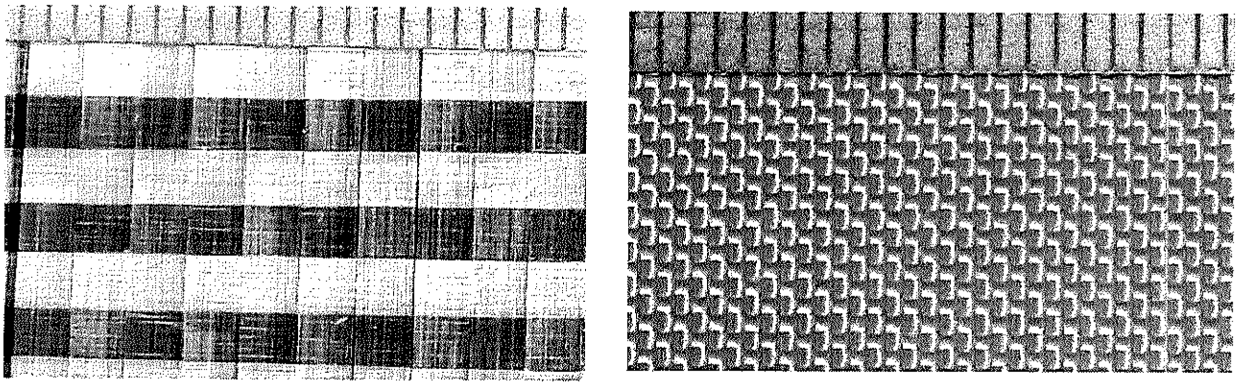
Figure 3: Plot of load, P, as a function of the squared diagonal of indentation, d^2, along the fibers direction, //, and normal to it, $\perp$, for the woven Tensylon tape.

Figure 4: Microhardness values of the woven samples along the orientation direction, $H_{||}$, and normal to it, $H_{\perp}$

Figure 5: Microindentation anisotropy of the woven samples investigated.

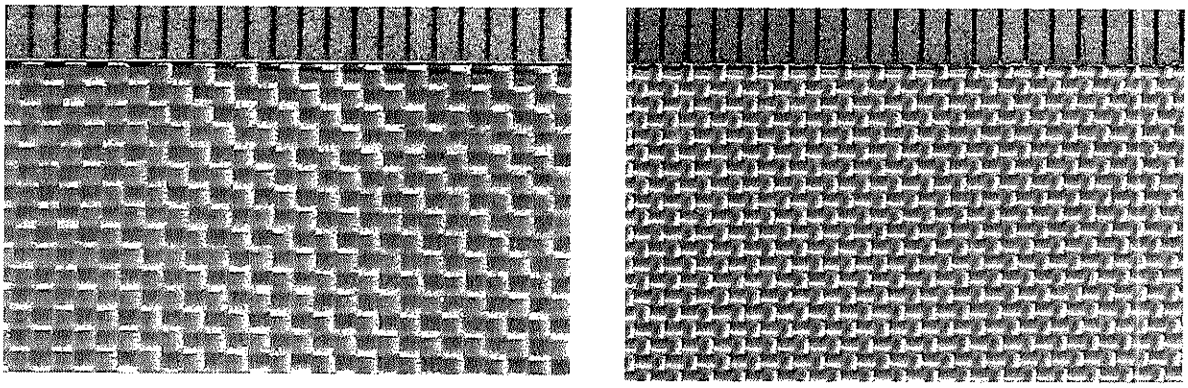
Figure 6: Microindentation anisotropy, ΔH, as a function of elastic modulus, E.

Figure 1.



Tensylon

Certran



Spectra

Dyneema

Figure 2.

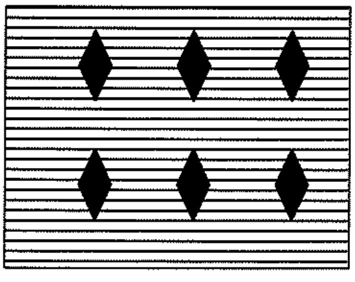


Figure 3.

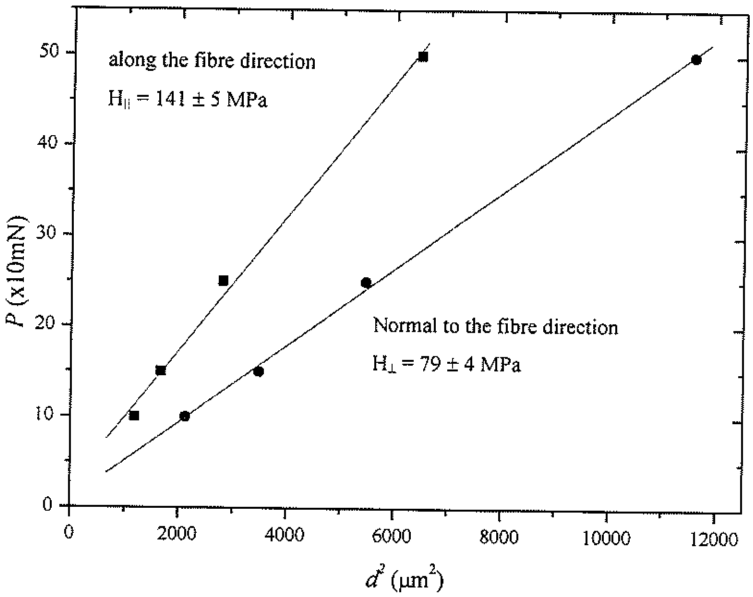
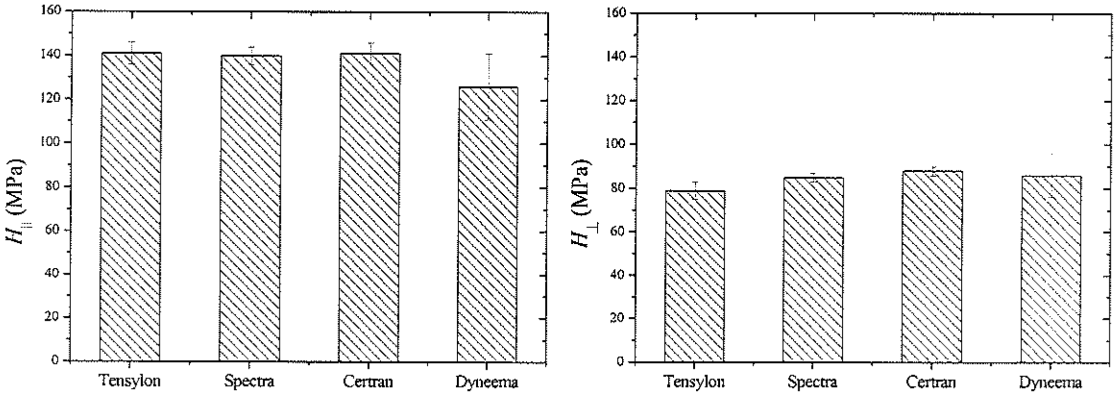

along the fibre direction
H|| = 141 ± 5 MPa
Normal to the fibre direction
H⊥ = 79 ± 4 MPa
P (x10mN)
0
10
20
30
40
50
0
2000
4000
6000
8000
10000
12000
d² (μm²)

Figure 4



$H_{\parallel}$ (MPa)
0
20
40
60
80
100
120
140
160
Tensylon
Spectra
Certran
Dyneema
$H_{\perp}$ (MPa)
0
20
40
60
80
100
120
140
160
Tensylon
Spectra
Certran
Dyneema

Figure 5.

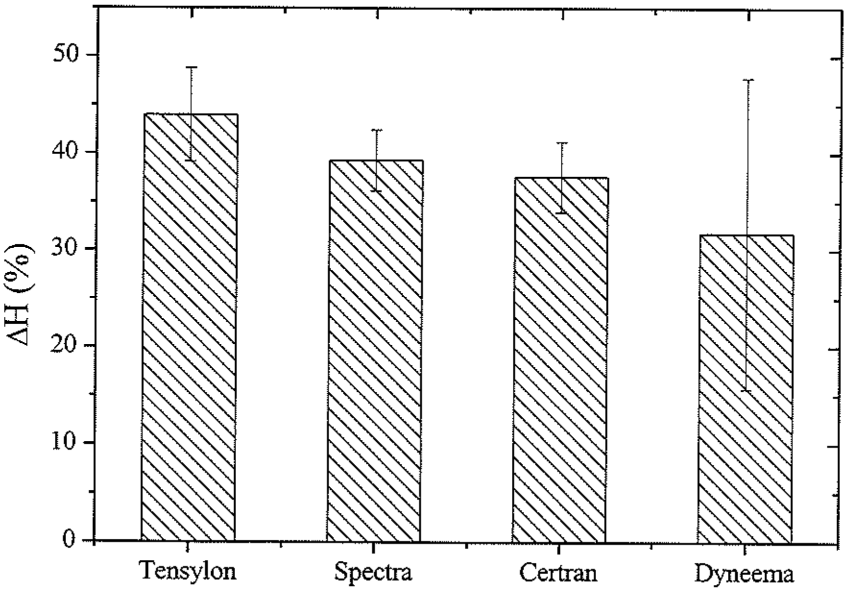
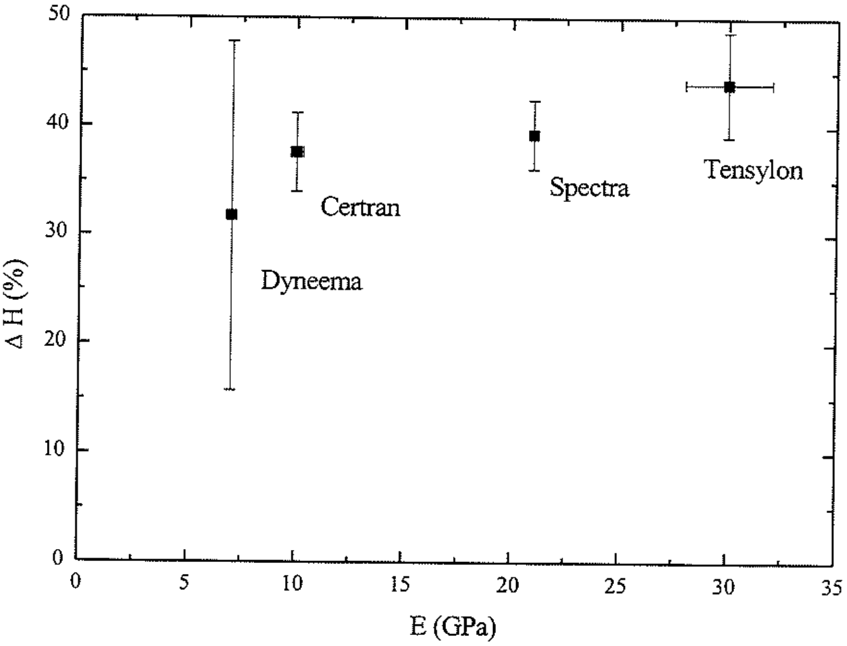


FIGURE 6


50
40
30
20
10
0
Δ H (%)
0
5
10
15
20
25
30
35
E (GPa)
Dyneema
Certran
Spectra
Tensylon