Mechanical Anisotropy of Oriented Polymers

Part 1 *A Yield Criterion for Uniaxially-Drawn Poly(ethylene terephthalate)*

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Measurements of tensile and shear yield stress have been made on strips cut at various angles to the draw direction from films of drawn amorphous poly(ethylene terephthalate). The data were well fitted by a criterion of the von Mises type but with modifications to allow for the anisotropy of the samples and also for a built-in compressive stress in the draw direction. In the tensile experiments a sharp neck is usually formed at an angle to the tensile direction and this angle is predicted with good accuracy by an application of the theory of plastic potential.

The built-in stress is closely related to the retraction stress which develops when the films are heated but not allowed to contract. In general the tensile yield stress and the tensile modulus are also closely correlated.

1. Introduction

Investigations of yield and plastic flow in metals have resulted in quite a good understanding of these phenomena in terms of movements of dislocations. Moreover, phenomenological treatments useful on a macroscopic scale had been developed before knowledge of the microscopic processes involved was available. The criterion for yielding proposed by von Mises that the second invariant of the deviatoric stress tensor

$$J_2' = \frac{1}{6}\left[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2\right] \quad (1)$$

where σ_1, σ_2, σ_3 are principal stresses, should reach a critical value, characteristic of the material, has generally been found to accord well with experience in complex stress situations.

In contrast, investigations of yield in ductile polymers have not been extensive and understanding of the process is not far advanced. In most cases, also, experiments which have been carried out have been limited to tensile yield of isotropic polymer samples which cannot give information on the form required for a yield criterion. Robertson and Joynson [1] have suggested that yield measurements on oriented polymer samples should be enlightening and have reported the results of shear experiments on drawn poly(2,6-dimethylphenylene oxide) and poly(4,4'-dioxydiphenyl-2,2-propane carbonate).

The packing together of polymer chains to the densities actually observed necessitates the existence of ordered domains (very small in size) even in amorphous polymers; drawing of the polymer should orient these domains so that their yield and flow properties can be more readily observed.

In the present investigation a systematic series of measurements of yielding in both tension and shear has been made on drawn films of amorphous poly(ethylene terephthalate)*.

2. Experimental

Films of drawn, initially amorphous, poly(ethylene terephthalate) were supplied by Plastics Division, ICI Ltd. The drawing was carried out by passing extruded film between two sets each of three rollers. The two sets of rollers rotated at different speeds, the ratio of the peripheral velocities giving the nominal draw ratio. Between the two sets of rollers the film was maintained at about 80° C by radiant heat. X-ray photographs confirmed that the undrawn film was amorphous; at the highest draw ratio used (5:1) the film was highly oriented and some crystallinity which was not estimated quantitatively had apparently developed, fig. 1.

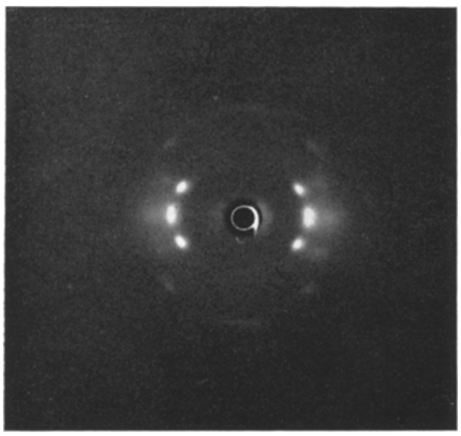

Figure 1 X-ray photograph of uniaxially-drawn poly(ethylene terephthalate) film (draw ratio 5:1). The draw direction and the collimated X-ray beam being at right angles and in the same vertical plane.

Tensile tests were performed on specimens cut from these uniaxially-drawn films using a dumb-bell-shaped die, sample dimensions were 0.5 cm wide and 2.54 cm long, the specimens being cut at different angles to the draw direction. The tests were performed using an Instron tensile test machine with CTM load cell and rubber-faced compressed-air grips and with a crosshead speed of 1 cm/min, corresponding to a nominal strain rate of 40%/min. The upper yield load was recorded. Generally, yielding occurred within a sharply-defined band only approximately parallel to the draw direction, the angle between this band and the tensile direction was measured with a goniometer eyepiece attached to a travelling microscope after the strip had been removed from the tensile test machine.

The apparatus used to carry out the experiments in shear was similar to that shown by Robertson and Joynson [1], modified so that the grips were pinned and screwed to prevent sample-rotation on tightening. The sample slots could accommodate specimens up to 5 mm wide and thicknesses from 0.2 to 0.5 mm without slipping occurring on shearing. The shear specimens were cut out by clamping the film between steel templates 4.5 mm wide and running a sharp scalpel along both edges of these templates. The orientation of the strip relative to the draw direction was fixed by clamping the templates with screws passing through holes in the sheet previously drilled with the help of a jig.

3. Results

Table II summarises the results for the various draw ratios investigated, the yield values quoted being means of three or four determinations. The tensile yield stresses (upper yield load divided by unstrained cross-sectional area) for the film with draw ratio 4.25:1 are plotted as a function of the angle θ between the draw and tensile directions in fig. 2. Fig. 3 shows the acute angle ϕ between the tensile axis and the neck as a function of θ for the same film.

For the shear experiments θ was defined as follows; in simple shear the shear direction was taken as the direction of lines which do not rotate during the deformation, the positive sense for angular measurements from this axis being the sense of rotation of other lines, and θ is the angle between this shear direction and the draw direction. In experiments ($90° < \theta < 180°$) in which the resolved tensile stress is negative (i.e. compressive) a yield drop was observed in the load and the yield stress was calculated from the maximum value. With a tension in the draw direction ($0° < \theta < 90°$) although a turnover in the load occurred so that the rate of load increase with deformation decreased markedly at higher strains there was, presumably because of rapid work-hardening, no maximum. There

*A preliminary account [2] of some of the shear results has appeared previously. At an advanced stage of the present work the authors became aware of similar experiments being carried out by I. M. Ward and co-workers at Bristol University.

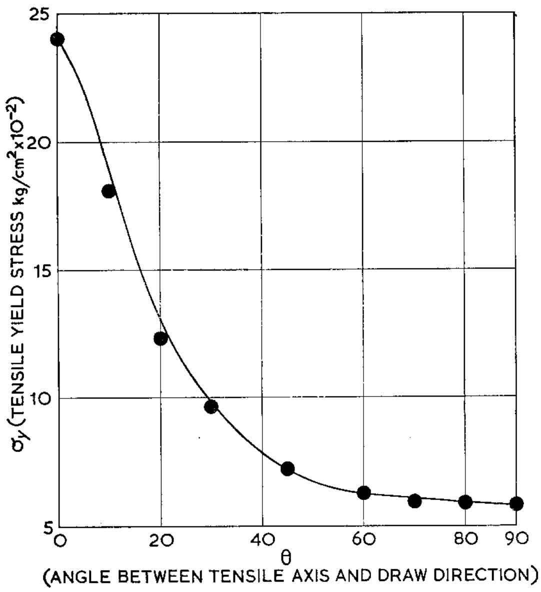

Figure 2 Tensile yield stress (σ_y) against θ (angle between the tensile axis and the draw direction) for uniaxially-drawn poly(ethylene terephthalate) film (draw ratio 4.25:1). In all curves the full line is the theoretical prediction and the dots experimental data.

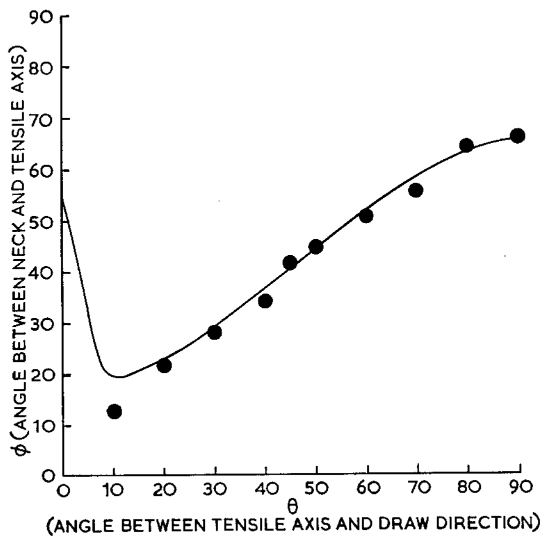

Figure 3 ϕ (angle between neck and tensile axis) against θ (angle between tensile axis and draw direction) for uniaxially-drawn poly(ethylene terephthalate) film (draw ratio 4.25:1).

was thus no obvious yield stress and an arbitrary procedure was adopted; the mean of the strains at which a load maximum had been observed was calculated and when there was no maximum the stress corresponding to this mean strain was taken as the yield stress. Results are shown in fig. 4 for the film with draw ratio 4.25:1.

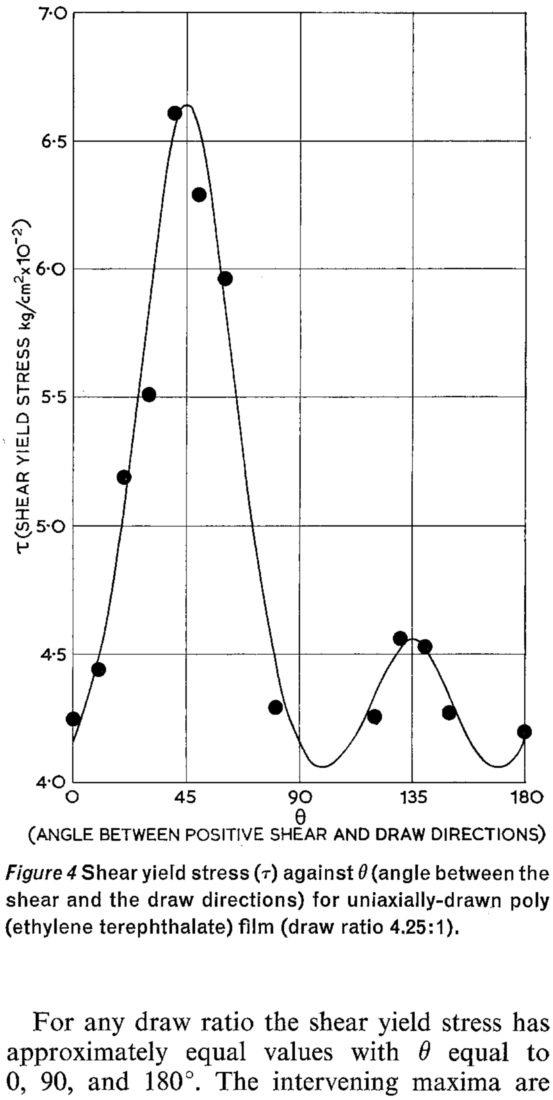

Figure 4 Shear yield stress (τ) against θ (angle between the shear and the draw directions) for uniaxially-drawn poly (ethylene terephthalate) film (draw ratio 4.25:1).

For any draw ratio the shear yield stress has approximately equal values with θ equal to 0, 90, and 180°. The intervening maxima are markedly unequal, the greater occurring when the resolved tensile stress in the draw direction acts in such a sense as to extend the oriented polymer chains.

4. Discussion

Robertson and Joynson have pointed out that it is not surprising that the yield stress should depend on whether the majority of the polymer chains in a drawn material are being further extended or allowed to retract. In a simple physical model for the drawn polymer, the oriented polymer chains can be considered to provide a frozen-in stress which becomes active as yield is reached and either reinforces or opposes the external stress.

Qualitatively, the experimental results of Robertson and Joynson on shear yield appear rather different from those obtained during the present investigation as these authors found only one maximum and one minimum yield stress in the range $0° \leqslant \theta \leqslant 180°$ (at $\theta = 60$ or $40°$, and 150 or 140° respectively for the two materials investigated). It is suggested, however, that the difference is a qualitative one and results from relatively larger frozen-in stresses with the polymers used by them.

There has been little investigation of yield criteria for polymeric materials. Thorkildsen [3] has investigated the behaviour of thin-walled tubes of poly(methyl methacrylate) under combined tension and internal pressure and found fair accord with von Mises' equation 1. Vincent [4] has observed that for a number of isotropic polymer samples the ratio of the shear and tensile yield stresses was very roughly the $1:\sqrt{3}$ required by the von Mises' criterion. It was of interest, therefore, to investigate the applicability to the oriented polymers of a development of the von Mises' equation for anisotropic materials due to Hill [5]. However, a further modification is necessary to allow for the built-in stress mentioned above.

For a material with three mutually orthogonal planes of symmetry, Hill's yield criterion, when the principal axes of anisotropy (intersections of the planes of symmetry) are taken as the Cartesian axes of reference, is

$$2f(\sigma_{ij}) = \mathrm{F}(\sigma_y - \sigma_z)^2 + \mathrm{G}(\sigma_z - \sigma_x)^2 + \mathrm{H}(\sigma_x - \sigma_y)^2 + 2\mathrm{L}\tau_{yz}^2 + 2\mathrm{M}\tau_{zx}^2 + 2\mathrm{N}\tau_{xy}^2 = 1 \qquad (2)$$

where F, G, H, L, M, N are constants.

In the application of Hill's criterion to the present data it was assumed that the draw direction is an axis of rotational symmetry. (This assumption appeared not unreasonable since contraction perpendicular to the draw direction was permitted during drawing both in the plane and perpendicular to the plane of the sheet. This anisotropy is not, however, borne out by the X-ray photographs as far as the crystalline part of the polymer is concerned and its justification must rest on the resulting fit of the data.) If the x-direction is a symmetry axis $\mathrm{G} = \mathrm{H} = \mathrm{L} - 2\mathrm{F}$, $\mathrm{M} = \mathrm{N}$, and if the y-axis is taken in the plane of the sheet and only stresses in the x, y-plane are considered, the yield criterion, equation 2, reduces to

$$\sigma_x^2 - \sigma_x\sigma_y + \alpha^2\sigma_y^2 + \beta^2\tau_{xy}^2 = \gamma^2 \qquad (3)$$

where

$$\alpha^2 \equiv \tfrac{1}{2}\left(\frac{\mathrm{F}}{\mathrm{G}} + 1\right), \; \beta^2 \equiv \frac{\mathrm{N}}{\mathrm{G}}, \; \gamma^2 \equiv \frac{1}{2\mathrm{G}}.$$

The frozen-in stress which was introduced to account for the difference in peak heights in the shear yield stress can easily be incorporated into the yield criterion by replacing σ_x by $\sigma_x - \sigma_0$. If a new set of axes (ξ, η) is chosen in the x, y-plane such that θ is the angle measured anticlockwise from the ξ-axis to the x-axis then

$$\begin{aligned}
\sigma_x &= \sigma_\xi\cos^2\theta + \sigma_\eta\sin^2\theta + 2\tau_{\xi\eta}\sin\theta\cos\theta\,,\\
\sigma_y &= \sigma_\xi\sin^2\theta + \sigma_\eta\cos^2\theta - 2\tau_{\xi\eta}\sin\theta\cos\theta\,,\\
\tau_{xy} &= -(\sigma_\xi - \sigma_\eta)\sin\theta\cos\theta + \tau_{\xi\eta}(\cos^2\theta - \sin^2\theta)\,.
\end{aligned}$$

For a simple tensile stress σ, in the ξ-direction, the yield criterion becomes

$$\sigma^2[\cos^4\theta + \alpha^2\sin^4\theta + (\beta^2 - 1)\sin^2\theta\cos^2\theta] + \sigma\sigma_0\,[3\sin^2\theta - 2] + \sigma_0^2 = \gamma^2 \qquad (4)$$

and for a shear stress τ ($= \tau_{\xi\eta}$) acting alone

$$\tau^2[(2 + \alpha^2)\sin^2 2\theta + \beta^2\cos^2 2\theta] - 3\tau\sigma_0\sin 2\theta = \gamma^2 - \sigma_0^2 \qquad (5)$$

In the formulation of the anisotropic yield criterion, Hill assumed that critical yield stresses were unchanged by the superposition of a hydrostatic pressure as has been found experimentally to be the case with metals. Unfortunately this is less likely to be so well justified an assumption in the case of polymeric materials because of the much lower bulk-compression modulus. From a different viewpoint it can be said that the yield strain in a polymeric material is much higher than is usual for a metal, and since the value of Poisson's ratio is similar in the two kinds of material, the volume-change is considerably higher with the former type; it is thus improbable that the yield criterion for a polymer does not involve at all the first stress invariant $J_1 = \sigma_1 + \sigma_2 + \sigma_3$. However, to take such considerations into account in the present anisotropic case would increase intolerably the number of disposable constants involved and, in view of the evidence that application of von Mises' criterion does not give large errors for isotropic materials, such applications were not considered worthwhile.

Although the modified Hill criterion has been presented in terms of the physical model of a built-in stress it is, in fact, the most general one that can be written consonant with the conditions of plane stress, independence of yield from hydrostatic pressure and cylindrical symmetry if only powers of the stresses up to the second are considered. If only first and second power terms are included, and the independence from hydrostatic pressure is assumed, the yield criterion must reduce to von Mises' in the isotropic case.

The four disposable constants, α, β, γ and σ_0 were determined by using three points on the curve of tensile yield against θ (at $\theta = 0$, 45, and 90°) and the difference of the peak heights (at $\theta = 45$ and 135°) in the shear yield curve and the theoretical curve for both tensile and shear constructed. If X, W, Y are the tensile yield stresses at 0, 45, and 90° and R and S the shear yield stresses at 45 and 135°, equations 4 and 5 give

$$\alpha^2 Y^2 + \sigma_0 (Y + 2X) = X^2 ,$$

$$R - S = \frac{3\sigma_0}{2 + \alpha^2} ,$$

$$\gamma = X - \sigma_0 ,$$

$$\alpha^2 + \beta^2 = \frac{4\gamma^2 - 4\sigma_0{}^2 + 2W\sigma_0}{W^2}$$

The first two equations gave α and σ_0 and the calculation of γ and β was then a matter of substitution. Some preliminary calculations showed that determination of all four constants by taking more points from the tensile results was impossible for good fits to all the tensile data which could be obtained over a wide range of σ_0 values by assigning appropriate values of α, β and γ. The quantity $(R - S)$ is the most sensitive to the magnitude of σ_0, and it was therefore most sensible to use this quantity in determining σ_0. However, as pointed out earlier, measurement of R is accompanied by considerable uncertainty and this must also be the case for σ_0.

Determination of the disposable constants in the manner described enables the complete yield stress against direction curves to be calculated for both tensile and shear stress. The theoretical curves are compared with experimental points for draw ratio 4.25:1 in figs. 2 and 4. The fit over the whole tensile curve is very good but this is hardly surprising as the curve was fitted at three of the experimental points. However the theoretical relation successfully predicts also the shear stress curve. In particular it is predicted that the shear yield stresses at 0, 90 and 180°, should be equal; this is found to be true to a good approximation experimentally, and the theoretical estimate of the common value is very satisfactory. (The minima in the theoretical curves occur close to, but not at, these values.) The theoretical estimate of the mean peak height is also in good agreement with the experimental value (table I).

The results obtained at all the draw ratios investigated are summarised in tables I and II.

By interpreting $f(\sigma_{ij})$ of equation 2 as a plastic potential, Hill obtained relations, equivalent to the Lévy-Mises equations for isotropic materials, between ratios of the plastic strain increments and the stresses. The angle between the neck formed in tensile yield of a thin strip and the tensile direction can then be calculated if the material is taken as rigid-plastic. The equation for the angle ϕ between the neck and the tensile direction becomes, after making the modifications necessary to allow for the built-in stress,

$$a \tan^2\phi - 2b \tan\phi - c = 0$$

where:
$a = 1 - 2(\alpha^2 - \beta^2 + 2)\sin^2\theta\cos^2\theta + (2\sin^2\theta - \cos^2\theta)\sigma_0/\sigma$;

TABLE I Summary of parameters used in the yield criterion derived from the experimental data, and comparison of experimental and theoretical results.

Draw ratio	σ_0 (kg/cm² × 10^{-2})	α	β	γ (kg/cm² × 10^{-2})	Shear yield stress Observed 0°	90°	180°	Calculated	Mean peak height $(RS)^{\frac{1}{2}}$ Observed	Calculated	Retractive stress at 80°C (kg/cm² × 10^{-2})
					(kg/cm² × 10^{-2})				(kg/cm² × 10^{-2})		
5.0	6.9	4.68	6.08	29.2	4.18	4.53	4.00	4.64	5.5	5.77	2.8
4.25	6.3	2.66	3.98	17.7	4.25		4.20	4.16	5.5	5.50	1.6
3.5	2.7	2.48	4.00	12.8	3.07	3.02	3.10	3.13	4.2	4.40	0.7
2.5	0.5	1.64	2.33	9.3	3.00	3.30	3.10	3.98	3.2	4.29	
1.0				6.0	3.10			2.89			

TABLE II Summary of tensile yield data.

$\theta°$	$D = 5$			$D = 4.25$			$D = 3.5$			$D = 2.5$		
	σ_y (kg/cm^2 $\times 10^{-2}$)	E (kg/cm^2 $\times 10^{-2}$)	$\phi°$	σ_y (kg/cm^2 $\times 10^{-2}$)	E* (kg/cm^2 $\times 10^{-4}$)	$\phi°$	σ_y (kg/cm^2 $\times 10^{-2}$)	E (kg/cm^2 $\times 10^{-4}$)	$\phi°$	σ_y (kg/cm^2 $\times 10^{-2}$)	E (kg/cm^2 $\times 10^{-4}$)	$\phi°$
0	36.0	14.3		24.0	11.2		15.5	8.5		9.8	4.8	54.5
10	25.1	9.6	12.0	17.6	11.6	12.5	12.6	7.7				42.5
20	15.0		20.0	12.3	4.4	21.5	9.6	4.6	20.0			39.5
30	10.5		30.5	9.6		28	7.5		26.0			38.0
40		3.5	38.0		3.9	34	5.8	2.9	39.0			
45	7.5		41.0	7.3		41.5				6.6	2.4	
50		2.9	44.0		2.4	44.5	5.2		39.0			50.5
60	6.7	2.2	55.0	6.3	1.6	50.5	4.8	2.1	53.0			58.0
70	6.1		56.0	5.9		55.5	4.5	2.0	59.0			65.5
80	5.2		65.0	5.8		64	4.8	1.9	57.5			66.0
90	5.9	2.3	67.0	5.8	1.8	66	4.8	2.0	61.0	5.6	2.3	75.0

*Instron strain gauge determinations, all other moduli were determined be dead weight experiments.

$b = \sin\theta\cos\theta\ [(\beta^2 - 2\alpha^2 - 1)\sin^2\theta - (\beta^2 - 3)\cos^2\theta - 3\sigma_0/\sigma]$;
$c = a + (2\alpha^2 - 1)\sin^2\theta + \cos^2\theta - \sigma_0/\sigma$, σ being the calculated tensile yield stress at an angle θ to the draw direction. The calculated neck angles from this equation are in good agreement with those measured. Fig. 3 shows the calculated and observed values at a draw ratio of 4.25:1. For all the higher draw ratios the pattern is similar. When the angle between the tensile and draw directions is large the neck deviates from the draw direction towards the tensile direction but as θ decreases ϕ decreases less rapidly, and at approximately 25° θ and ϕ become equal and the neck lies in the draw direction. With smaller values of θ the calculations suggest that the neck and the tensile axis will lie on opposite sides of the draw direction and for $\theta < 10°$ ϕ increases rapidly with decreasing θ to 54.7° at $\theta = 0$, the value expected also for isotropic materials. No experimental measurements of ϕ could be made of $\theta = 0$ except for films with the lower draw ratio (2.5 : 1) as the neck was insufficiently sharp. Generally, therefore, the rise in ϕ at low θ was not observed although otherwise the agreement of theory and experiment was good. For a draw ratio of 2.5:1 the full curve was obtained (fig. 5). The predicted minimum in ϕ is clearly shown in the results and the observed value at ϕ at $\theta = 0$ is close to the theoretical. Overall, however, agreement of theory and experiment was not as good as at higher draw ratios because of the difficulty in characterising with sufficient accuracy the rather small deviation from isotropy at this draw ratio.

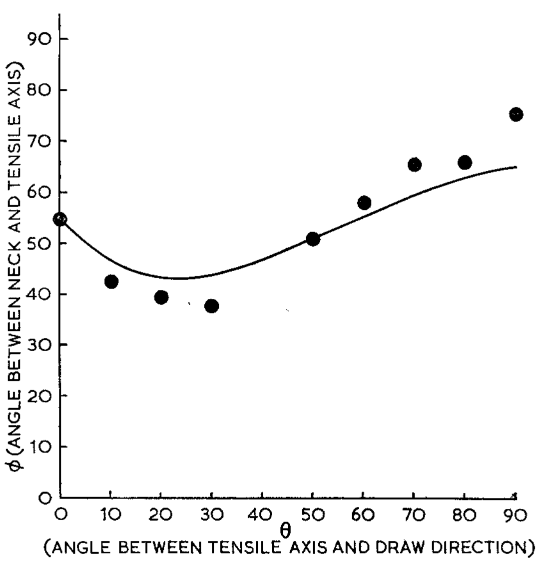

Figure 5 ϕ (angle between neck and tensile axis) against θ (angle between tensile axis and draw direction) for uniaxially-drawn poly(ethylene terephthalate) film (draw ratio 2.5:1).

On heating, drawn films of poly(ethylene terephthalate) will retract so that the physical reality of a frozen-in stress, such as has been postulated above as a mathematical convenience, can be demonstrated. Pinnock and Ward [6] have shown that for amorphous fibres at low draw ratios a well-defined retraction stress is developed if the fibres are held at their initial length in hot water. Similar measurements on the films used in the present experiments gave the values given in table I. These values are of the same order as the values of σ_0 deduced from the yield measurements, but are lower by a factor of about three. In view of the difficulties in determining σ_0 mentioned earlier, it is reasonable to identify σ_0 tentatively as essentially this retraction stress released when yielding begins.

There is a close correlation between the tensile yield stress and the tensile modulus (more accurately with the reciprocal of the tensile compliance as measurements were made with a simple stress tensile which would give a simple elongation only if applied in the direction of a principal axis). In fig. 6 values of the tensile yield stress corrected for the frozen-in stress (i.e. calculated from equation 4 using the appropriate values of α, β, γ, from table I but putting $\sigma_0 = 0$), $\sigma_y{}^c$, have been plotted against measured values of the reciprocal compliance. Whether modulus is altered by change of draw ratio or change of the angle between tensile and draw directions $\sigma_y \simeq E/50$ is a fair approximation for the yield stress. The implication is that the yield strain changes little but no measurements are available to check this directly. Physically this could be the case if yielding commenced as soon as some structures (such as the ordered domains whose existence is deduced from the density) become critically strained. From structures with a more-or-less biased distribution of orientations (dependent on draw ratio) those structures in the tensile direction would be most strained and would yield first.

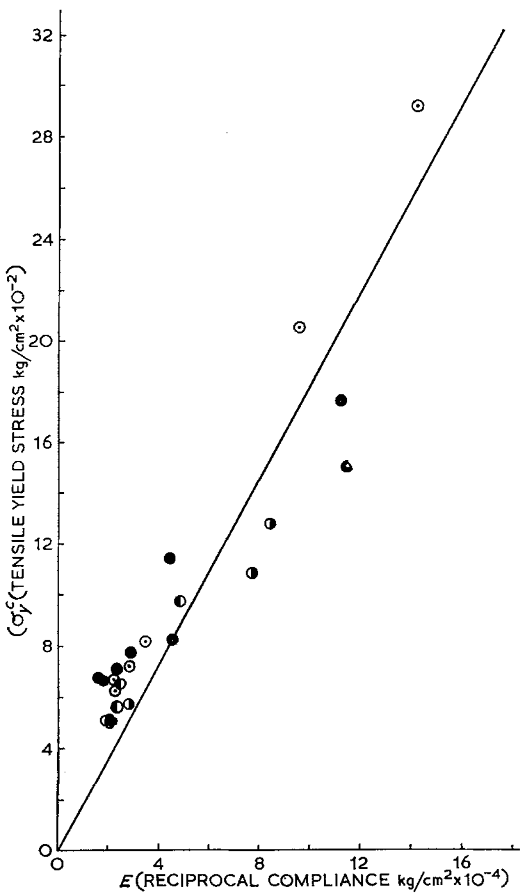

Figure 6 Corrected tensile yield stress $\sigma_y{}^c$ against reciprocal compliance for all angles and draw ratios. (⊙, $D = 5$; ●, $D = 4.25$; ◑, $D = 3.5$; ◐, $D = 2.5$.)

Acknowledgement

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