Mechanical anisotropy in oriented polychlorotrifluoroethylene

C. L. Choy and S. H. Fung
Department of Physics, The Chinese University of Hong Kong, Hong Kong

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The dynamic tensile modulus (E) and loss (tan δ) of various oriented samples of polychlorotrifluoroethylene have been measured at 0°, 45° and 90° to the draw direction over the range of −100 to 160°C. For the cold-drawn samples the mechanical anisotropy at the lowest temperature is determined by the overall chain orientation resulting in $E_0 > E_{45} > E_{90}$. Above the γ relaxation (20°C) a shear process is activated leading to a change in the anisotropy pattern to $E_0 > E_{90} > E_{45}$. Cold-drawing followed by annealing gives rise to further changes so that $E_{90} > E_0 > E_{45}$ above the β relaxation (120°C). The effect of annealing has been attributed to the relaxation of the amorphous regions and the development of lamellar texture, and the anisotropy in tan δ/E at the β relaxation is found to be consistent with the interlamellar shear model.

INTRODUCTION

Polychlorotrifluoroethylene (PCTFE) shows three relaxations which have been extensively studied by dynamic torsional[1–3] and dielectric[4,5] measurements. The α relaxation at 140°C (1 Hz) is exhibited only by samples of the highest crystallinity and is associated with the occurrence of chain-folded lamellar spherulites. The loss peak of the β relaxation at 100°C decreases with increasing crystallinity and is clearly related to the glass–rubber transition in the amorphous regions. The γ peak at about −30°C decreases in magnitude and shifts to lower temperature as crystallinity increases, so it is probably composed of two overlapping relaxations. Both relaxations have been attributed to the motion of a small section of chain backbone, with the higher temperature process occurring in the amorphous region and the lower temperature process in the crystallites.

It has recently been shown[6–13] that the study of the anisotropy of mechanical modulus and loss of oriented samples can give important information on the mechanical processes responsible for the relaxations. Not a single study has been reported on the mechanical anisotropy of PCTFE. The investigation described in this paper is concerned with the mechanical anisotropy of drawn PCTFE of two different crystallinities (0.39 and 0.63), and the effect of annealing on these materials. Structural information obtained from birefringence, wide- and small-angle diffraction measurements are also used in the interpretation of the mechanical data.

EXPERIMENTAL

Sample preparation

Two series of isotropic sheets of about 1.5 mm thickness were prepared from commercial PCTFE (Kel-F, 3M Co. Ltd) by compression moulding at 250°C. The first series were quenched from the melt into water at room temperature while the second series were cooled at about 2°C/min from the melt to room temperature. There are no visible spherulites in the quenched sheets but the slow-cooled sheets are spherulitic. The volume fraction crystallinities χ as determined by hydrostatic weighing are 0.39 and 0.63 for the quenched and slow-cooled samples, assuming the density of the amorphous and crystalline phases to be 2.077 and 2.187, respectively[14].

Suitably shaped samples (10 cm long and 7.5 cm wide) were cut separately from the quenched and slow-cooled sheets and drawn at 1 cm/min on an Instron tensile testing machine. The 'natural' draw ratio of the quenched samples was found to increase with temperature, so samples of draw ratios (λ) 1.9, 2.7 and 3.7 were prepared for mechanical, birefringence and X-ray measurements by drawing at 22, 60 and 90°C, respectively. One more sample of lower λ (1.35) was also prepared at 22°C for birefringence measurements. Since the highest temperature used is only 40°C above the glass transition (52°C) all these samples can be regarded as cold-drawn. Only one drawn sample ($\lambda = 4$) was prepared at 90°C from slow-cooled sheets. This sample was silky in appearance and was therefore thought to contain microvoids.

Annealed samples were also prepared from the oriented quenched sheets ($\lambda = 3.7$) and slow-cooled sheets ($\lambda = 4$) by: (i) annealing at 190°C for 8 hours while being held at constant length, and (ii) annealing at 205°C for 3 min with both ends free. During annealing procedure (ii) both samples shrank by about 30%, and the draw ratio of the quenched and slow-cooled samples reduce to 2.6 and 3, respectively.

Birefringence and X-ray diffraction measurements

The birefringence of the quenched and drawn films were measured using a tilting compensator with a Leitz polarizing microscope. Wide-angle X-ray diffraction photographs were taken on all the samples using a Phillips Camera and filtered CuKα radiation. Small-angle X-ray photographs were taken using a Franks Camera manufactured by Searle Instrument Ltd.

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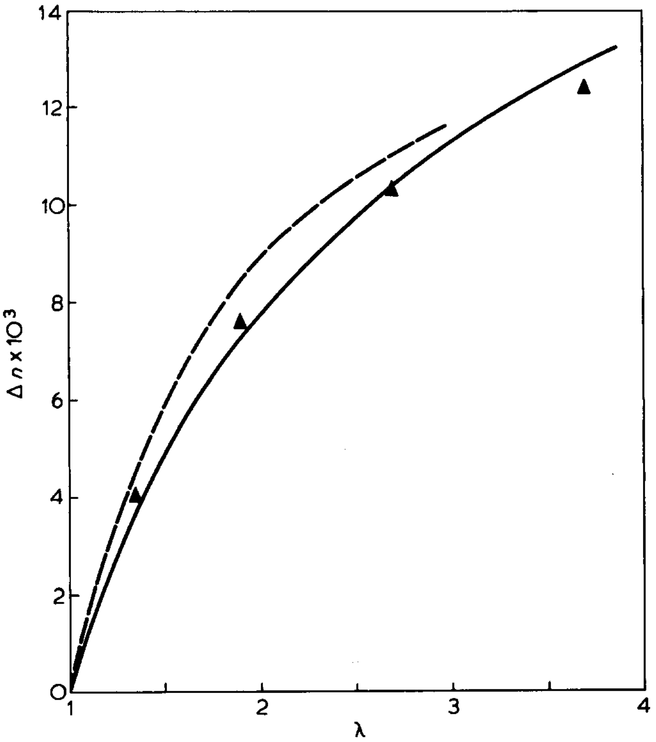

Figure 1 Variation of the birefringence Δn of PCTFE with draw ratio λ. The points are our data while the broken line denotes the data of Hashimoto *et al.*[15]. The full line represents the prediction of the aggregate model

Mechanical measurements

Dynamic tensile measurements at 90 Hz were made from −100° to 160°C using a viscoelastic spectrometer (Iwamoto Seisakusho Co. Ltd). Samples of length 35 mm and width 2.5 mm were cut at 0°, 45° and 90° to the draw direction and the tensile modulus E and loss tangent tan δ were measured along these directions.

RESULTS AND DISCUSSIONS

Summary of recent structure studies

Hashimoto *et al.*[15] have recently investigated the structure of isotropic and drawn films of PCTFE by depolarized light scattering, wide-angle X-ray diffraction and birefringence measurements. Light scattering measurements show that the isotropic quenched sample contains a random array of crystallites small compared with the wavelength of incident light. Upon drawing the superstructure remains essentially a random aggregation of crystallites but the crystalline chains tend to orient towards the draw direction. The amorphous chains also orient towards the draw direction and their contribution to the total birefringence is only a little smaller than that of the crystallites. Both the crystalline orientation function f_c and the birefringence vary with draw ratio in accordance with the prediction of the aggregate model[16,17] assuming pseudoaffine deformation

Hashimoto *et al.*[15] have also studied isothermally crystal-

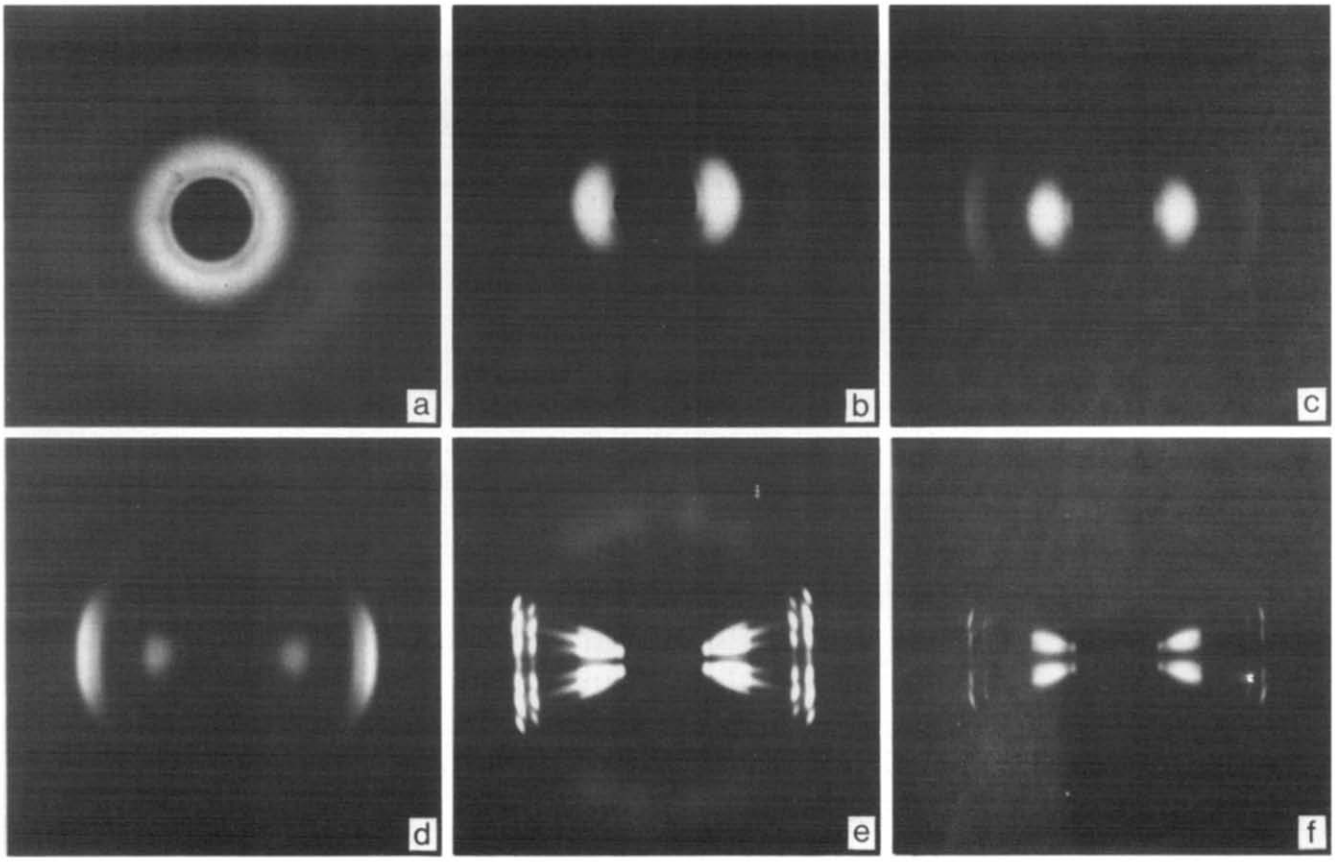

Figure 2 Wide-angle X-ray patterns for quenched PCTFE of crystallinity 0.39. The draw axis is along the vertical direction. (a) isotropic; (b) draw ratio: λ = 1.9; (c) λ = 2.7; (d) λ = 3.7; (e) annealed taut at 190°C; λ = 3.7; (f) annealed free at 205°C; λ changes from 3.7 to 2.6

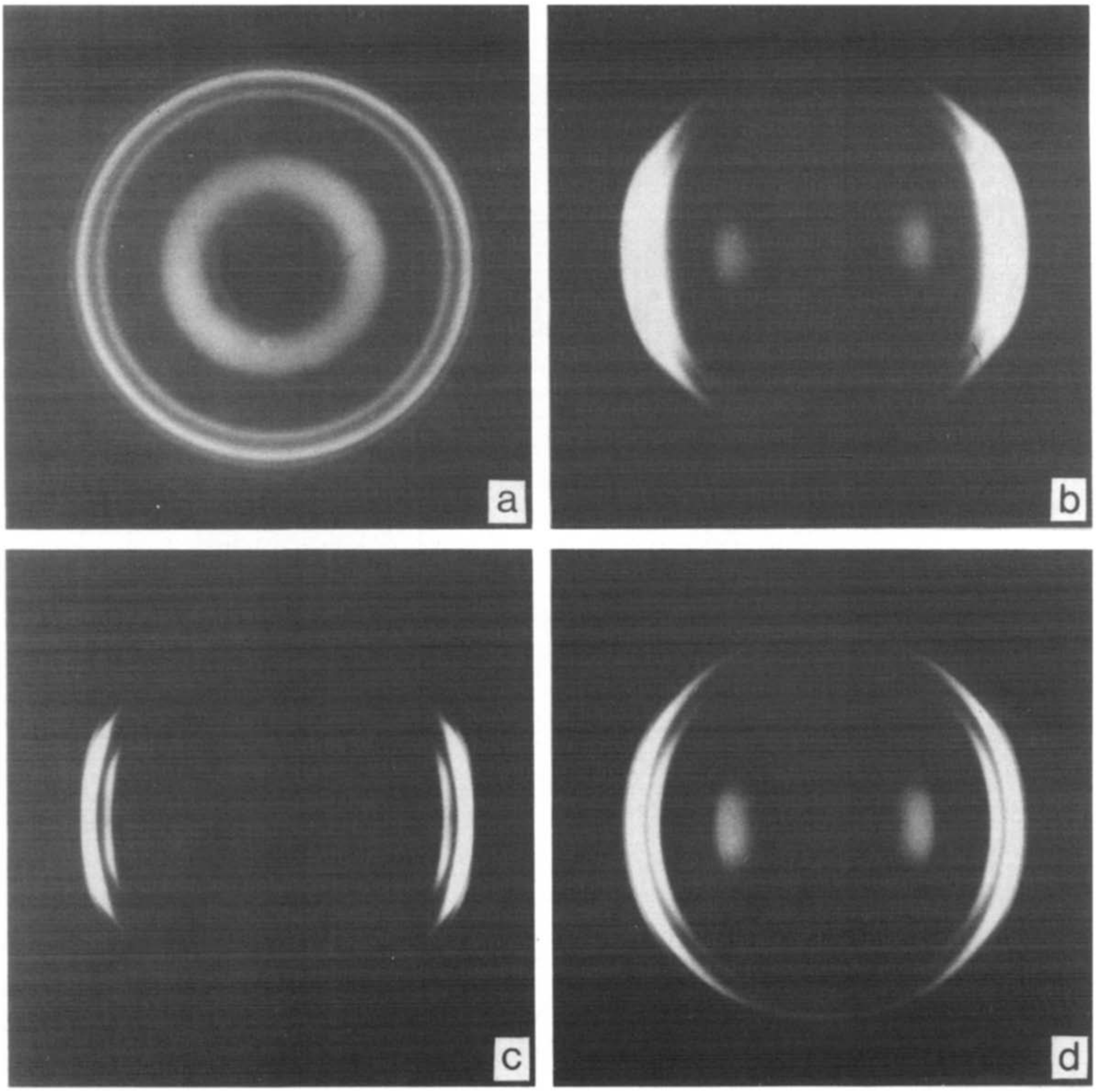

Figure 3 Wide-angle X-ray patterns for slow-cooled PCTFE of crystallinity 0.63. The draw axis is along the vertical direction. (a) Isotropic; (b) draw ratio λ = 4; (c) annealed taut at 190°C; λ = 4; (d) annealed free at 205°C; λ changes from 4 to 3

lized PCTFE. For crystallization temperatures higher than 150°C the samples have a well-developed spherulitic superstructure, which is probably similar to the morphology of our slow-cooled materials. Upon drawing the spherulitic material exhibits about the same birefringence as that of the quenched material with the same draw ratio. However, f_c for the drawn spherulitic material is smaller, which indicates that the amorphous chain orientation in this material is enhanced.

Birefringence and X-ray diffraction data

The birefringence of the quenched and drawn sheets used in our investigation is shown in *Figure 1*. These sheets were drawn at temperatures varying from 22 to 90°C but the results agree with those obtained on materials drawn at room temperature[15], implying that the average chain orientation is not much affected by draw temperature within the above range. *Figure 1* also indicates that the increase of birefringence with draw ratio is consistent with the prediction of the aggregate model[16,17] if we take the birefringence of a fully aligned sample to be 19×10^{-3}.

Figures 2 and *3* show the wide-angle X-ray diffraction patterns for PCTFE taken with the incident X-ray beam normal to both the draw direction and the plane of the sheets. The PCTFE crystals have an hexagonal unit cell with spacings of 6.438 Å along the *a* and *b* axes, and 41.5 Å along the *c* axis[18]. The (10 *l*), $0 \leqslant l \leqslant 5$, diffractions are superimposed at a Bragg angle 2θ of 14° to 18°. It is seen from *Figure 2* that the isotropic quenched sample (χ = 0.39) gives a single diffuse diffraction ring; as the draw ratio increases this splits into two rings. The decrease in arc width and the rise in intensity show that the crystalline orientation increases with draw ratio. Previous work[15] gives $f_c \simeq 0.7$ for samples with draw ratio >3. Subsequent annealing of the highest drawn sample (λ = 3.7) at 190° and 205°C produces crystal twinning (*Figures 2e* and *2f*) but there is very little loss in *c*-axis orientation. The slow-cooled samples, which have a higher crystallinity (χ = 0.63), exhibit similar but sharper patterns. The twinned crystal structure is, however, absent in the drawn and annealed materials.

Unfortunately, no small-angle X-ray patterns have been observed for any of the samples. Since both the slow-cooled

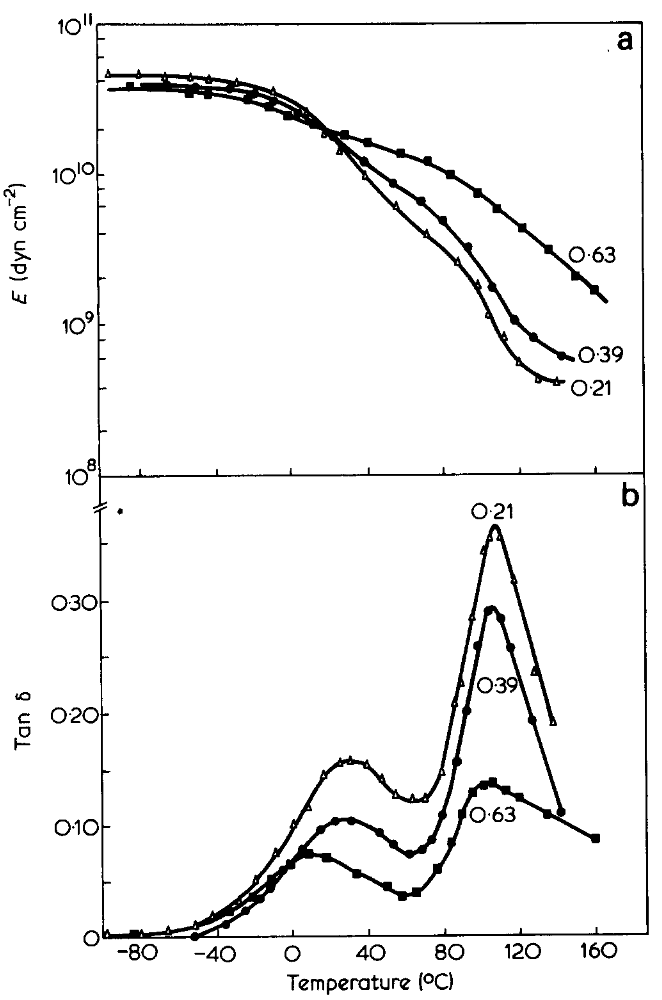

Figure 4 Temperature dependence of the (a) tensile modulus and (b) loss tangent for isotropic PCTFE. The numbers beside the curves denote the crystallinities

and the quenched and annealed samples are expected to have a lamellar texture the absence of small-angle patterns may probably be attributed to the fact that the long period is larger than 300 Å, i.e. beyond the detection range of the small-range X-ray camera used in the present study. In this respect we note that previous studies[5,19] of isotropic samples indicate that the long period varies from 500 to 1300Å depending on crystallization conditions. Other cameras can, of course, be used to measure a larger long period but they do not provide the information we need, namely, the orientation of the lamellae.

Crystallinity dependence of mechanical data

Figures 4a and *4b* show the dynamic tensile modulus E and loss tangent $\tan\delta$ of the isotropic quenched ($\chi = 0.39$) and slow-cooled ($\chi = 0.63$) materials. For comparison we have also shown the data for a sample of $\chi = 0.21$ which was prepared by quenching a very thin (0.3 mm) sheet from the melt to room temperature. Within the present crystallinity range only the β(110°C) and γ (about 30°C) relaxation peaks are observed, with the possibility of a small contribution from the α process appearing on the high temperature side of the β process for the highly crystalline ($\chi = 0.63$) sample. We also see from *Figure 4* that $\tan\delta$ at the β and γ relaxations decreases with increasing crystallinity in a manner similar to that revealed by dynamic torsional studies[1–3]. An interesting feature in the modulus, which was also observed in torsional work, is that below the γ relaxation E decreases with increasing crystallinity but the trend is reversed at higher temperature.

Mechanical anisotropy of drawn materials

We first consider the quenched samples ($\chi = 0.39$). *Figures 5a–5c* show the variation of E with draw ratio at −80°, 60° and 130°C, respectively. Below the γ relaxation the pattern of mechanical anisotropy is very simple, with $E_0 > E_{45} > E_{90}$. This anisotropy can be attributed to the overall chain orientation, with the much higher E_0 arising

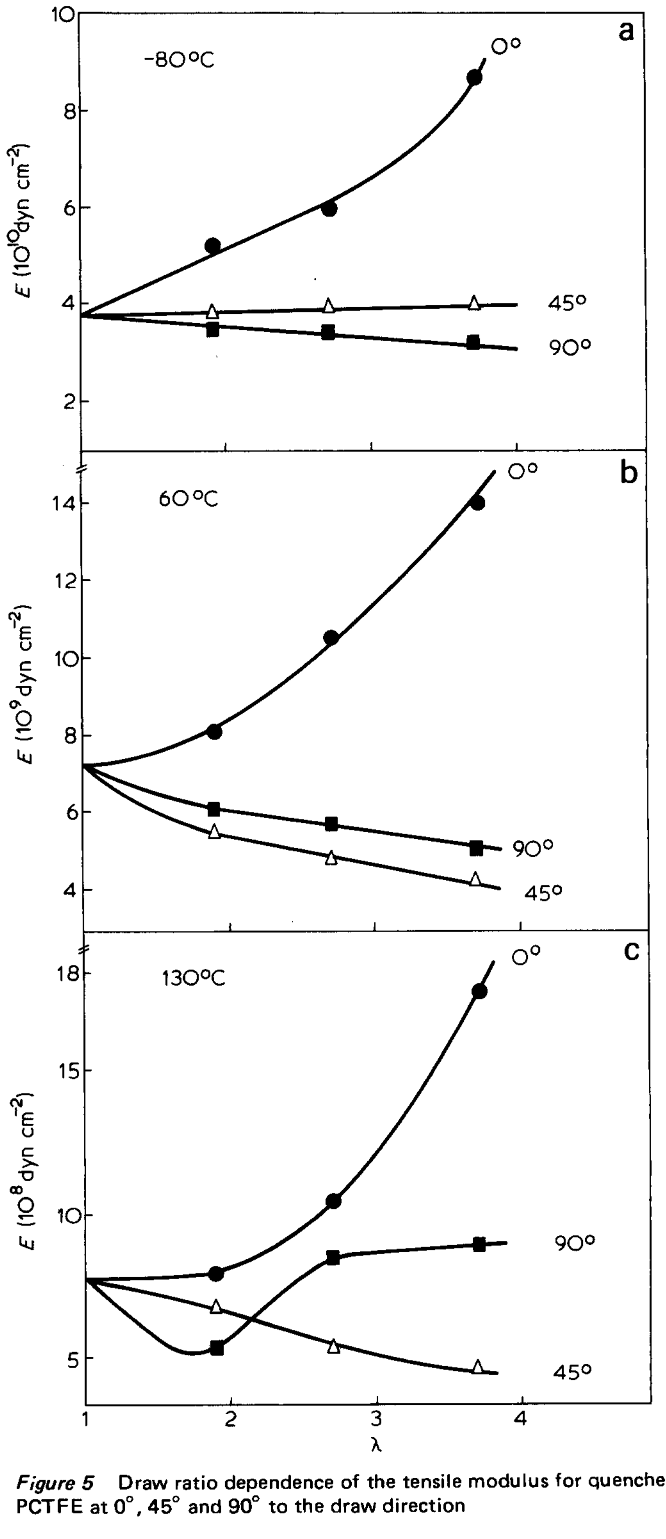

Figure 5 Draw ratio dependence of the tensile modulus for quenched PCTFE at 0°, 45° and 90° to the draw direction

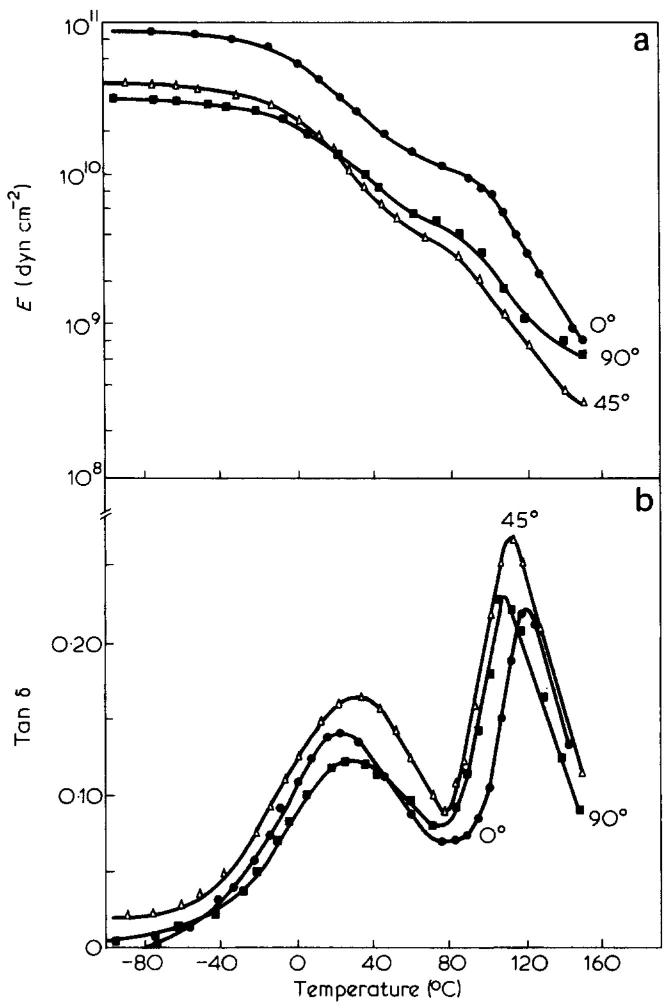

Figure 6 Temperature dependence of the (a) tensile modulus and (b) loss tangent for quenched PCTFE (χ = 0.39) which has been drawn to λ = 3.7. 0°, 45° and 90° denote the angle between the tensile axis and draw direction

from the greater strength of the covalent bonds. However, on going through the γ relaxation E_{45} drops faster than E_{90} (see also *Figure 6*) so that the pattern becomes $E_0 > E_{90} > E_{45}$ above 20°C. There is also a further drop in E_{45} relative to E_{90} at the β relaxation. These results, together with the fact that $\tan\delta_{45} > \tan\delta_0 \geqslant \tan\delta_{90}$ at the two relaxations, suggest that a shear process is operating above room temperature, and *a priori* it could be attributed to either shear on planes parallel to the *c*-axis (*c*/*c* shear) or interlamellar shear. Since Hashimoto *et al.*[15] have shown that no crystalline lamellae are present in the quenched materials *c*/*c* shear seems to be the more probable mechanism.

It is also seen from *Figures 4b* and *6b* that while the β peaks in $\tan\delta_{45}$ and $\tan\delta_{90}$ are located at the same temperature as that for the isotropic material the peak in $\tan\delta_0$ is shifted upwards by about 10°C. This shift to higher temperature reflects the reduction in molecular mobility in the amorphous region, which arises from chain orientation and the presence of strained tie molecules between the crystallites. Similar feature has been observed in other polymers such as poly(ethylene terephthalate)[1,20]

Figure 7 shows that the slow-cooled sample (χ = 0.63) exhibits similar mechanical anisotropy as the quenched material but the magnitude of the β peaks are much lower because of the smaller proportion of amorphous regions. Since lamellae are present in this material the occurrence of an interlamellar shear process cannot be ruled out. However, the activation of such a shear process would be considerably hindered by constraints imposed on the amorphous regions by molecular orientation and interlamellar tie molecules.

Mechanical anisotropy of annealed materials

Annealing removes constraints in the interlamellar regions and thus produces changes in the patterns of mechanical anisotropy (*Figures 8–11*). For the low-crystallinity samples E_{45} is lower than E_0 and E_{90} throughout the whole temperature range. However, the most interesting feature is the crossover between E_0 and E_{90} at the β relaxation (about 120°C) for all the samples except the high-crystallinity sample annealed at 190°C, for which E_0 is still slightly higher than E_{90} at 160°C. Probably for the latter sample the annealing temperature is not high enough to remove all the contraints imposed by interlamellar ties.

Takayanagi[6] has proposed a model to explain the mechanical anisotropy of drawn and annealed materials. In this model the amorphous region is assumed to be in series with the crystalline region along the draw direction, while in the perpendicular direction the two regions are in parallel. The modulus along the draw direction E_0 is expected to have a large drop at the major relaxation (the β relaxation

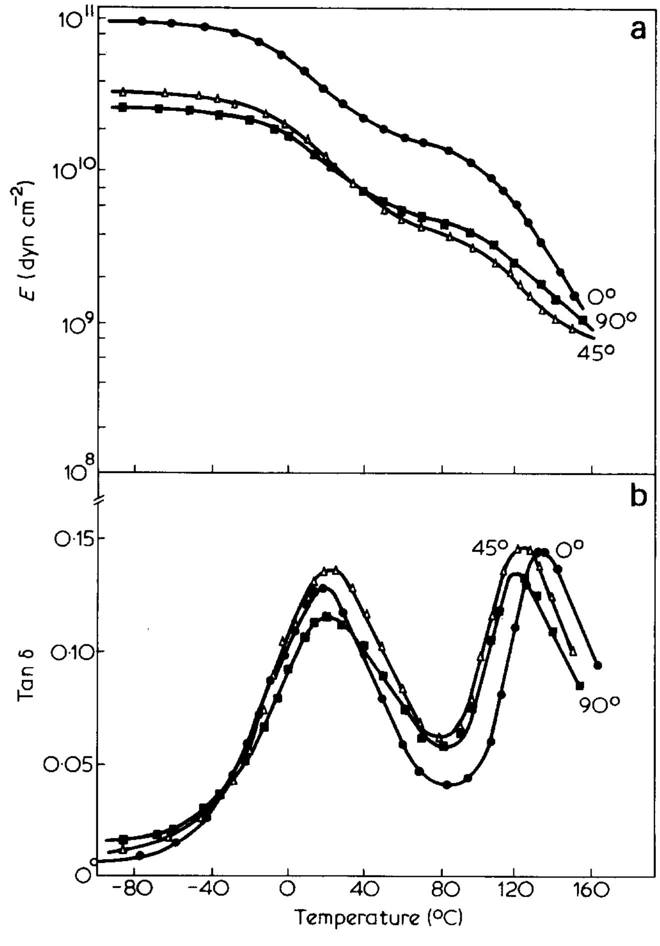

Figure 7 Temperature dependence of the (a) tensile modulus and (b) loss tangent for slow-cooled PCTFE (χ = 0.63) which has been drawn to λ = 4

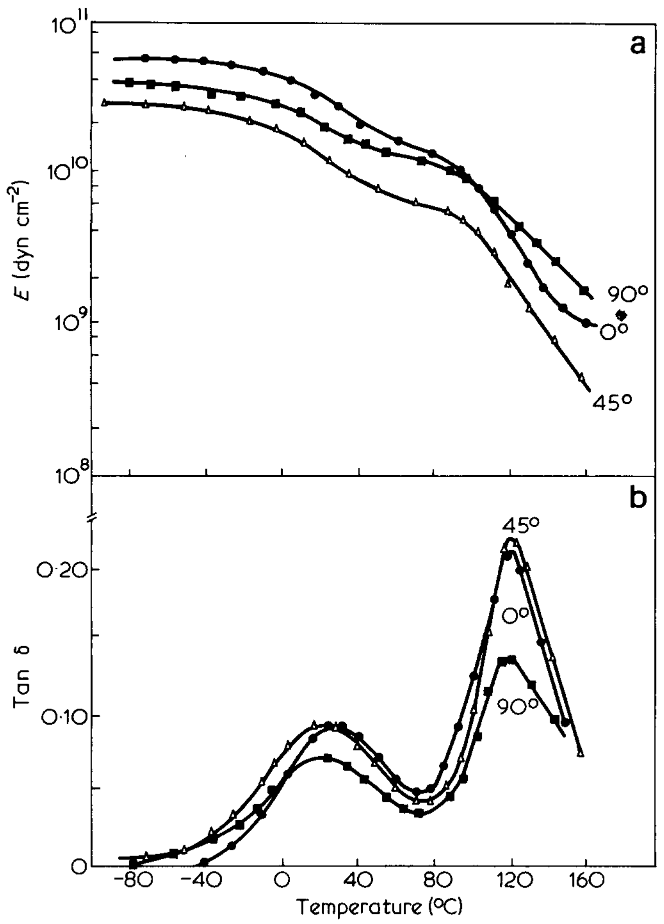

Figure 8 Temperature dependence of the (a) tensile modulus and (b) loss tangent for quenched PCTFE which has been drawn to λ = 3.7 and then annealed taut at 190°C

in the present case) since above this relaxation the modulus of the amorphous region becomes very small. In the perpendicular direction the fall in modulus is less pronounced since the crystalline region still supports the applied stress. Thus the model predicts that while at low temperature $E_0 > E_{90}$ there is a crossover at the β relaxation, in agreement with our results (*Figures 8a, 9a,* and *11a*).

Ward[21] has pointed out that in order to convert the Takayanagi model to a three-dimensional model, shear strains as well as tensile strains must be taken into account. This has indeed been done in the interlamellar shear model of Davies *et al.*[11]. Assuming that the lamellar plane normals are distributed symmetrically about the draw direction, they have derived the following expression:

$$\frac{\tan\delta}{E} = (1-\chi)J''_a\,\overline{\sin^2\gamma\cos^2\gamma} \qquad (1)$$

where J''_a is the imaginary part of the shear compliance of the interlamellar material, γ is the angle between the applied stress direction and the lamellar plane normal and the bar denotes average over all lamellar planes.

Since we expect annealing to produce a lamellar texture with relaxation of interlamellar ties, the interlamellar shear process should be activated especially at the β relaxation, which is associated micro-Brownian motion in the amorphous regions. However, in order to make a quantitative comparison between our mechanical data and equation (1) one would have to obtain the distribution of the lamellar planes from low-angle X-ray measurements. Unfortunately, this is not possible because, as mentioned previously, no low-angle X-ray patterns have been observed for our samples. Nevertheless, as shown in *Table 1* for the three well-annealed samples, the anisotropy of $\tan\delta/E$ at the β relaxation is similar to those observed at the β relaxation of oriented low-density polyethylene and the α relaxation of oriented high-density polyethylene, which have been attributed to interlamellar shear processes[11]. We therefore assume that for the annealed PCTFE samples the distribution of the lamellar plane normals are cylindrically symmetric about the draw direction, and proceed to analyse the data according to equation (1). The function

$$\overline{\sin^2\gamma\cos^2\gamma}$$

has been calculated[11] in terms of θ, the angle between the lamella normal and the draw direction, for the two following cases: (i) all the lamellae normals lie at the same angle $\theta = \theta_0$; (ii) the lamellae normals are uniformly distributed between $\theta = 0$ and $\theta = \theta_0$. Assuming case (i) our data are consistent with the interlamellar shear model if $\theta_0 = 21°$ for the low-crystallinity samples annealed at 190°C and 205°C and $\theta_0 = 25°$ for the high-crystallinity sample annealed at 205°C. Assuming case (ii) the corresponding values for the low and high-crystallinity samples are 29° and 38°, respectively. These values are also quite similar to those for low and high-density polyethylene.

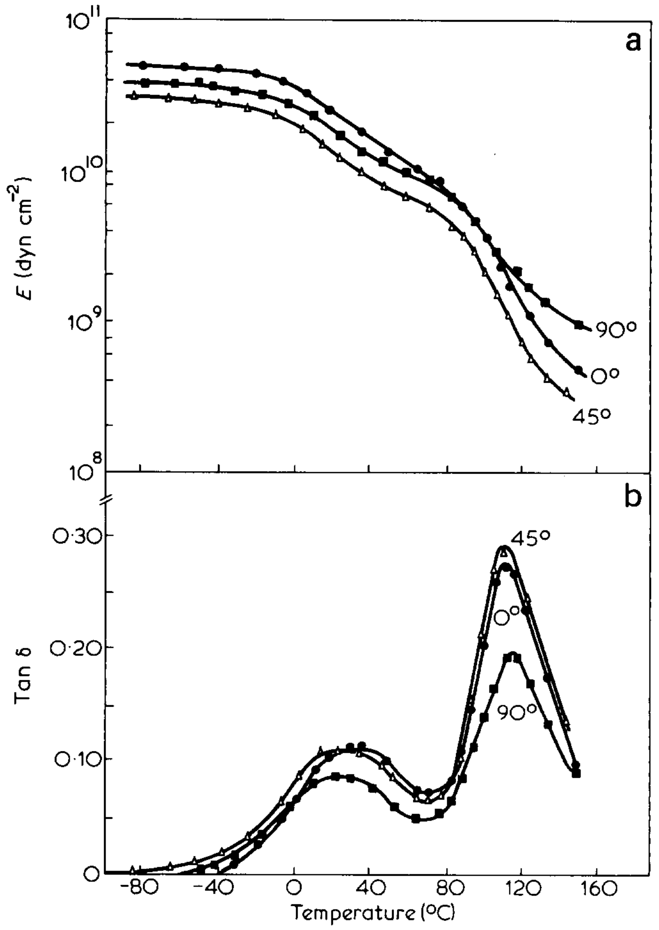

Figure 9 Temperature dependence of the (a) tensile modulus and (b) loss tangent for quenched PCTFE which has been drawn to λ = 3.7 and then annealed free at 205°C

Table 1 Tensile modulus (E) and loss ($\tan\delta$) for drawn and annealed PCTFE measured at the β peak

	Crystallinity 0.39 Annealed at 190°C			Crystallinity 0.39 Annealed at 205°C			Crystallinity 0.63 Annealed at 205°C		
	0°	45°	90°	0°	45°	90°	0°	45°	90°
$\tan\delta$	0.20	0.21	0.14	0.27	0.28	0.19	0.18	0.16	0.14
E (10^{10} dyn cm^{-2})	0.38	0.18	0.48	0.18	0.10	0.23	0.27	0.20	0.30
$\tan\delta/E$	0.53	1.2	0.29	1.5	2.8	0.83	0.67	0.80	0.47
Relative $\tan\delta/E$	1	2.3	0.55	1	1.9	0.55	1	1.2	0.70

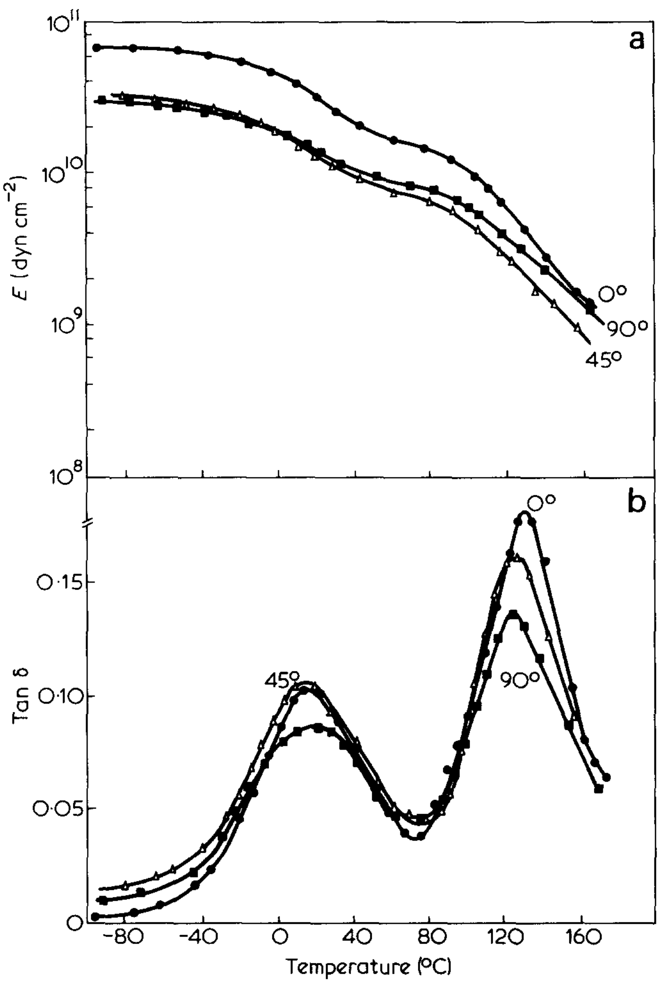

Figure 10 Temperature dependence of the (a) tensile modulus and (b) loss tangent for slow-cooled PCTFE which has been drawn to λ = 4 and then annealed taut at 190°C

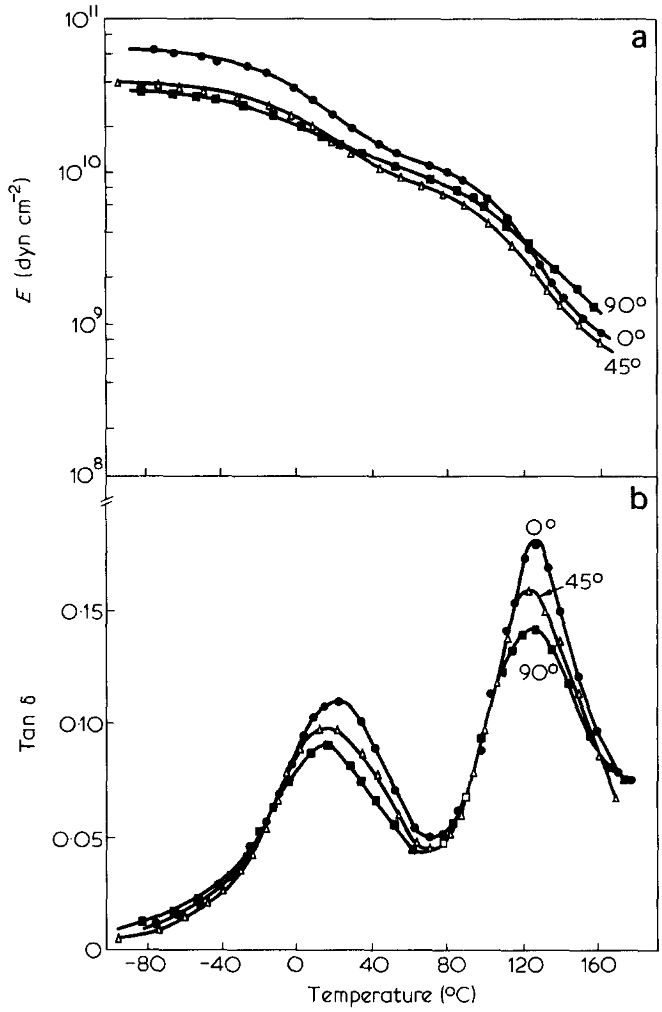

Figure 11 Temperature dependence of the (a) tensile modulus and (b) loss tangent for slow-cooled PCTFE which has been drawn to λ = 4 and then annealed free at 205°C

We also note that equation (1) predicts that $\tan\delta/E \propto 1 - \chi$. The crystallinity of our two samples ($\chi = 0.39$ and $\chi = 0.63$) remains roughly unchanged after annealing for 3 min at 205°C, so the $1 - \chi$ ratio is $(1 - 0.39)/(1 - 0.63) \simeq 1.7$. As seen from *Table 1* the observed $\tan\delta/E$ values for the low-crystallinity sample are about 1.8 to 3.5 times that for the high-crystallinity sample. Although not in quantitative agreement with equation (1) the results are certainly of the right order of magnitude, and the poor agreement may arise either from the idealized nature of the model or that J''_a decreases somewhat with increasing crystallinity (see equation (1)).

The mechanical anisotropy at the γ relaxation is not consistent with the simple model for interlamellar shear. The nature of this relaxation is expected to be more complicated since, as mentioned previously, it is associated with motion in both the amorphous and crystalline regions.

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