Letters

Dielectric relaxation in polychlorotrifluoroethylene

Previous work on polychlorotrifluoroethylene (PCTFE) has revealed three main relaxations [1-5], the α being associated with crystalline regions, the β with disordered regions and the γ arising from crystalline (γ_c) and amorphous (γ_a) regions. However, the α relaxation was considered to arise partly [5] or largely [1] in the fold surfaces of the chain folded lamellae and not entirely in their interior. In order to clarify the mechanisms of relaxation measurements have been made on specimens arranged as shown in Fig. 1.

Specimen (a) was a disc (≏ 51 mm diameter by 0.6 mm thick) cut from a compression moulded sheet which had been heated to 250° C and then drawn to a ratio of about 4:1 by extension at about 208° C and subsequently isothermally crystallized (whilst held under extension) in the manner for a 0.80 specimen as designated by Scott *et al* [1] (i.e. crystallized for 1 day at 200° C, 1 day at 190° C and 3 days at 180° C and cooled to room-temperature giving a specimen of nominal crystallinity of about 80%). The presence of orientation was checked with wide angle X-ray photographs (Fig. 2) and the degree of crystallinity was checked by density measurements. The specimen was coated with silver paint to give a three-terminal guarded-electrode system. Specimen (b) (of Fig. 1) was prepared by cutting strips 2 mm wide from the same sheet, turning them through 90° and placing them side by side to give a specimen of the required size with the draw direction as shown. The surfaces were smoothed and were then coated with silver paint to give a similar three-terminal guarded-electrode system. Each specimen was examined by placing it in a shielded electrode assembly with a brass electrode system matching the electrodes on the specimens and with chimneys surrounding the outgoing leads so that the assembly could be immersed in an oil bath at constant temperature (± 0.5° C). Measurements were made over a range of frequency using a G.R. 1615A Capacitance Bridge at a series of temperatures from room to 200° C and the results are shown in Fig. 3, including data obtained on unoriented specimens of similar crystallinity (80%). Since the dipole moment of PCTFE is perpendicular to the chain (*c*-) axis a significant anisotropy would be expected if the relaxation arose mainly in the interior of the lamellae but little anisotropy if it arose in the folds at the surfaces of lamellae.

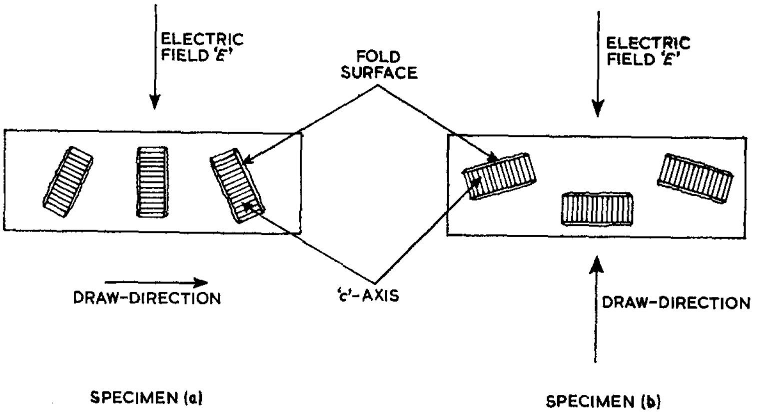

Figure 1 Relationship between the draw-directions of PCTFE specimens (a) and (b) and the applied electric field *E*.

A marked anisotropy is observed in Fig. 3 with appreciably larger values of loss peak and relaxation magnitude ($\epsilon_S - \epsilon_\infty$) for the α-relaxation for specimens with the draw direction perpendicular to the applied electric field than those for the draw direction parallel to the field. The magnitude of the loss peaks for the unori-

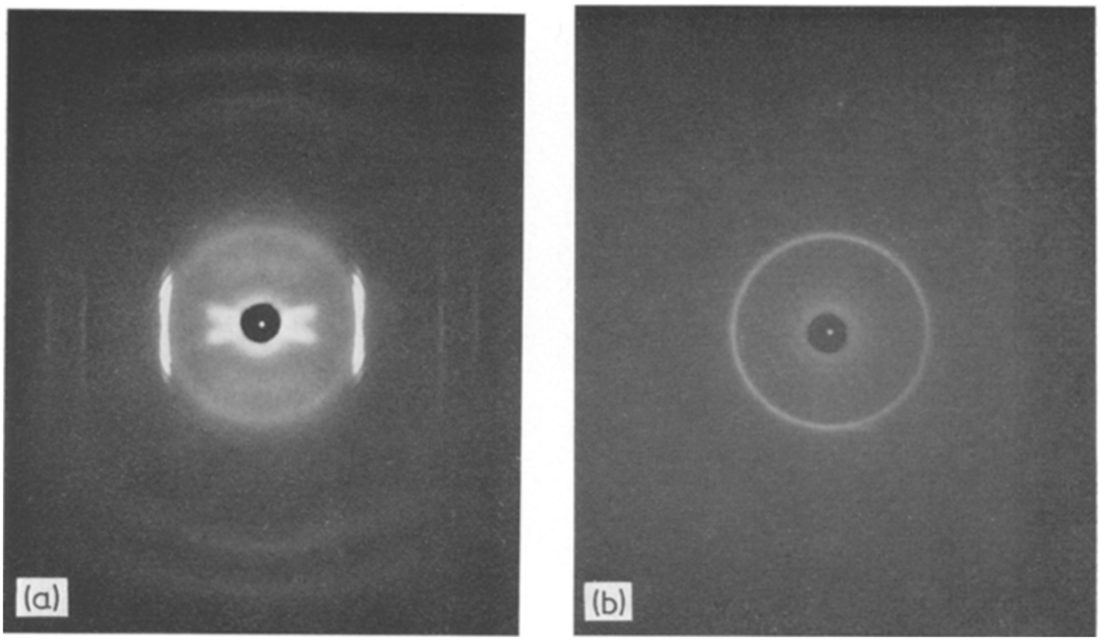

Figure 2 Flat plate wide angle X-ray photographs of (a) specimen (a) with draw-direction vertical, (b) Unoriented 0.80 specimen.

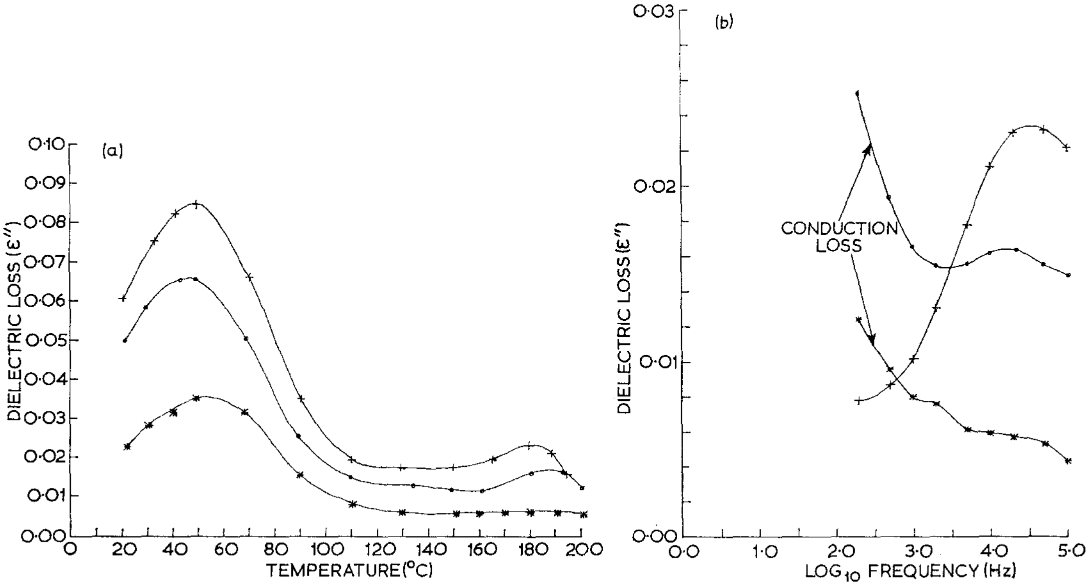

Figure 3 (a) Plots of loss factor ϵ'' at 10 kHz against temperature for PCTFE specimens of nominal crystallinity 80 ± 2%: + Specimen (a) with draw-direction perpendicular to the electric field; ○ Unoriented disc; * Specimen (b) with draw-direction parallel to the electric field. (b) Plots of loss factor ϵ'' against $\log_{10}$ frequency for PCTFE specimens of nominal crystallinity 80 ± 2%: + Specimen (a) at 188 °C with draw-direction perpendicular to the electric field; ○ Unoriented disc at 193 °C; * Specimen (b) at 190 °C with draw-direction parallel to the electric field.

ented specimens were intermediate between those for the different draw directions. This shows that the α-relaxation arises mainly from the interior of the lamellae in specimens of nominally 80% crystallinity with little contribution from the chain folds. (A similar conclusion has been found for low-density polyethylene [6]). A similar anisotropy is observed for the γ-relaxation but this may arise to a small extent from changes in the γ_a component from oriented amorphous regions as well as from changes in the γ_c component.

Some measurements have also been made on unoriented PCTFE specimens of about 75 to 80% crystallinity after annealing for various times up to 10^5 min at 200°C in order to thicken the lamellae. Despite some inconsistencies the activation energy for the α-relaxation showed a definite trend of increasing as annealing time increased, from 2.3 to 3.0×10^5 J mol^{-1}, but there was no marked change in $\epsilon_S - \epsilon_\infty$. These effects are consistent with the above conclusion. The results will be used in order to test existing theory [5] assuming that this relaxation arises mainly in the interior of lamellae. The activation energy for the γ-relaxation was little affected by annealing at this temperature.

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Anisotropic electrochemical concentration cell: a system based on oriented β-alumina ($NaAl_{11}O_{17}$) as solid electrolyte

As a by-product of our interest in the electron microscopic [1] studies of layered solids and measurement of ionic migration in organic solids [2], we have been led to a brief investigation of a novel electrochemical cell in which the concentration difference occurs not in the electrolyte compartments, as is generally the case, but in the electrodes. The cell is based on β-alumina (composition close to $Na_20.11Al_2O_3$) the material now used in the high-power output, sodium-sulphur secondary battery developed at the Ford Motor Company [3-5] and elsewhere [6, 7].

The crystal structure [8, 9] of β-alumina (Fig. 1) reveals its unusual properties. The hexagonal solid has the lattice constants $a_0 = 5.58$ and $c = 22.45$Å. Parallel to the basal plane of the hexagonal cell are sheets of atoms arranged such that four layers of oxygens are in cubic closest packing. These spinel-like blocks, within which the Al atoms occupy both octahedral and tetrahedral holes, are spaced well apart by Al-O-Al columns and within the inter-spinel spaces the Na^+ ions are arranged amongst a set of nearly equivalent sites. The Na^+ ions are, consequently, exceptionally mobile which accounts for the very high (ionic) conductivity [6] of β-alumina.

We argued that if a single crystal of β-alumina were used as a conducting medium sandwiched between two electrodes each consisting of an inert metal immersed in an aqueous solution of Na^+ ions, then an emf could be generated, provided there is a concentration (strictly "activity") difference between the electrodes. This emf, which is proportional to the logarithm of the activities, should, however, be produced only when the crystal is oriented so as to permit ready migration of Na^+ ions along the basal planes from one electrode to the other. On turning the crystal through a right-angle, the emf should vanish because Na^+ migration is impossible along the *c*-direction of the solid electrolyte. This is indeed observed and the salient details of the experiment now follow.

The β-alumina used was obtained (via Mr K. Williams) from commercially available, fused, cast bricks. These bricks fracture readily, and, with care, single crystals of up to 1 cm diameter and a few mm in thickness may be extracted. The following concentration cell was set up: