JOURNAL OF MATERIALS SCIENCE 9 (1974) 1099–1103

Dielectric relaxation in polychlorotrifluoroethylene

M. E. BAIRD, P. BLACKBURN
Department of Applied Physics, UWIST, Cardiff, UK

The effect of increasing lamellar thickness in bulk polychlorotrifluoroethylene (PCTFE) by various methods (annealing and increasing time and temperature of crystallisation) on the parameters of the α and γ relaxations has been studied.

For the α relaxation a consistent increase in temperature of maximum loss and activation energy with increasing lamellar thickness confirms the strong suggestion of earlier work [6] on oriented specimens and shows that the α relaxation arises mainly in the interior of the lamellae with little contribution from the chain folds.

No systematic changes in these parameters with increasing lamellar thickness was found for the γ relaxation and this is explained by the presence of γ_c and γ_a components in crystalline and amorphous regions respectively. The component γ_a (as well as the γ_c one) shows a marked anisotropy in magnitude with respect to the draw direction in oriented specimens relative to the direction of the applied electric field. This implies a "lining up" of the chain molecules parallel to one another in amorphous regions.

The non-existence of analogous short chain compounds and experimental scatter prevented detailed checking of the consistency of the data for the α relaxation with the theory for the $\alpha_c - C_c$ model [5].

1. Introduction

Previous work on polychlorotrifluoroethylene (PCTFE) has revealed 3 main relaxations [1-5]. These consist of the α, β and γ processes arising in descending order of temperature (at a given frequency). The α relaxation has been shown to be associated with crystalline regions, the β with disordered regions and the γ arising from crystalline (γ_c), and amorphous (γ_a) regions. However, the exact nature of the α relaxation has been in doubt. It was considered to arise partly [5] or largely [1] in the fold surfaces of chain folded lamellae and not entirely in their interior.

Preliminary measurements of ours with oriented specimens [6] showed a marked anisotropy with the α relaxation, strongly suggesting that the α relaxation arises mainly in the interior of the chain folded lamellae (in specimens of 80% crystallinity) with little contribution from chain folds. Recent work [7, 8] on single crystals suggests that the folds in bulk polymer specimens may be fairly loose and with lamellae of about 500 Å thick in PCTFE, the folds may then contain an appreciable number of carbon atoms. Even though there might be a slight preferred orientation in the folds, we would expect virtually normal segmented motion, so that even in the oriented specimens the distribution of dipole rotation axes will probably be reasonably random. This should then give little or no anisotropy to the α relaxation. Moreover, such motion is more likely to be involved in the β relaxation than the α. Even if the folds are relatively "tight", the most likely motion of the folds is "waggling" out of their plane and assuming one central and two side equilibrium positions, then a movement from the central position to either of the two side positions involves changes in dipole moment along the c-axes of the lamellae and along random directions in the planes at right angles to the c-axes. Although the equivalent changes along three axes at right angles may not be exactly equal, it seems likely that any anisotropy observed would be small, in contrast to the experimental findings. However, it is impossible to be precise, but experimental data described in this paper will show the increase of the activation energy ΔH and temperature of maximum loss $T_{\max}$ (at a given frequency) for the dielectric α relaxation with increasing lamellar thickness, as obtained by annealing, by crystallization at increasingly higher temperatures and by crystallization for progressively longer times at a high temperature. These confirm the strong suggestion of the orientation work and show that the α relaxation arises mainly in the interior of the lamellae (e.g. as in Fig. 1) with little contribution from the chain folds, since relaxation arising from chain fold motion (α_c – C_f model) should yield ΔH and T_{max} values independent of lamellar thickness [5].

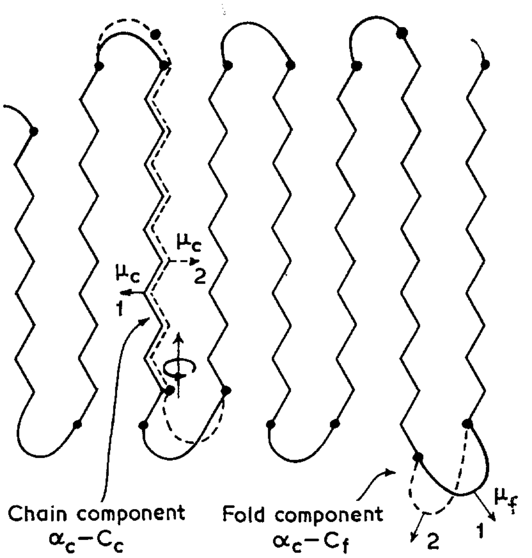

Figure 1 Model for process $\alpha_c - C$ (slightly rough fold surface and independent interior chain and fold motions). From Hoffman *et al.* [5].

2. Experimental and discussion

The polymer used was Kel F 81, Grade 3, KF 6060, of purity 99.9 % and with a number average molecular weight $\overline{M}n$ of approx. 190 000 supplied by Minnesota Mining and Manufacturing Co Ltd. Except when otherwise stated, unoriented disc specimens approximately 51 mm in diameter by 1.5 mm thick were used. Thermal treatment of the disc specimen was carried out whilst immersed in silicone oil in small trays in an air oven. Each specimen was cleaned with carbon tetrachloride and the electrodes were applied and measurements made with a G.R. 1615A Capacitance bridge as described previously [6].

2.1. α relaxation

2.1.1. Effect of annealing

The PCTFE specimens were crystallised at 170° C for one week after cooling from the melt and subsequently annealed at 200° C for various times up to 10^5 min. The actual crystallinity of the samples ranged between 70 and 80% as evaluated by density measurements [8a]. Typical data shown in Fig. 2 indicate a small but definite increase in T_{max} with annealing time. (Average rate of change 7 × 10^{-5}° C min^{-1}.) Correspondingly, plots of loss factor against log frquency at an approximately constant test temperature show that the frequency of maximum loss f_m decreases with increasing annealing time.

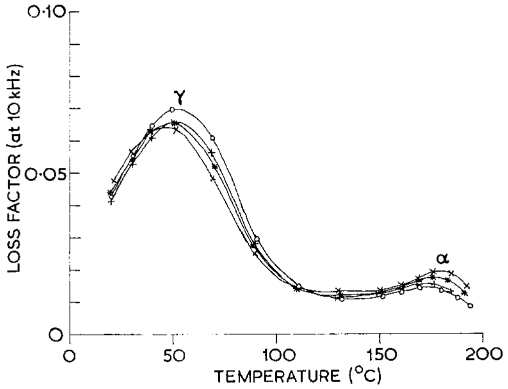

Figure 2 Loss factor (at 10 kHz) versus temperature (° C) for specimens annealed at 200° C for different times (after crystallization at 170° C for one week). (○) no annealing; (+) 10^3 min; (∗) $10^{3.7}$ min; (×) 10^5 min. Crystallinity 70 to 80%.

2.1.2. Effect of temperature of crystallization

Specimens were crystallized for one week (after cooling from the melt) at various temperatures ranging from 160 to 200° C. The results are shown in Fig. 3. The temperature of maximum loss increases quite significantly with rising crystallization temperature and hence with increasing lamellar thickness. The crystallinity of the specimens ranged between 66 and 80%. Plots of loss factor against log frequency for the different specimens at a given test temperature showed a corresponding decrease of frequency of maximum loss f_m with increasing crystallization temperature.

2.1.3. Effect of time of crystallization

Samples were crystallized for different times at

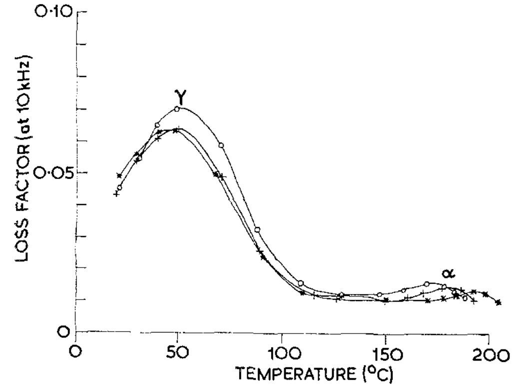

Figure 3 Loss factor (at 10 kHz) versus temperature (°C) for specimens crystallized for one week at different temperatures. (○) Isothermally crystallized at 160°C; (+) isothermally crystallized at 190°C; (*) isothermally crystallized at 200°C. Crystallinity 66 to 80%.

200° C after cooling from the melt and typical data are shown in Fig. 4. The crystallinity of the specimens ranged between 55 and 80%. The results show a definite increase in T_{max} with rising time of crystallization (note that the peak for 1700 min specimen, with a crystallinity of 55%, is largely a β peak). Correspondingly, plots of loss factor against log frequency at an approximately constant test temperature for the different specimens showed a definite fall in frequency of maximum loss f_m with increasing crystallization time.

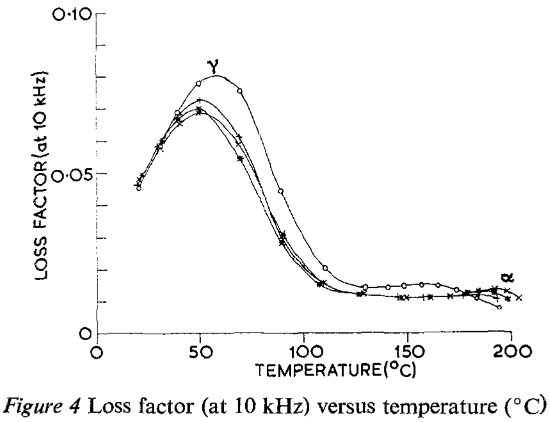

Figure 4 Loss factor (at 10 kHz) versus temperature (°C) for specimens crystallized for different times at 200°C. (○) Crystallized for 1700 min; (+) crystallized for 2850 min; (*) crystallized for 5250 min; (×) crystallized for 8500 min. Crystallinity 55 to 80%.

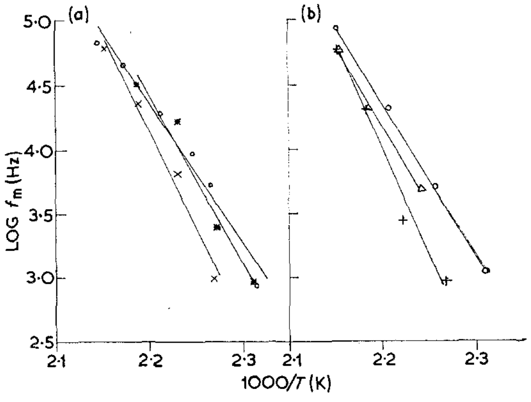

Figure 5 (a) Plots of log $_{10}$ (f_m) versus 1000/T(K) for the α relaxation in specimens annealed for different times: (○) 0 min; (*) 10^4 min; (×) 10^5 min. (b) Plots of log $_{10}$ (f_m) versus 1000/T(K) for the α relaxation in specimens crystallized at different temperatures; (○) 170°C; (△) 180°C; (+) 190°C.

2.1.4. Loci plots

Plots of log frequency of maximum loss f_m against 1000/T (T being the temperature on the Kelvin scale) are shown in Fig. 5, for the first two methods of inducing changes in lamellar thickness. The frequency of maximum loss was obtained by interpolation between the experimental data of loss factor versus log frequency (using the computer) and the straight lines drawn through the corresponding points in Fig. 5 were those obtained by the method of least squares fit. The activation energies ΔH were calculated as

$$-2.303\,R\left[\frac{\mathrm{d}\log_{10}f_m}{\mathrm{d}(1/T)}\right]$$

and clearly ΔH increases with increasing annealing time and with rising crystallization temperature. The effect of annealing time is shown in more detail in Fig. 6 which includes data from two different sets of samples. Clearly ΔH increases significantly for the α relaxation (but there is no change in the activation energy for

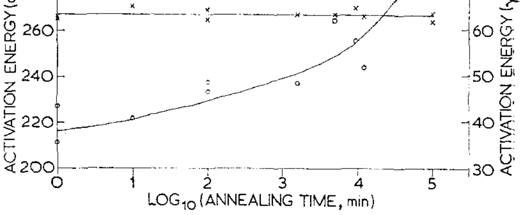

Figure 6 Plots of experimental activation energy ΔH versus $\log_{10}$ (annealing time in min) for the α (○) and γ (×) relaxations. Crystallinity 70 to 80%.

the γ relaxation. This is discussed in more detail later on).

The data for the different times of crystallization at 200° C were not sufficiently well resolved in plots against log frequency to allow a plot of $\log f_m$ against $1000/T$ to be drawn.

2.1.5. *Measurements of lamellar thickness*

Low-angle X-ray measurements were made with a Kratky slit collimated camera and after slit height correction the Bragg equation was applied to the small angle peak and the resulting spacing taken as a measure of the average periodicity [10, 11]. Certain difficulties arise in relating this periodicity to the lamellar thickness and in view of this we have assumed that the low angle spacing d is a rough measure of lamellar thickness [9]. In Figs. 7 and 8 are shown the variation of temperature of maximum loss T_{max} with log d and the variation of ΔH with d.

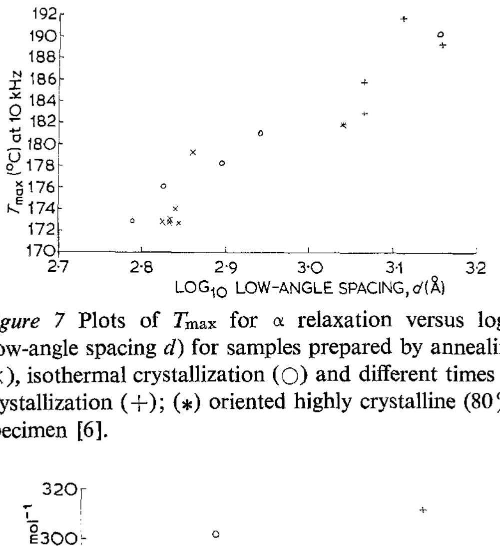

Figure 7 Plots of T_{max} for α relaxation versus $\log_{10}$ (low-angle spacing d) for samples prepared by annealing (×), isothermal crystallization (○) and different times of crystallization (+); (∗) oriented highly crystalline (80%) specimen [6].

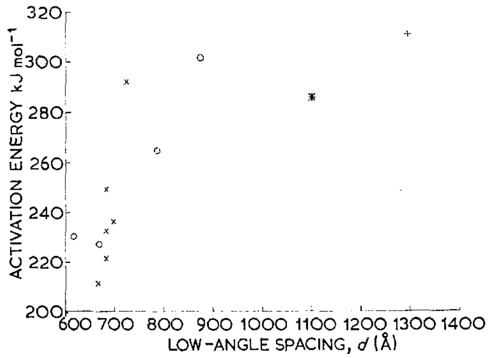

Figure 8 Plots of experimental activation energy ΔH for α relaxation versus low angle spacing d for samples prepared by annealing (×), isothermal crystallization (○) and different times of crystallization (+); (∗) oriented highly crystalline (80%) specimen [6].

In Fig. 7 each method of increasing lamellar thickness gives rise to an increase of T_{max} within the limits of experimental error. Despite some scatter in the data, there is clearly a significant increase in T_{max} with log d and a reasonable correlation between the data for the three methods of increasing lamellar thickness. However, the scatter in the data does not allow accurate curve fitting for checking for consistency with the theory for the $\alpha_c - C_c$ model [5] or for assessing whether chain twisting is occurring. Similarly, in Fig. 8, due to experimental errors and difficulties in assessing slopes of the plots of $\log f_m$ against $1000/T$, the experimental errors in ΔH are appreciable (about ± 10%). However, the correlation coefficient between the data is 0.78 which is significant at the 1% level. Thus, despite the scatter in the data, due probably to the comparatively large error in ΔH, there is a clear relationship between the variables, ΔH increasing as spacing d is made larger.

Thus the gross changes observed in T_{max} and ΔH are consistent with the $\alpha_c - C_c$ model [5] but the scatter in the experimental data precludes any detailed checking. Further measurements on single crystals of PCTFE might yield results with less experimental scatter and which perhaps could be analysed in a more detailed fashion. This work is at present being attempted.

2.2. γ relaxation

The loss peaks for the γ relaxation previously shown in Figs. 2 to 4 show little or no systematic changes (apart from a fall in magnitude due to increasing crystallinity) with the varying parameters (i.e. annealing time, or time or temperature of crystallization), and similarly in Fig. 6 the activation energy ΔH for the γ relaxation is quite unaffected by annealing time. This behaviour almost certainly arises because the γ relaxation consists of overlapping components from the crystalline (γ_c) and amorphous (γ_a) regions. The γ_a component gives a peak at a slightly higher temperature (T_{max}) at a given frequency than the γ_c one and similarly it has a slightly higher activation energy than the γ_c component. In the various methods used for thickening the lamellae the crystallinity and proportion of γ_c component increases somewhat as the lamellar thickness increases with a probable increase in T_{max} and ΔH for the γ_c component but at the same time the proportion of γ_a component (with a higher T_{max} and ΔH than for the γ_c component) is being reduced. Thus one may expect to see little change in $T_{\max}$ or ΔH for the overall γ relaxation as observed. To check on consistency of the behaviour of $T_{\max}$ and ΔH as the lamellar thickness increases with the predictions of the γ_c – A model [5] measurements will have to be made on single crystals of PCTFE. This work is at present being attempted in our laboratory.

Data presented in previous work [6] clearly showed the anisotropy of (mainly) the γ_c component as would be expected from the γ_c – A model [5]. Measurements made in a similar way on oriented specimens of PCTFE of relatively low crystallinity ($\approx$ 35%) also showed a marked anisotropy (Fig. 9) in what must be mainly the γ_a component. This is consistent with a "lining up" of the molecular chains in amorphous regions with orientation. This is also supported by a definite anisotropy observed with the dielectric β relaxation (Fig. 9).

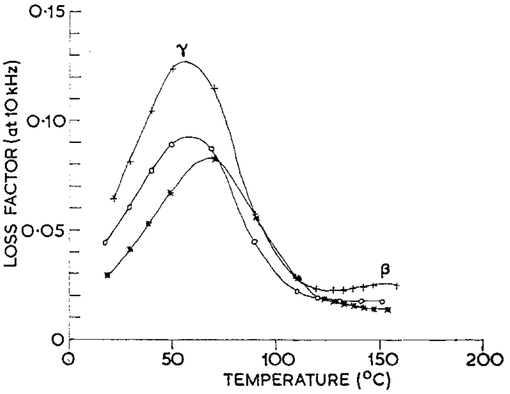

Figure 9 Loss factor (at 10 kHz) versus temperature (°C) for isotropic (○) and drawn specimens with draw direction perpendicular (+) and parallel (∗) to the applied field. Crystallinity approximately 35%.

3. Conclusions

The increase in temperature of maximum loss $T_{\max}$ and activation energy ΔH for the α relaxation with increasing lamellar thickness in bulk PCTFE confirm the strong suggestion of earlier work on oriented specimens [6] and show that the α relaxation arises mainly in the interior of the lamellae (e.g. α_c – C_c model [5]) with little contribution from the chain folds. Experimental scatter in the data prevents detailed checking of the consistency of the experimental data with the theory for the α_c – C_c model.

No systematic changes in the behaviour of $T_{\max}$ and ΔH are found with increasing lamellar thickness for the γ relaxation because of the presence of γ_c and γ_a components. Both γ_c and γ_a components showed a marked anisotropy in magnitude with respect to the orientation direction relative to the applied electric field. For the γ_a component this indicates a "lining up" of the molecular chains parallel to one another in the amorphous regions.

A more detailed check on the theoretical models (e.g. α_c – C_c and γ_c – A) [5]) may be possible with data from single crystals of PCTFE which might give less experimental scatter. This work is at present being attempted.

References

1. A. H. SCOTT, D. J. SCHEIBER, A. J. CURTIS, J. I. LAURITZEN, JUN. and J. D. HOFFMAN, *J. Res. Nat. Bur. Stand.* **66A** (1962) 269.
2. S. I. REYNOLDS, V. G. THOMAS, A. H. SHARBAUGH and R. M. FUOSS, *J. Amer. Chem. Soc.* **73** (1951) 3714.
3. G. P. MIKHAILOV and B. I. SAZHIN, *Sov. Phys.-Tech. Phys.* **1** (1957) 1670.
4. L. HARTSHORN, J. V. L. PARRY and E. RUSHTON, *Proc. I.E.E.* **100** 2A (3) (1953) 23.
5. J. D. HOFFMAN, G. WILLIAMS and E. PASSAGLIA, *J. Polymer Sci. C* **14** (1966) 173.
6. M. E. BAIRD and P. BLACKBURN, *J. Mater. Sci.* **7** (1972) 836.
7. A. KELLER, *Kolloid Z.* – Z. fur Polym. **231** (1969) 386.
8. F. C. STEHLING and L. MANDELKERN, *J. Polymer Sci.* B **7** (1969) 255.

8a. J. D. HOFFMAN and J. J. WEEKS, *J. Res. Nat. Bur. Stand.* **60** (1958) 465.

9. Written communication from Professor P. H. Geil, Division Macromolecular Science, Case Western Reserve Univ, Cleveland, Ohio, USA.
10. G. KORTEVE and C. G. VONK, *Kolloid Z.* – Z. fur Polym. **225** (1968) 124.
11. S. KARESH and J. M. SCHULTZ, *J. Polymer Sci. A-2* **9** (1971) 85.

Received 12 November 1973 and accepted 11 January 1974.