Anisotropy of dielectric relaxation in poly(ethylene terephthalate) fibres

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Dielectric measurements have been made on poly(ethylene terephthalate) (PET) fibres in the frequency range 0.5–10 kHz in temperature range $-120°$–$+30°$C with the applied electric field parallel and perpendicular to the fibre axis. Considerable directional anisotropy was observed in the β-relaxation process, which was independent of frequency. The observed dielectric anisotropy has been related to the structural parameters thus leading to a value $\langle\cos^2\psi\rangle = 0.21$, where ψ is the angle between the dipole moment vector responsible for this relaxation and the molecular chain axis. Activation energy for this process in PET fibres (9 kcal/mol) was lower than that reported for PET films and extruded rods.

INTRODUCTION

Molecular orientation in natural and drawn synthetic fibres is responsible for their various physical properties. Due to the molecular orientation, anisotropy arises in various optical, electrical and mechanical properties of fibres. Anisotropy of dielectric properties of fibres has been little investigated since its first observation over two decades ago by Shaw and Windle[1]. This behaviour may provide a new method for characterizing the orientation in fibres.

The present paper describes a study of the anisotropy of dielectric properties of polyethylene terephthalate (PET) fibres in their β-relaxation region.

EXPERIMENTAL

PET fibres in the form of multifilament zero twist yarns (76 denier, 36 filaments) of draw ratio 3.92, supplied by Shri Synthetics, Ujjain, were used in this work.

Dielectric measurements at frequencies 0.5, 1, 5 and 10 kHz were carried out on a General Radio Capacitance Bridge 716 CS using a two terminal connection for the cell in the temperature range $-120°$ to $+30°$C. The cell is described in detail elsewhere[2]. Liquid nitrogen was used for cooling. The specimen compartment was filled with dry nitrogen. Temperature was measured by a thermocouple kept in close vicinity to the specimen.

In order to hold the fibres parallel and perpendicular to the test condenser plates, sample discs were prepared as described below.

Fibres wound uniformly on a rectangular frame were embedded into low density polyethylene on a compression moulding machine at 140°C to obtain air bubble-free moulds of ~1 mm thickness. A circular disc of appropriate dimensions (diameter ~1.3 cm) was cut from such a mould to serve as the sample disc with fibre axis parallel to the disc surfaces. For preparing the disc with fibres perpendicular to disc surfaces, several moulds prepared as described above were piled one over the other (keeping the alignment of fibres mutually parallel) and remoulded on the compression moulding machine into a thick block. From this mould, sections of appropriate dimensions were cut and faces were polished to obtain sample discs with fibre axis perpendicular to the disc surface.

A third sample disc of polyethylene was prepared under similar conditions. Data for this disc were used as reference for obtaining the results for fibres from the measurements on composite discs. The disc surfaces were silver coated for better electrode contact. Volume fractions of fibres in the composite discs were determined from the densities of composite discs and of their two components.

RESULTS AND DISCUSSION

Evaluation of dielectric parameters of fibres

Evaluation of the real part of the dielectric permittivity of fibres from data on the mixture is an intricate, theoretical problem and exact solution can be obtained only in some extreme cases[3,4]. The authors' recently proposed[5] empirical method for determining dielectric constant from the data in a limited range of composition of mixtures, could not be applied for these data on a single composition of the mixture However, the imaginary part of the dielectric parameters in the mixture may be described sufficiently well[6] by using the assumption that the complex dielectric permittivity is additive in the mixture. According to this

$$\epsilon_m^* = (1-\nu)\epsilon_f^* + \nu\epsilon_p^* \qquad (1)$$

where ϵ_f^*, ϵ_p^* and ϵ_m^* are complex permittivities of the fibre, polyethylene and the mixture, respectively, and ν is the volume fraction of polyethylene. Thus it can be shown that

$$(\tan\delta)_f = [(\tan\delta)_m - \nu(\tan\delta)_p](1-a)^{-1} \qquad (2)$$

where $a = \nu\epsilon_p'/\epsilon_m'$. The prime denotes the real part of the

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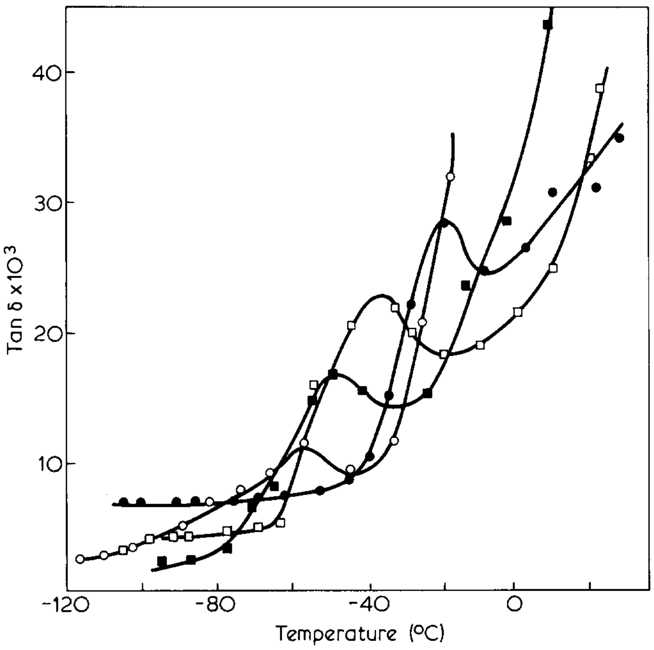

Figure 1 Variation of dissipation factor (tan δ) with temperature at different frequencies for PET fibres with applied electric field perpendicular to the fibre axis (90° case)

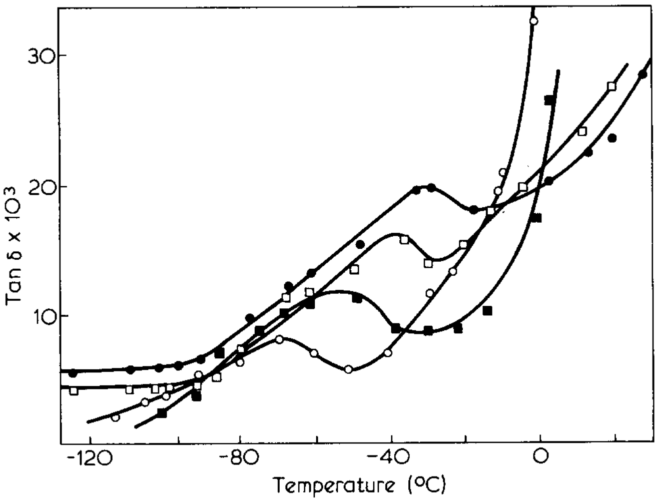

Figure 2 Variation of dissipation factor (tan δ) with temperature at different frequencies for PET fibres with applied electric field parallel to the fibre axis (0° case)

dielectric permittivity and the subscripts f, p and m have same meaning as in equation (1). It may be seen that if ϵ'_p and $(\tan\delta)_p$ were replaced by the respective quantities for air, i.e., unity and zero respectively, then the equation (2) would reduce to the form: $(\tan\delta)_f = (\tan\delta)_m$, which is generally used for air–fibre or other mixtures containing air as one of the components.

For the present case of a polyethylene – PET fibre mixture, equation (2) cannot be much simplified because $(\tan\delta)_p$ is not negligible compared with $(\tan\delta)_m$ and moreover the relaxations of both the components in the temperature range studied are overlapping. In the application of equation (2), a constant value of a based on the average value of ϵ'_m was used over the whole temperature range because the variation of ϵ'_m was very small.

Evaluation of the real part of the dielectric permittivity for fibres from these data was not possible with sufficient precision due to uncertainties in the theoretical expressions and the observed low variation in ϵ'_m. The present discussion is therefore limited to the tan δ parameter).

In *Figures 1* and *2*, values of $(\tan\delta)_f$ calculated from the present data on polyethylene and the composite discs compare well with the reported values[6–9] for PET films, thus justifying the application of equation 2 for this mixture.

Dielectric anisotropy

Figures 1 and *2* show the variation of tan δ for PET fibres (the subscript f will be dropped hereafter) with temperature when the fibre axis was perpendicular (90° case) and parallel (0° case) to the applied electric field. In both 0° and 90° cases a relaxation peak is observed, whose position shifts to lower temperature with the lowering of frequency. This peak corresponds to the already identified β-relaxation process of PET[6–9]. Furthermore, on going from the 90° case to the 0° case the following behaviour is noted at all the frequencies:

peak height $(\tan\delta_{max})$ lowers considerably,
peak shifts to lower temperature by 5°–10°C,
peak becomes broader

The Arrhenius plots obtained from these data as well as from the data on PET films[6,8] are shown in *Figure 3*. The activation energy thus obtained for PET fibres is 9.1 kcal/mol for the 0° case and 8.4 kcal/mol for the 90° case. These values are lower than the values 12.7 and 13.9 kcal/mol for biaxially oriented PET films[8], 15.5 kcal/mol for PET extruded rods[7] and 12.4 kcal/mol for unoriented PET films[9]. The lower value of the activation energy of fibres might imply a higher degree of restriction on the mobility of relaxing units in the fibres than in other forms of PET.

Unlike the case of oriented PET films[8], the present values of activation energy for PET fibres for 0° and 90° cases may not be indicative of anisotropy of activation energy, as the difference of slopes of the Arrhenius plots in the two cases is not greater than the experimental precision. However, these data on fibres show that $(f_m)_{0°} > (f_m)_{90°}$, which is contrary to the observations on PET films[8] which need further investigations for any reasonable explanation of this observation. The difference of $(f_m)_{0°}$ and $(f_m)_{90°}$, however, is hardly beyond the experimental precision.

The exact group responsible for β-relaxation process of

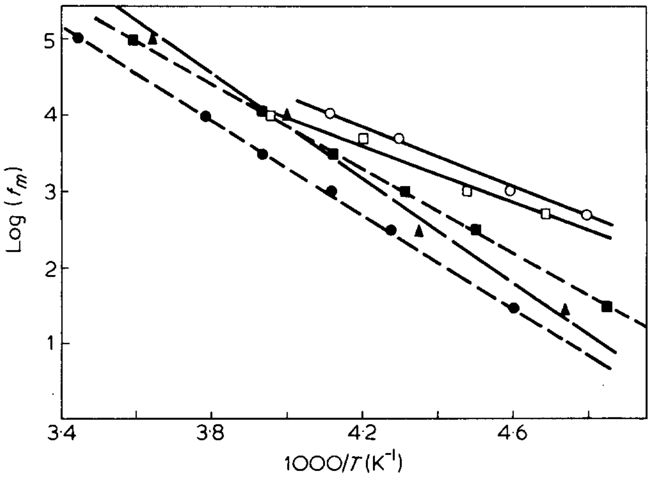

Figure 3 Arrhenius plots, log f_m as function of reciprocal temperature from these data on PET fibres and the reported values[6,8] for PET films. ○ – PET fibres (0° case); □ – PET fibres (90° case); ● – PET films (ref 8) (0° case); ■ – PET films (ref 8) (90° case) and ▲ – PET films (ref 6)

Table 1 Values of $\tan\delta_{max}$ and $(\tan\delta_{max})_{90°}/(\tan\delta_{max})_{0°}$ at different frequencies

Frequency (kHz)	$(\tan\delta_{max})_{90°} \times 10^3$	$(\tan\delta_{max})_{0°} \times 10^3$	$(\tan\delta_{max})_{90°}/(\tan\delta_{max})$
1	28.8	20.0	1.44
5	22.6	16.2	1.40
1	16.6	12.0	1.38
0.5	11.5	8.3	1.39

PET is a point of controversy. Various authors have attributed it to the motion of end-groups[9], the glycol residues[10], carbonyl groups[11] and $-C_2H_4-$ units[11]. We would, therefore, use the term 'dipole unit' to denote the group responsible for this relaxation.

Due to the orientation in the fibres the dipole units would be so arranged that the components of their dipole moment along and perpendicular to the fibre axis are unequal. If γ be the angle between the dipole moment vector of the units and the direction of applied electric field, then the average value of $\cos^2\gamma$, i.e. $\langle\cos^2\gamma\rangle$, will be 1/3 for a randomly oriented (i.e. isotropic) structure, whatever the direction of applied electric field. For uniaxially oriented fibre structure the values of $\langle\cos^2\gamma\rangle$ for cases when the electric field direction is parallel (0° case) and perpendicular (90° case) to the fibre axis may be expressed[6] as follows:

$$\langle\cos^2\gamma\rangle_{0°} = \frac{1}{2}[1 - \langle\cos^2\psi\rangle - (1 - 3\langle\cos^2\psi\rangle)\langle\cos^2\theta\rangle]$$

$$\langle\cos^2\gamma\rangle_{90°} = \frac{1}{4}[1 + \langle\cos^2\psi\rangle + (1 - 3\langle\cos^2\psi\rangle)\langle\cos^2\theta\rangle] \tag{3}$$

where θ is the angle between a given polymer chain and the draw direction (fibre axis) and ψ is the angle between the dipole moment vector of the relaxing unit and the chain axis.

Thus the mean square dipole moment $\langle\mu^2\rangle$ of the relaxing dipole units will have a component along the applied electric field direction dependent on the direction of the electric field. For this case of a uniaxially oriented system:

$$\langle\mu^2\rangle_{0°} = \langle\mu^2\rangle\langle\cos^2\gamma\rangle_{0°}$$

and

$$\langle\mu^2\rangle_{90°} = \langle\mu^2\rangle\langle\cos^2\gamma\rangle_{90°} \tag{4}$$

The directional anisotropy of dipole moment components should be directly observable in the dielectric relaxation strength. As already stated the absolute values of ϵ' could not be precisely determined in this experiment, the observed anisotropy in $\tan\delta$ has been related to the structural anisotropy due to the dipole moment components, in the same way as done by Hsu and Kwan[8]. Since the area under the plot of ϵ'' *versus* reciprocal of temperature multiplied by activation energy is a measure of dielectric relaxation strength[12], hence the anisotropy expected in dielectric relaxation strength should also appear in ϵ'' multiplied by the activation energy, E. Considering the low variation of ϵ'_m in these data as well as the low anisotropy in the real part, ϵ', of dielectric permittivity of PET films[6], it would be reasonable to consider that $\tan\delta$ varies as ϵ''. Hence the anisotropy of $\langle\cos^2\gamma\rangle$ may be related to that of $(\tan\delta_{max})E$. Thus

$$\frac{(\tan\delta_{max})_{90°} \times E_{90°}}{(\tan\delta_{max})_{0°} \times E_{0°}} = \frac{\langle\cos^2\gamma\rangle_{90°}}{\langle\cos^2\gamma\rangle_{0°}} \tag{5}$$

The value of $(\tan\delta_{max})_{90°}/(\tan\delta_{max})_{0°}$ is close to 1.4 at all the frequencies of measurement (*Table 1*), thus indicating frequency independence of the dielectric anisotropy in these fibres. The value 1.4 seems in agreement with the value 1.3 for extruded rods[7] of draw ratio 3.3, and the value 2.1 for biaxially oriented films[8] of draw ratio 5. This might indicate the possibility of an increase in the dielectric anisotropy with increasing draw ratio of fibres.

The right hand side of equation (5) involves two quantities, viz. $\langle\cos^2\theta\rangle$ and $\langle\cos^2\psi\rangle$, of which the former is related to f, the Herman's orientation factor[13], $f = (3\langle\cos^2\theta\rangle - 1)/2$. This could be determined for these uniaxially oriented fibres by optical birefringence or X-ray diffraction measurements. The values of optical birefringence $\Delta n = 0.187$ and the draw ratio 3.92 for these fibres lead to $\langle\cos^2\theta\rangle = 0.82$ according to the method of Ward *et al.*[14,15]. The Herman's orientation factor determined from X-ray diffraction method for these samples is 0.89[16] thus giving a higher value of $\langle\cos^2\theta\rangle$. Using the value of $\langle\cos^2\theta\rangle = 0.82$, we find that $\langle\cos^2\psi\rangle = 0.21$ would result in the right-hand-side of equation (5) consistent with the experimental value of the left-hand-side.

Thus the dielectric anisotropy coupled with the optical birefringence or X-ray diffraction could be used as a means of determining $\langle\cos^2\psi\rangle$, which in turn might help in deciding which dipole unit is responsible for the relaxation process. The value $\langle\cos^2\psi\rangle = 0.21$ would be consistent with the ester group dipole moment according to Flory's contention[17] that the dipole moment of the ester group is inclined at an angle of about 20°–30° to the C=O bond. This it seems reasonable to attribute the β-relaxation in PET to the mobility of ester groups in the main chain.

In conclusion we may say that the dielectric β-relaxation of oriented PET fibres is anisotropic. An increase in the anisotropy of this process with the increasing draw ratio may be expected. The activation energy for this process in PET fibres is lower than that in films or extruded rods of PET. The observed anisotropy in $\tan\delta_{max}$ can be used to determine the direction of the dipole moment vector with respect to the molecular chain axis.

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