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The dielectric response of a commercial polybutylene terephthalate

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Contour maps of complex relative permittivity within the range −170 to +175° C and 0.1 Hz to 3 MHz are presented for a commercial polybutylene terephthalate. The interdependence of ε' and ε'', as required by the Kramers–Krönig relations, is particularly apparent. Individual dispersion regions are attributed to α- and β-relaxation processes and to Maxwell–Wagner–Sillars polarizations. Possible explanations are proposed for the structure which is apparent in the α-peak.

1. Introduction

Polybutylene terephthalate (PBT), also known as polytetramethylene terephthalate (PTMT), is a thermoplastic polyester used widely in the fabrication of injection-moulded components. Although one of the important engineering polymers, there have been comparatively few published studies of the dielectric and other physical properties of this material. Most interest has centred on the solid-state transition between the alpha and beta crystalline forms in PBT [1–13] which are reported to be reversible and stress-dependent [4–13]. A number of studies have utilized nuclear magnetic resonance (NMR) C-13 and chemical shift anisotropy [13–20] to investigate the nature of molecular motions in PBT materials of varying degrees of crystallinity. A few studies have employed dynamic mechanical measurements [21–24] or dielectric relaxation techniques [24–28]. The present paper provides more comprehensive dielectric data over an extended and continuous range of temperature and frequency.

2. Experimental details

VALOX 315 polybutylene terephthalate powder (General Electric Plastics) was pre-dried at 130° C and pressed into sheets at 260° C following the procedure described in an earlier paper [29]. For measurements of complex relative permittivity and d.c. resistance, samples of approximate dimensions 25 mm × 20 mm × 0.4 mm were cut from the sheet and aluminized on opposite faces to form matching electrodes. Permittivity data were obtained using the capacitative-T wide-band bridge of Pratt and Smith [30]. A Keithley Instruments 602 electrometer was used to obtain the d.c. resistance. Sufficient time was allowed to exclude the influence of transient currents. Control of sample temperature was achieved by a baffled flow of dry nitrogen gas at the desired temperature.

3. Results and discussion

3.1. Presentation of experimental results

The temperature–frequency variation of complex relative permittivity for VALOX 315 PBT is presented in Figs 1 to 3. Plots of the temperature variation of ε' and ε'' at 16 selected frequencies are shown in Figs 1 and 2, respectively. A useful alternative method of data presentation is given in Fig. 3, which shows the corresponding loss tangent as contours of equal tan δ values. Arrhenius plots of the logarithm of the frequency at which maximum loss occurs against reciprocal temperature are shown in Fig. 4 for the α- and β-processes.

The interdependence of ε' and ε'' required by the Kramers–Krönig dispersion relations is well illustrated by the observations presented here. Several distinct regions are apparent in the constant-frequency plots of the temperature variation of ε' and ε'' (Figs 1 and 2) and in the contour map of tan δ (Fig. 3). In general, the magnitude of ε' increases with increasing temperature and/or decreasing frequency, although the rate of change varies widely between regions. The individual features are discussed below.

3.2. Low-temperature β and related processes

At the lowest temperatures the value of ε' increases initially at a slow rate with increasing temperature or decreasing frequency from about 3.35 to about 3.60, and then at a more rapid rate from 3.60 to 3.70. The contour at $\varepsilon' = 3.65$ extends approximately from −95° C at 0.3 Hz, through −50° C at 1 kHz, to 35° C at 3 MHz and corresponds quite closely to the locus of the broad peak of moderate intensity which occupies most of the low-temperature region in the tan δ contour map (Fig. 3).

The location of this broad peak is in reasonable agreement with that observed for the β-process in early dynamic mechanical investigations [21, 22], which noted two dispersions with low-frequency peaks in the vicinity of 60° C (α) and −80° C (β). The latter has been attributed to restricted local motions of carbonyl groups and glycol residues. More recently, Chang and Slagowski [23] reported a progressive reduction in the magnitude of the dispersion with increasing crystallinity in agreement with the generally accepted view that

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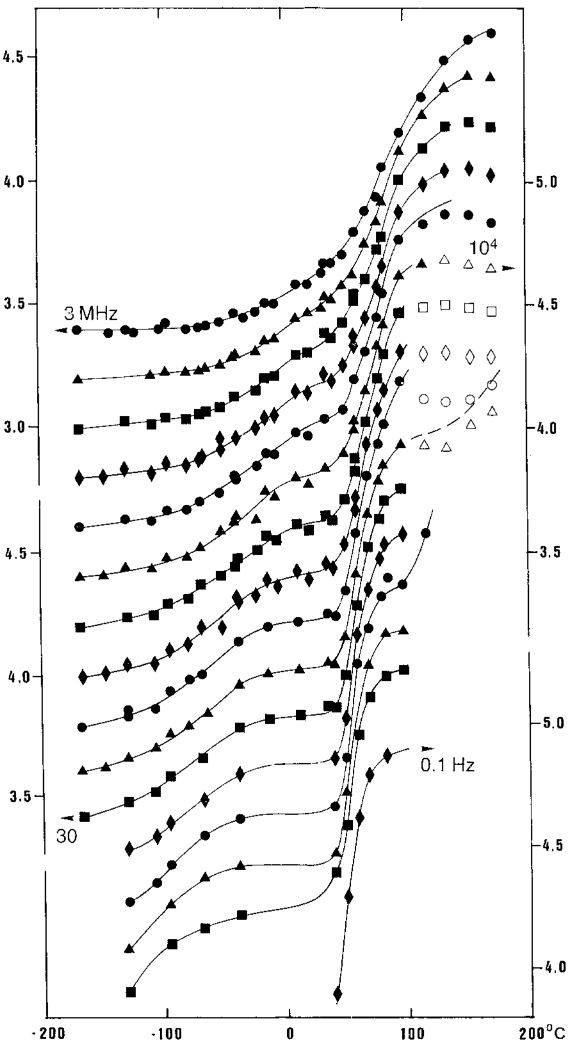

Figure 1 Constant frequency plots of the temperature variation of real relative permittivity of VALOX 315 PBT at half-decade intervals from 0.1 Hz to 3 MHz. Successive curves are displaced vertically by 0.2 in the interests of clarity.

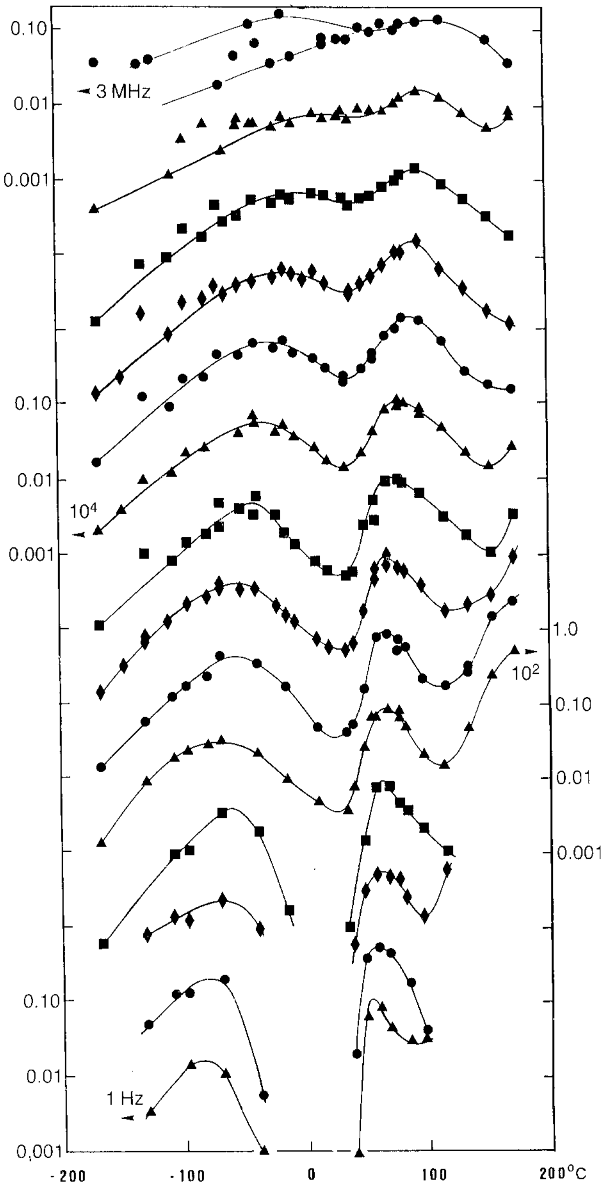

Figure 2 Semi-logarithmic plots of the temperature variation of imaginary relative permittivity of VALOX 315 PBT at half-decade intervals from 1 Hz to 3 MHz. Successive curves are displaced vertically by one logarithmic decade.

the local motions are associated with amorphous regions in PBT.

Leung and Choy [24] note that the β-process in drawn samples of PBT is not greatly affected by orientation, thereby providing further evidence that the motions are quite localized. Drawing produces partial alignment of the chains with a consequential closer packing and reduction of free volume leading to hindering of any extensive segmental motions.

Illers and Breuer [22] reported an asymmetry of the 0.1 Hz dynamic mechanical β-peak, which they attribute to the superposition of a lower-temperature component involving motion of $-CH_2$ groups and a higher-temperature component involving -COO- motions. Low-frequency asymmetry of the β-peak is not apparent in the present work. This is to be expected, as the $-CH_2$ component will not contribute significantly to the dielectric loss peak.

On the basis of chemical shift anisotropy and magic-angle spinning, Jelinski and co-workers [14–19] suggest that the aromatic rings in the amorphous regions of PBT undergo increasingly rapid 180° ring flips with increasing temperature. They further suggest that the phenyl rings in the crystalline domains are essentially fixed or static, and that there exists an intermediate region in which the 180° ring flips occur very slowly (at 70° C). Garbow and Schaefer [20] also report that some of the phenyl groups in PBT at ambient temperatures undergo large-amplitude motions consistent with 180° ring flips superimposed on oscillations and wiggling motions. Similar behaviour has been reported for polydian carbonate [31] and other materials [17].

The activation energy for the β-process calculated from the Arrhenius plot (Fig. 4) is 57 kJ mol^{-1}. Values from 50 to 55 kJ mol^{-1} have been reported previously [24, 28].

At near-ambient temperatures the real relative permittivity, ε', attains a reasonably constant value ($3.8 < \varepsilon' < 3.9$). In the corresponding contour map or three-dimensional model of ε' (not shown here) the plateau narrows with increasing frequency, extending from approximately -60 to $+40$° C at 0.1 Hz and from -5 to $+45$°C at 1 kHz, but only from 60 to 70° C at 3 MHz. The contour at $\varepsilon' = 3.85$ coincides approximately with the line of the ε'' minimum, or

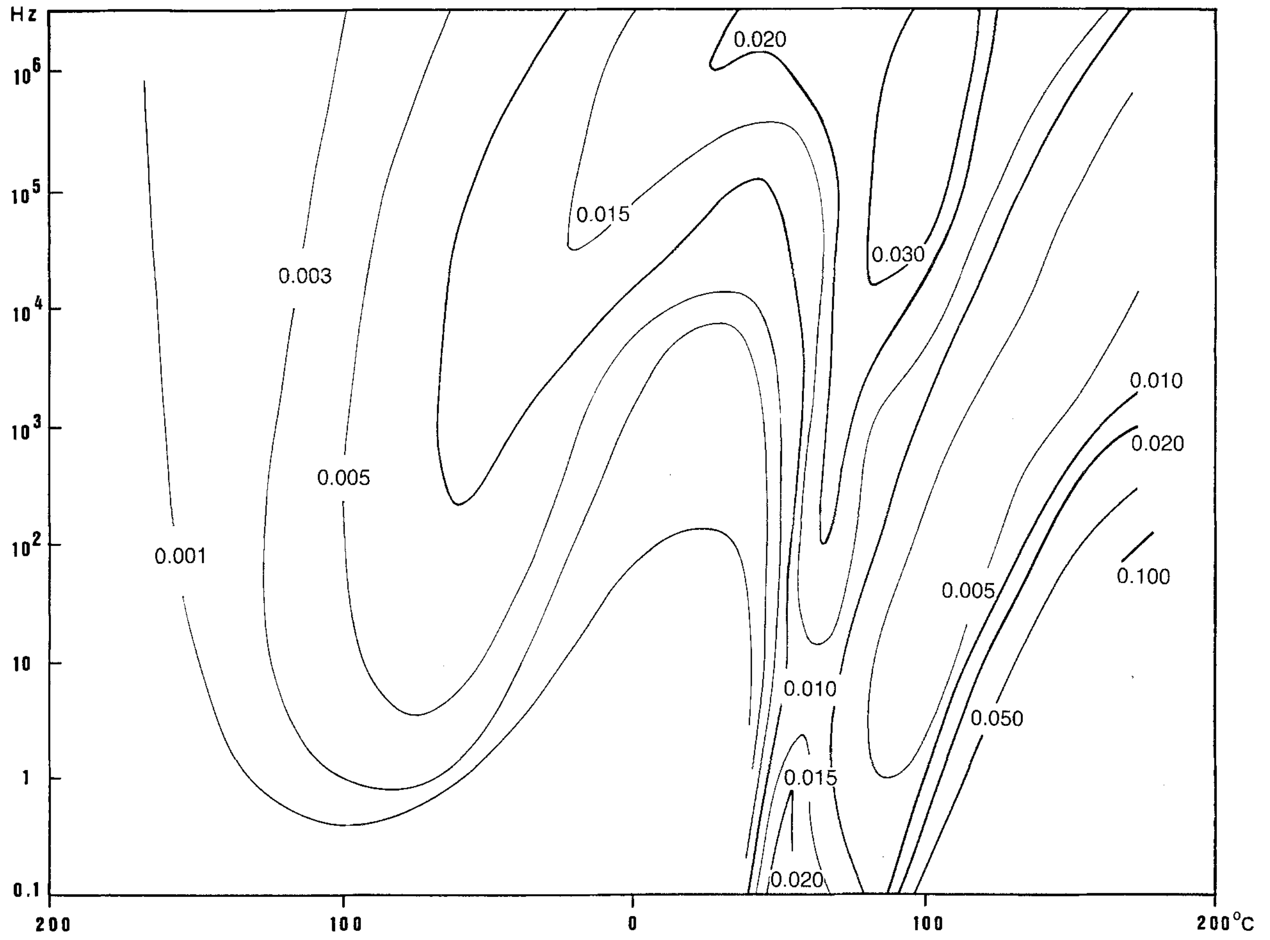

Figure 3 Contour map showing the temperature–frequency variation of tan δ for G.E. VALOX 315 polybutylene terephthalate.

trough, which extends from 0° C at 0.1 Hz, through 35° C at 1 kHz, to 65° C at 3 MHz.

3.3. High-temperature α-process and Maxwell–Wagner–Sillars (MWS) processes

At moderate temperatures the magnitude of ε' increases rapidly from 3.9 to 4.6, changing most rapidly in the vicinity of the contour at $\varepsilon' = 4.3$ which extends from about 50° C at 0.1 Hz, through 70° C at 1 kHz, to 105° C at 3 MHz. The location of the contour coincides with the peak of the sharper and more prominent dispersion in the temperature variation of ε'' (Fig. 2) and in the contour map of tan δ (Fig. 3). It is attributed to the primary (α-) relaxation associated with substantial micro-Brownian motion of molecular segments.

The shape of this dispersion region, as shown in the tan δ contour map (Fig. 3), suggests that there is more than one process involved over the frequency range of the investigation. At moderately low frequencies (3 Hz to 1 kHz) the glass transition in PBT appears as a narrow dispersion region which is clearly separated from the β-peak and from the region of increasing loss beyond 100° C. Such behaviour differs from that of the polycarbonate of bisphenol-A for which the α-peak occurs at substantially higher temperature and merges into the MWS disperison region below about 1 Hz [29].

The sharpness and magnitude of the α-peak in the tan δ contour map (Fig. 3) below 3 Hz suggests an admixture of the α-relaxation with some low-frequency process. The temperature and frequency at which this process occurs indicates a relaxation associated with the motion of a large molecular segment, or considerable constraint of the moving entity, or a substantial displacement of the motion. One explanation would be that the relaxation involves MWS polarization processes between either individual crystallites in the crystalline domains, or between alpha and beta crystalline forms within the crystallites. Brereton *et al.* [5] suggest that a boundary between the crystalline forms may be generated in an individual crystallite, and Dobrovolny-Marand *et al.* [13] report that some residual beta crystalline PBT is present even at zero stress.

The width of the dispersion increases at frequencies higher than 1 kHz, a shoulder appears on the high-temperature side of the α-peak and, at 3 MHz, it is no longer possible to distinguish the location of the β-peak on the low-temperature side. The shape of the tan δ contours on the high-temperature side of the peak suggests the admixture of an additional process with the α-relaxation. Leung and Choy [24] have previously noted substantial overlapping of the α- and β-peaks in ultrasonic longitudinal elastic wave measurements at 2.5 MHz.

The Arrhenius plot for the α-process (Fig. 4) separates into two straight lines of differing slope at about 1 kHz. The activation energies derived from the slopes are 220 and 420 kJ mol^{-1} above and below 1 kHz, respectively. Values from 205 to 460 kJ mol^{-1} are reported elsewhere [24, 32].

Considerable attention has been devoted to the

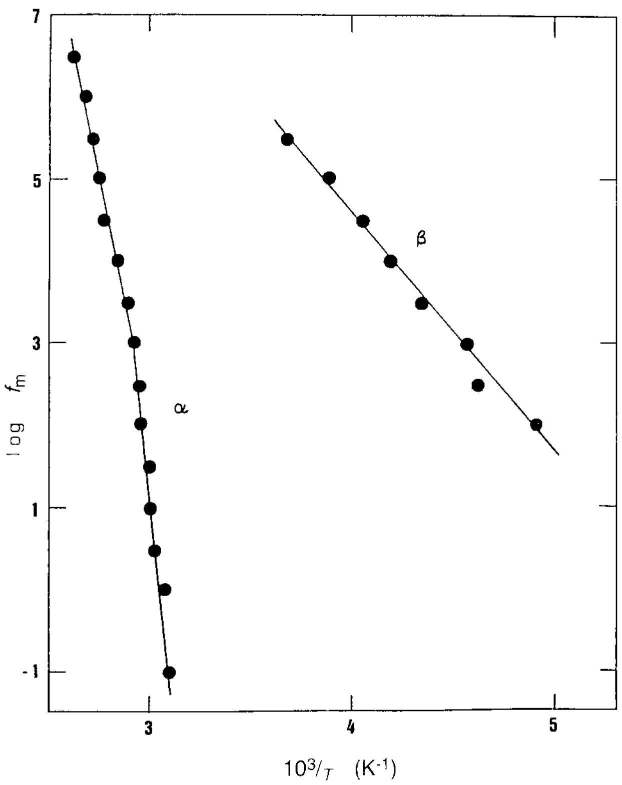

Figure 4 Arrhenius plot of the logarithm of the frequency at which maximum loss occurs for the α- and β-processes in VALOX 315 PBT.

study of the crystalline phase transition in PBT [1–20]. X-ray diffraction [4, 5], Raman spectroscopy [5], differential scanning calorimetry (DSC) [8], Fourier transform infrared spectroscopy [6, 7, 9, 13] and various NMR techniques [12, 14–19] have been used to monitor the reversible alpha $\rightleftharpoons$ beta transformation which changes the dominant conformation of the aliphatic tetramethylene group from the *gauche–trans–gauche* sequence in the unstressed state to the more extended all-*trans* sequence under stress. The transformation occurs at strains as low as 5% [12], and the critical stress level for the alpha → beta transition has been found to be a function of temperature [8]. Perry *et al.* [12] report more efficient packing of the aromatic rings and, hence, more hindered motion of phenyl groups in the alpha phase.

The occurrence of this crystalline phase transformation may provide an explanation for the asymmetry observed in the α-peak of PBT at higher frequencies on the assumption that changes between alpha and beta crystalline forms also occur under conditions of compressive stress. A slight spring pressure is used in the sample cell of the permittivity bridge to maintain contact between the sample and the electrodes. As the temperature rises, the resultant stress may exceed the critical value for the crystalline transition, and could lead to the creation of a form of beta PBT in which molecular motion is less hindered than in the more closely-packed alpha form. Such conjecture would at least be consistent with the lower value of the apparent activation energy for the "α-process" in this region. However, it is difficult to envisage how compression of the sample could induce a change to a more extended conformation in the crystalline regions.

It is considered more probable that the asymmetry of the α-peak arises from the interaction of amorphous and crystalline regions of the PBT. At higher temperatures, recrystallization of the PBT can occur and a progressive change in the degree of crystallinity with increasing temperature might be expected. One possibility is that α- and α′-relaxation processes of amorphous material within, respectively, amorphous and crystalline domains are involved. Large-scale dipole-driven motion of polymer molecules or segments should be more difficult in crystalline regions than in less ordered amorphous regions, leading to a higher rather than a lower activation energy. On the other hand, the interaction of two processes of similar activation energies, but separated by 20 or 30° C, can produce an apparent activation energy for their combined effect which is lower than that of each component alone. Deconvolution of the peak into its constituent parts may resolve the issue.

Increased crystallinity would be expected to have two conflicting effects on an α-process which is normally considered to involve amorphous materials or regions. First, the reduced proportion of amorphous material should lead to a reduced magnitude of the dispersion. Second, the increased hindrance to molecular motion should require greater expenditure of energy per moving segment. In dielectric experiments the applied electric field will tend to induce motion in dipoles in amorphous and crystalline domains alike. Their response will vary in relation to the frequency, the temperature and their interaction both with neighbouring atoms in the same molecule and with adjacent polymer chains.

At higher temperatures, ε' (Fig. 1) increases more slowly from about 4.6 to 4.8, and the contour at $\varepsilon' = 4.75$ follows approximately the line of the minimum or trough in the temperature variation of ε'' (Fig. 2) and the contour map of tan δ (Fig. 3), the latter extending from about 80° C at 0.1 Hz, through 130° C at 1 kHz, to 175° C at 100 kHz. The reliability of apparent ε' values at the highest temperatures is diminished as a result of dimensional changes in the sample.

At the highest temperatures, ε' increases more rapidly beyond about 4.8 and losses increase rapidly beyond the contour at $\varepsilon'' = 0.100$ which extends from 90° C at 0.1 Hz, through 115° C at 10 Hz, to 175° C at 1 kHz. These losses are attributed to Maxwell–Wagner–Sillars (MWS) polarization processes at interfaces between crystalline and amorphous regions in the semi-crystalline PBT. The degree of crystallinity is estimated from DSC measurements to be 33%.

4. Conclusions

The dielectric properties of a commercial polybutylene terephthalate have been measured over an extended and continuous range of temperature and frequency without recourse to Fourier transform analysis or to a change of experimental technique.

An extremely broad β-dispersion occurs at temperatures below ambient, and partially merges with the α-dispersion at the highest frequencies. A narrow α-dispersion associated with the glass transition is clearly separated from the low-frequency high-temperature region of MWS polarization losses.

Evidence is presented for the existence of two additional relaxation processes which interact with the α-dispersion at high and low frequencies, respectively. It is postulated that the low-frequency process is associated with MWS polarization processes involving crystallites. As yet, the nature of the higher frequency process is not fully resolved.

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