A dielectric study of molecular relaxation in linear polyethylene*

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Although the dielectric β glass–rubber relaxation has previously been observed in dipole-decorated branched polyethylenes and in linear polyethylene containing several mole per cent chlorine, it has not been observed in linear polyethylene containing very low dipole concentrations. Dielectric relaxation has been studied here in a linear polyethylene specimen (containing a few carbonyl groups per 1000 methylene units) in the hope of observing the β process. The isochronal loss peak for the β relaxation is not well resolved from that for the α relaxation. However, it is found that the β process is very apparent as an increment in the isochronal dielectric constant scans. This was taken advantage of in characterizing the relaxation. In comparing the results with previous work it is found that there is a progression in the β relaxation $T_{\max}$ location towards higher temperature as the degree of crystallinity increases through branched and linear polyethylene specimens.

(Keywords: dielectric relaxation; linear polyethylene; beta process)

INTRODUCTION

In the study of polymeric molecular relaxation, polyethylene (PE), with its relatively simple molecular structure, has been a material of great interest. PE exhibits at least three relaxation processes, labelled α, β and γ in order of decreasing temperature[1–5]. The α process has its origin in motions in the crystalline portion of the semicrystalline polymer. The dielectric α process in dipole-decorated (with carbonyl groups or chlorine) PE is directly associated with the crystal motions. However, mechanically, the process is associated with softening of the amorphous fraction, which is enabled by attainment of mobility of the crystal stems that are connected to the amorphous phase. The β process is attributed to the glass–rubber transition in the amorphous fraction. The γ relaxation also has its origins in the amorphous fraction and is thus a subglass process. It is presumed to involve more localized motions than the β process[2,3].

The β process in branched polyethylene (BPE) is quite prominent but in linear polyethylene (LPE) it is much less so. In fact, dielectrically it is difficult to detect. There are two reasons for this. The first is connected with the time–temperature behaviour in comparison with the other relaxations. The β process is well resolved from the γ relaxation at moderate frequencies. This is not true with respect to the α process, however. The α process occurs at a higher temperature than the β but its activation energy is lower. This means that the α and β processes become better resolved in isochronal scans as frequency increases. This is the opposite to the usual situation, where isochronal scan resolution improves at lower frequency.

The other aspect of experimentally characterizing the β process concerns the effect of the semicrystalline environment. In wholly amorphous polymers, the glass–rubber relaxation is rather narrow in isochronal scans and moderately so in isothermal log frequency scans. However, in semicrystalline polymers, the presence of the crystal surfaces and the connections of the amorphous chains to them have an immobilizing effect. The latter effect shows up in both the kinetic and quasi-equilibrium properties of the glass–rubber relaxation[2,3]. Kinetically, the distribution of relaxation times is tremendously broadened in comparison to an unconstrained, completely amorphous polymer. It is also shifted to longer times isothermally or higher temperature isochronally. The strength of the relaxation, an equilibrium property, is also affected. The constrained chains find themselves unable to relax completely; the relaxation strength is reduced. In PE, and especially in LPE, these effects combine to render the β process quite broad and also obscured by the α process. Only at relatively high frequency (>1 kHz), where the improvement in resolution alluded to above is operable, can any hint of the β relaxation be observed dielectrically in LPE in isothermal scans. At higher frequencies still, this improvement is compromised by the melting process occurring at the attendant higher temperatures. There is a relatively limited window of frequency and temperature where the β process can be observed. So far, it has been observed dielectrically only in a few isochronal scans at high frequency in an LPE decorated by chlorination (5.4 wt% Cl, 22 Cl/1000 CH_2)[6]. The Cl content is sufficient to affect the morphology appreciably; the crystallinity is suppressed significantly.

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In the present work, measurements of dielectric relaxation in a lightly oxidized LPE (about three carbonyl groups per 1000 CH_2), where the morphology approaches that of undecorated LPE, were made. It was found that the β process could be detected. The relaxation strength was estimated and the location on a loss map defined.

EXPERIMENTAL

Sample preparation

Polyethylene is not naturally dielectrically active. However, it can be oxidized to provide a sufficient number of carbonyl dipoles to render it useful in dielectric experiments. Extensive experiments have been carried out on such specimens[6]. The polymer used in the present work was the same as that studied previously[6]; it is an antioxidant-free Marlex 6050 fluff obtained from the Phillips Petroleum Company. The sample density was 0.961 g cm^{-3} with a melt temperature of 133°C. The density indicates a degree of crystallinity of 75% and heat of fusion results gave 68% (ref. 6). It was rendered dielectrically active by milling in air. The carbonyl content, as determined by comparing the intensities of the loss peaks with specimens previously studied[6], was about 3 $C{=}O/1000\,CH_2$.

The polymer was melt-pressed using a disc-shaped mould between two sheets of Teflon, which aided in sample removal. The melt-pressing was done at 150°C and 2000 psi (13.8 MPa). The sample was cooled slowly overnight under pressure. The sample was 0.559 mm thick with a diameter of 57.05 mm. Both sides of the sample were gold-coated, rendering the surface conductive. A circular ring of gold was removed from the bottom side of the sample so that when positioned in the capacitor the central sample plate would be insulated from the sample ground ring. The sample was kept in a desiccator during the various stages of preparation prior to running the experiment.

Dielectric measurements

The dielectric measurements were conducted using a parallel-plate cell, described previously[7], based on the design of Yoshihara and Work[8]. Briefly, the capacitor had a solid upper plate with a smaller, central, lower plate circled by three concentric rings separated by gaps. The sample extended out to the first ring only. The dielectric properties of the sample were measured across the central plate, whereas the dielectric properties of the air were measured across one of the outer rings. Both the plate and the air capacitance ring had a corresponding ground ring. The air capacitance measurements were used to correct the sample capacitance values for the effects of changing sample thickness due to thermal expansion and flow.

An EG&G 5206 two-phase lock-in analyser coupled with a General Radio 1616 precision capacitance bridge was used to take the capacitance and conductance data[7]. The lock-in/bridge combination was interfaced with a CRDS (PDP-11) computer system.

Measurements were taken at increments of approximately 7°C during a heating run from -190 to 120°C. At each equilibrated temperature, measurements of capacitance and conductance were taken at frequencies of 5, 10, 20, 50, 100, 200 and 1000 Hz, and 2, 5, 10 and 20 kHz. This was followed by measurement of the air capacitance and conductance at 1.23 kHz. From the results obtained it would appear that the dielectric loss at 10 and 20 kHz is not as reliable as the other frequencies, the values being somewhat higher than expected. It is known that in bridges of this type the loss is less reliable at the high end of the frequency range.

Prior to the experiment, a gaseous nitrogen flush of the system was conducted at room temperature for 20 min. The cell was cooled by pouring liquid nitrogen directly into the Dewar. Care was taken to cool the sample at a rate of less than 2°C min^{-1} in order to avoid freezing-in artefacts. The fully cooled chamber was allowed to sit for 3 h before the experiment was begun. The data were taken over the frequencies in nearly isothermal mode and through an ascending series of temperatures. However, data acquisition over the 13 frequencies required about 40 min at each temperature, and thermal drifts were noticeable. Therefore as each frequency was measured, the temperature was recorded from thermocouples embedded in the lower and upper plates of the cell.

RESULTS AND DISCUSSION

General observations

A plot of dielectric loss *versus* temperature for LPE is shown in *Figure 1*. The α and γ processes are seen as prominent loss peaks. The corresponding dielectric constant scans are shown in *Figure 2*. It should be noticed in *Figure 2* that the influence of temperature on specimen density is a prominent feature. That is, decreasing density causes the unrelaxed dielectric constant (ε) to decrease with increasing temperature. This is the phenomenon quantified by the Clausius–Mosotti relation[9] where $(\varepsilon-1)/(\varepsilon+2)$ is proportional to density. Because the specimen is relatively non-polar the effect is much more noticeable than usual in comparison with the relaxational changes. Nevertheless, the dielectric constant increments associated with the relaxation processes are clearly evident. The most important result of the present work is that the increment associated with the β process is plainly evident. In fact it is much more evident than the corresponding peak in the loss. In *Figures 3* and *4* the loss and dielectric constant, respectively, at 10 kHz have been plotted separately for clarity. In *Figure 3* it may be seen that the β loss process is only suggested as a broad shoulder next to the α process peak. In *Figure 4*, however, the increment in the constant is quite visible. Returning to *Figure 2*, it may be seen that the envelope of relaxed γ processes is a further aid in establishing the unrelaxed base for the increment of the β process.

Argand plots and Cole–Cole parameters

As an aid in establishing the strength of the β process, strengths were found for the α and γ processes via fits of the Cole–Cole function[10] to Argand plots. Due to its breadth, the fitting of the γ process is admittedly rather speculative and approximate. It was accomplished as follows. First, a value for the relaxed dielectric constant ε_R at -89°C was found directly from the Argand plot. Then an ε_R *versus* temperature line was established by joining the -89°C value with the ε_R envelope at slightly higher temperatures than is apparent in *Figure 2*. Then ε_R values were taken from this line at -104 and -117°C. The Cole–Cole fitting at -104 and -117°C was then

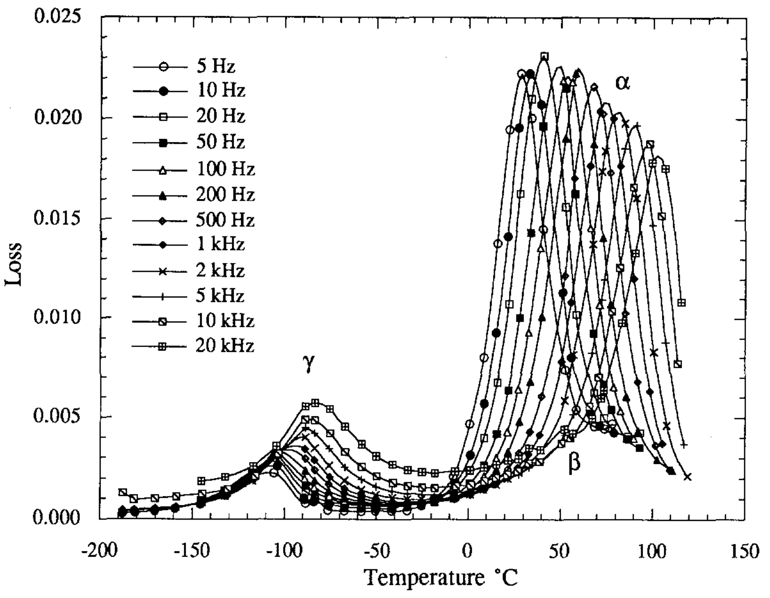

Figure 1 Plots of dielectric loss *versus* temperature for LPE

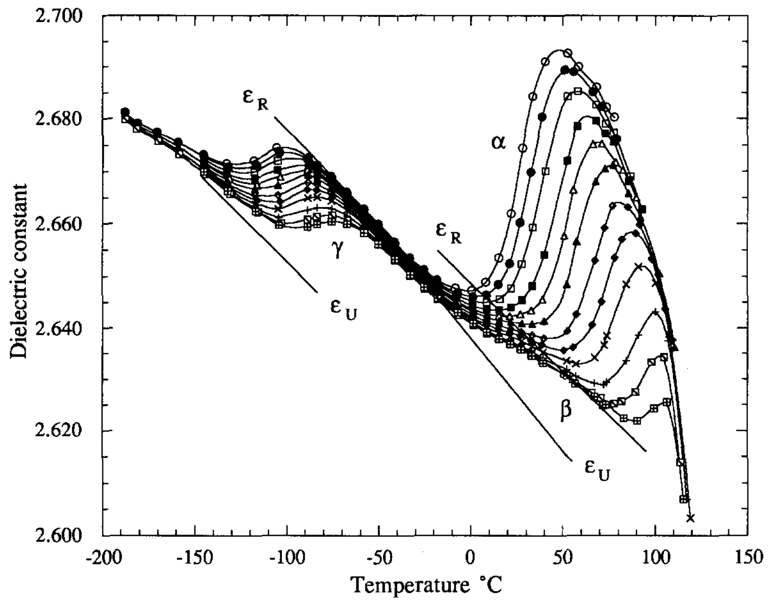

Figure 2 Plots of dielectric constant *versus* temperature for LPE. Symbols as in the key to *Figure 1*. ε_R and ε_U are the relaxed and unrelaxed dielectric constants, respectively

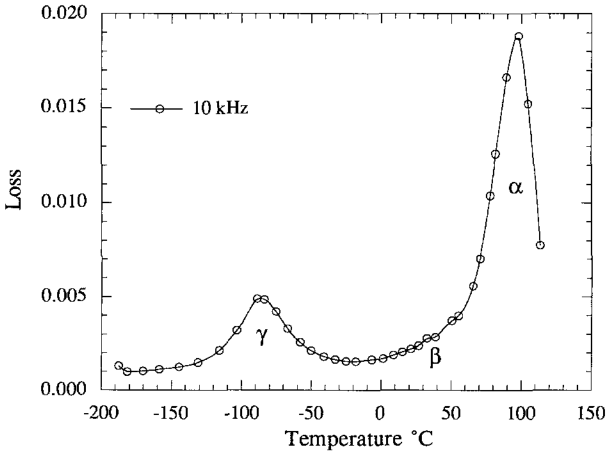

Figure 3 Dielectric loss *versus* temperature at 10 kHz

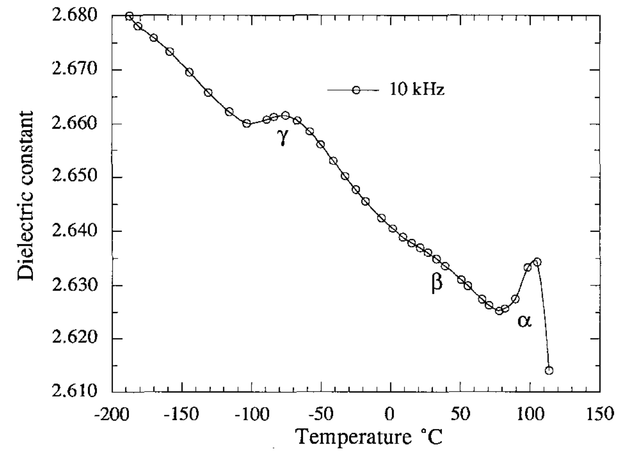

Figure 4 Dielectric constant *versus* temperature at 10 kHz

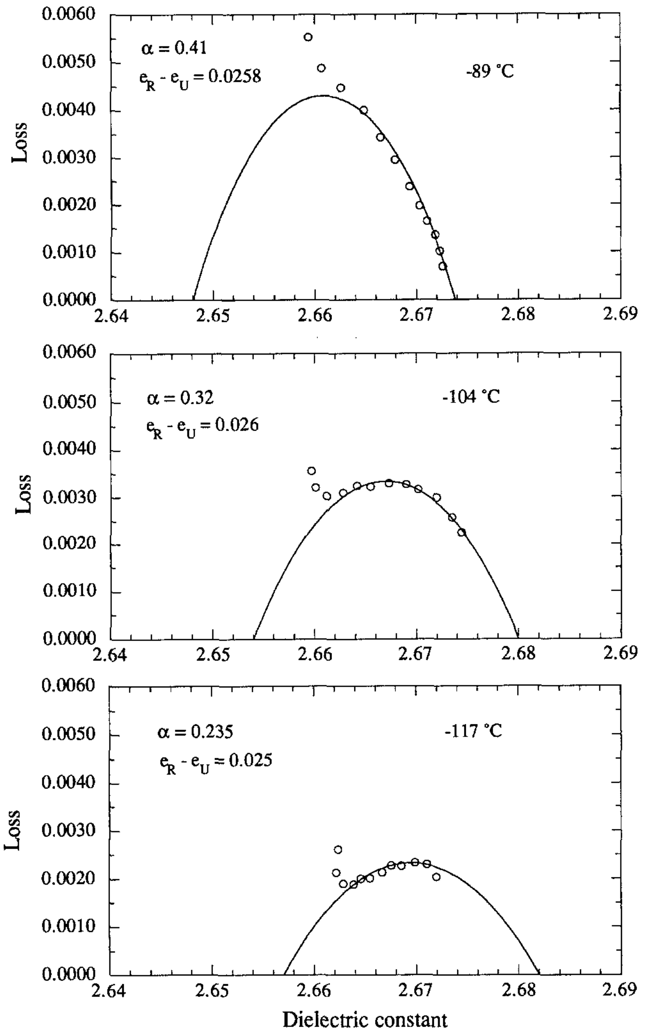

Figure 5 Cole–Cole fit for the γ process at three temperatures

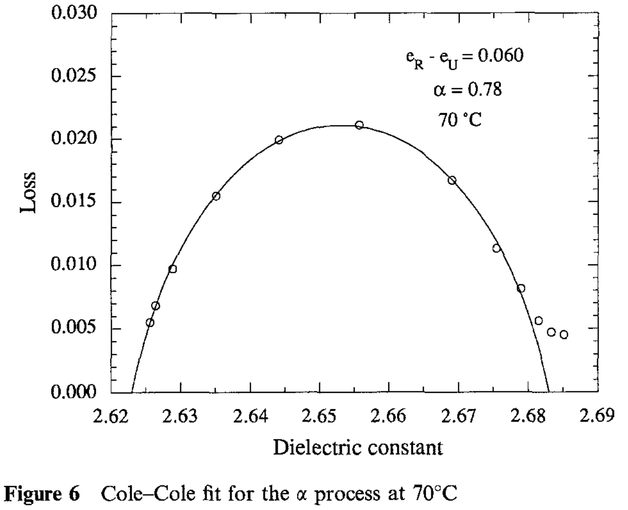

Figure 6 Cole–Cole fit for the α process at 70°C

made with the constraint of the already fixed ε_R values. In turn, the ε_U -104 and -117°C values were used to approximate the -89°C ε_U value and, from this, the Cole–Cole fit at this latter temperature was completed. *Figure 5* displays the fits for the γ process at three temperatures. *Figure 6* is a plot for the α process.

It may be noticed for the γ process (*Figure 5*) that the width parameter ($=1$ for single relaxation time) has quite low values and is strongly temperature dependent. The width of the isothermal log frequency process narrows strongly with increasing temperature. It is this phenomenon that is responsible for two features of the γ process isochronal loss curves in *Figure 1*: the first feature is that they are skewed towards low temperature; the second is that $\varepsilon''_{\max}$ increases with increasing frequency. Both of these are due to the isothermal width narrowing with increasing temperature. This effect is common for subglass processes and has been commented on before[2–4,6,7].

The α process is very narrow, with the width parameter ($=0.78$) approaching single relaxation time. This is due to the single jump nature of the dipolar reorientation process in the crystal[3,11].

The limiting dielectric constant lines in *Figure 2* were drawn to be consistent with the limiting ε_R, ε_U values of *Figures 5* and *6*.

Loss map

The loss peaks in *Figure 1* were used to find $T_{\max}$ at each frequency for both the α and γ processes. These are plotted in the form of a loss map in *Figure 7*. For the β process, the temperatures of the inflection points in the mid-range of the dielectric increments in *Figure 2* were used.

Also shown in *Figure 7* are similar data, from ref. 6, for both oxidized and chlorinated BPE and for chlorinated LPE. For the α relaxation, it may be seen that there is a progression at constant temperature towards lower $\log f_{\max}$ as one proceeds from the BPE specimens to chlorinated LPE to oxidized LPE. This is due to the progressively thicker crystals encountered, causing a slowing in the reorientation rate of the chains[3,11]. It should also be noticed that there is a distinct difference between LPE and BPE in the activation energy for the γ process (17 *versus* 12 kcal mol^{-1}). The behaviour in the β region is commented on in the next section.

The β relaxation

The loss map, enlarged in the β region, is shown in *Figure 8*. There is a progression towards higher temperature or lower frequency in proceeding from chlorinated BPE to oxidized BPE to chlorinated LPE to oxidized LPE. It is apparent that the connections to the crystal surface have a substantial constraining effect on the dynamics. At 1 kHz, the shift in $T_{\max}$ is over the range

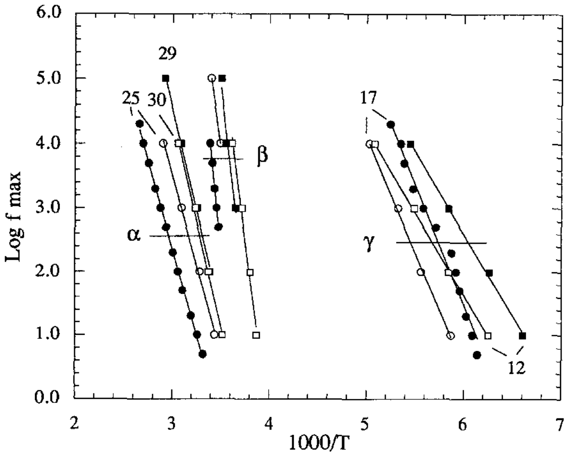

Figure 7 Loss map for the α, β and γ processes. ●, Oxidized LPE; ○, chlorinated LPE; ■, oxidized BPE; □, chlorinated BPE. Activation energies (in kcal mol^{-1}) are indicated (see *Figure 8* for those for the β process)

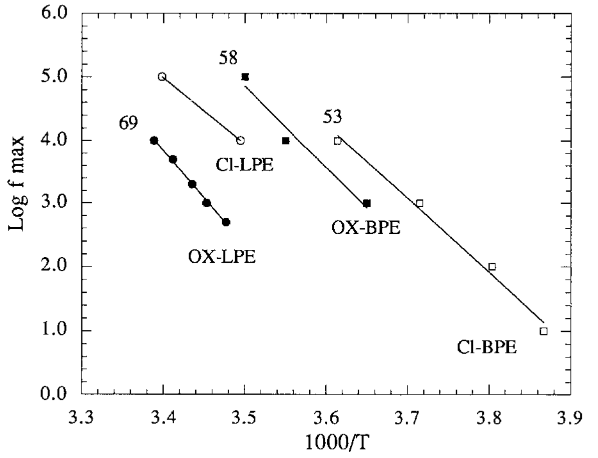

Figure 8 Loss map, as in *Figure 7*, enlarged in the β region. Activation energies (in kcal mol^{-1}) are indicated

270–290 K as the degree of crystallinity increases (through 22, 27, 42, 68%, ref. 6) over the specimens.

The strength of the β process relative to that of the γ relaxation is of interest. It appears from *Figure 2* that the β relaxation strength at 70°C is very approximately 0.015 as opposed to 0.025 for the strength of the γ relaxation at -100°C (*Figure 5*). If the partitioning of dipoles between the crystal and amorphous phases, suggested in ref. 6, is accepted then the Kirkwood–Onsager correlation factor for the γ process is very approximately 0.06. The correlation factor for the combined γ, β relaxations at 50°C would be of the order of 0.2. This would indicate a high degree of constraint indeed for the amorphous phase. However, there are too many uncertainties in determining the amorphous phase dipolar concentration to put much emphasis on the value.

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