

The glass transition and molecular motions of poly(chlorotrifluoroethylene)

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Molecular motions in poly(chlorotrifluoroethylene) have been studied over the range -150 to $+200^\circ\text{C}$ by thermal/mechanical techniques with the specific intent of clarifying the glass transition (T_g) of this polymer. An extremely broad Γ relaxation, centred at $\approx -15^\circ\text{C}$ and associated with an activation energy of 17 kcal mol^{-1} , is proposed to be a predominantly amorphous phenomenon involving small scale motions. A β relaxation peak at $\approx 95^\circ\text{C}$ with an activation energy of 64 kcal mol^{-1} represents the amorphous segmental mobility and its onset at $75 \pm 2^\circ\text{C}$ is assigned as the T_g . This value for the T_g of poly(chlorotrifluoroethylene) is supported by dynamic mechanical, thermomechanical and differential scanning calorimetric techniques. We are unable to support the existence of an α relaxation at 140 – 150°C , i.e. $T_g < T < T_m$, occasionally cited in the literature.

(Keywords: poly(chlorotrifluoroethylene); glass transition; molecular motions)

INTRODUCTION

Poly(chlorotrifluoroethylene) (poly(CTFE)) is a very important polymer with a unique combination of chemical, mechanical, electrical and optical properties. One of the major applications of poly(CTFE) is in barrier technology in which advantage is taken of its transparency and the fact that its water vapour permeability is the lowest of all known plastics. The glass transition temperature, T_g , is an important parameter for understanding the structure–property relationships. Although poly(CTFE) has been a commercial material since 1957, no reliable value has been assigned to its T_g .

Conflicting views on the T_g of poly(CTFE) have been expressed in a recent review article¹. Using specific volume *versus* temperature measurements, a T_g of 52°C has been reported for poly(CTFE)². However, there is also general agreement that a relaxation at $\approx 95^\circ\text{C}$ in mechanical and dielectric relaxation studies corresponds to the glass transition^{3–5}. Thus the literature lacks a definite, reliable value for the T_g of poly(CTFE). The result of this study is to propose $T_g = 75 \pm 2^\circ\text{C}$ based on dynamic mechanical analysis (d.m.a.), thermomechanical analysis (t.m.a.) and differential scanning calorimetry (d.s.c.).

EXPERIMENTAL

Materials

Two commercial grade poly(CTFE) resins were used in this study. Resin A had a molecular weight $M_w = 8.5 \times 10^5$ and resin B had $M_w = 3 \times 10^5$. The two resins exhibited melt crystallization (T_{cc}) temperatures of 175 – 176°C and subsequent reheat melting temperatures (T_m) of 213 – 214°C . These values were obtained by d.s.c. at $10^\circ\text{C min}^{-1}$ and are typical of a poly(CTFE).

All the characterization work was carried out on the moulded plaques. Resin A was compression moulded at

$\approx 250^\circ\text{C}$ into a plaque $\approx 1.25\text{ mm}$ thick and cooled in press (CIP). Resin B was moulded similarly but quick quenched in ice-cold water. The crystallinities of these samples have been estimated to be 30 – 50% by d.s.c.

Viscosity

The intrinsic viscosity $[\eta]$ of the samples was measured at 135°C with 2,5-dichlorobenzotrifluoride as the solvent. The intrinsic viscosity was converted to the weight average molecular weight (M_w) as follows:

$$[\eta] = 6.15 \times 10^{-5} (M_w)^{0.74}$$

Dynamic mechanical analysis

Two different instruments were used for d.m.a. A Rheometrics dynamic spectrometer, RDS-7700II, was operated in the torsion/rectangular geometry (shear mode) at a frequency of 10 rad s^{-1} (1.6 Hz) using a strain of 0.1% . The data was collected at 10°C intervals between -130 and 200°C . A Polymer Laboratories DMTA unit was operated in the bending deformation geometry (tension mode with shear correction) at a frequency of 1 Hz , a strain of $\approx 0.3\%$ and a heating rate of 3°C min^{-1} over the range -130°C – 200°C . Activation energies were calculated from two additional scans at 0.1 and 100 Hz .

Thermomechanical analysis

A Perkin–Elmer TMS-2 was used in the expansion mode. The sample was heated in a helium atmosphere at $10^\circ\text{C min}^{-1}$ from 0 to 200°C .

Differential scanning calorimetry

A Perkin–Elmer DSC-2C was used to measure the specific heat over range 0 – 170°C at a heating rate of $10^\circ\text{C min}^{-1}$ with a sample of 25 mg . A DuPont 9900 DSC was used to obtain the transition temperatures under the following conditions: argon atmosphere, $\approx 10\text{ mg}$ sample crimped in an aluminium pan and rates of $10^\circ\text{C min}^{-1}$ for melting/crystallization and $20^\circ\text{C min}^{-1}$ for glass transition determination.

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RESULTS AND DISCUSSION

The two poly(CTFE) resins, $M_w = 3 \times 10^5$ and 8.5×10^5 , were characterized by two types of d.m.a. unit to obtain the relaxation patterns. The materials were also characterized by t.m.a. and d.s.c. techniques. All the methods suggest $T_g = 75 \pm 2^\circ\text{C}$ for poly(CTFE).

Dynamic mechanical analysis

D.m.a. of resin A on the Rheometrics dynamic spectrometer (1.6 Hz, torsional deformation) exhibits two relaxations based on the shear modulus (G') and damping ($\tan \delta$) curves (Figure 1). Similar analysis on the Polymer Laboratories DMTA unit (1 Hz, bending deformation) provides an identical relaxation pattern (Figure 2).

 Γ Relaxation

The Γ relaxation peak is quite broad and extends over a range of 150°C (Figures 1 and 2). Obviously, it must involve contributions from several components. It is pointed out in the literature that the Γ peak is a composite of both crystalline (lower temperature component) and amorphous peaks⁵. While we confirm the composite

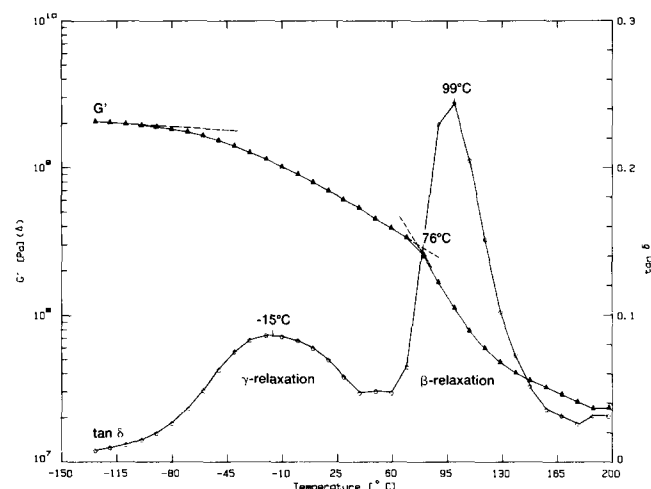


Figure 1 Dynamic mechanical analysis of poly(CTFE) resin A using Rheometrics dynamic spectrometer

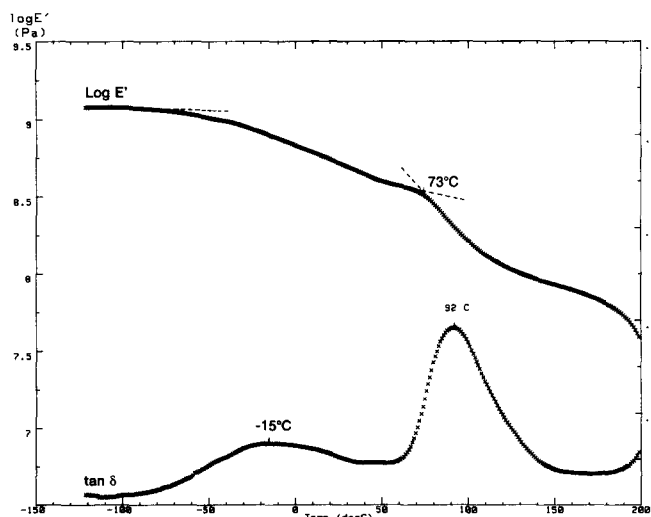


Figure 2 Dynamic mechanical analysis of poly(CTFE) resin A using Polymer Laboratories DMTA unit

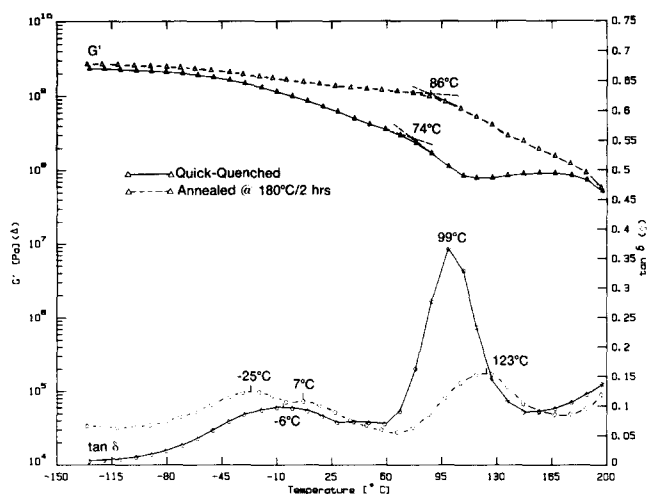


Figure 3 Effect of thermal history on relaxation strengths for Γ and β processes in poly(CTFE) resin B

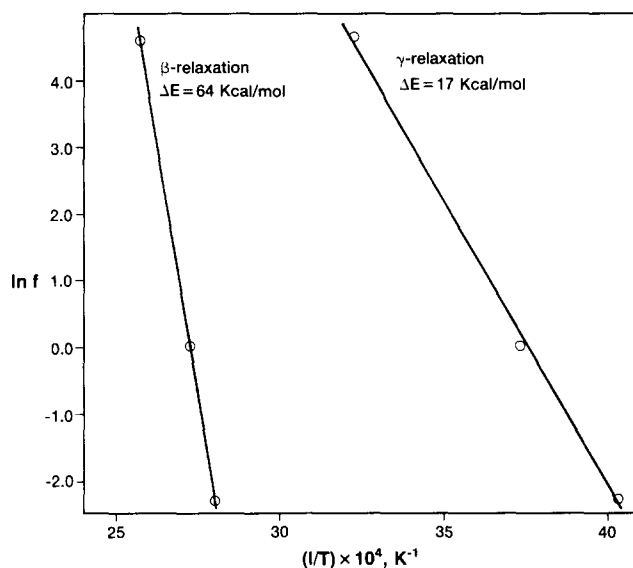


Figure 4 Activation energies for Γ and β relaxations of poly(CTFE) resin B

nature of the Γ peak (e.g. $\tan \delta$ curves in Figure 3), we stress that the Γ peak originates predominantly from the amorphous phase. For example, consider a substantial drop in the Γ relaxation strength on annealing, i.e. a change in shear modulus ($\Delta G'$) between -100 and $+75^\circ\text{C}$ (Figure 3). We believe that the Γ peak involves the following types of motion: small units of the polymer chain, perhaps 3–4 carbon atoms long⁶; loose chain ends within the amorphous and crystalline phases; and small scale or local motion of the amorphous segments, perhaps up to 10 carbon atoms long^{6,7}. This transition is known to occur at $\approx 0.75T_g$ (references 6 and 7). With a T_g of 75°C for poly(CTFE), the local chain motion would occur at -12°C , which is about the maximum in the Γ relaxation.

In addition to the motions of the moieties mentioned above, chemical heterogeneities (e.g. head–tail and tacticity) at the short chain level may also contribute to the extreme broadness of the Γ relaxation. From the frequency (f) dependence of the relaxation temperatures (Figure 4), an activation energy (ΔE) of 17 kcal mol^{-1} has been established for the Γ peak. This is in line with

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