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Positron lifetime spectroscopy characterization of thermal history effects on polycarbonate

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The effect of a short-term anneal above T_g on the free volume cavity size and concentration and on the fracture toughness of polycarbonate is examined. The positron annihilation lifetime (PAL) technique is used to measure the change in free volume concentration and cavity size during isothermal relaxation experiments at 10, 20 and 30° C. An activation energy of 16.5 kJ mol^{-1} is calculated for the relaxation of the annealed polycarbonate, compared to 12.3 kJ mol^{-1} for the unannealed material. The fracture toughness and brittle fracture morphology of compact tension specimens are unchanged by the anneal. The similarity in the PAL parameters and physical properties between the unannealed polycarbonate and the material annealed above T_g suggests that the short-term anneal does not appreciably alter the structural state of glassy polycarbonate.

1. Introduction

Understanding the relationship between mechanical properties and molecular structure in polymers is a necessary precursor to the prediction of physical responses, such as fracture toughness, yield strength, and creep resistance. In pursuit of this understanding, an investigation of polycarbonate, a structural polymer with a unique combination of high fracture toughness and strength, was performed using the positron annihilation lifetime technique and fracture tests. The structural state of a glassy polymer can be characterized in part by the amount of free volume present at a given temperature. The molecular motions and thus the mechanical properties of the polymer depend on this structural state. The thermal history of the polymer can alter the structural state, and this change is reflected in the kinetics of molecular relaxations [1, 2]. Annealing polycarbonate for short periods of time at temperatures above its glass transition temperature (T_g) is thought to erase the polymer's previous thermal history and release the frozen-in stresses associated with manufacturing [3]. In addition, physical ageing effects such as an increase in polymer density, enthalpic changes in T_g, suppression of a secondary relaxation and growth of spherulitic surface regions, produced by ageing heat treatments below T_g, are thought to be thermoreversible by annealing above T_g and then cooling [1, 3–7]. It was the purpose of this research to measure the effect of short-term annealing above T_g on the structural state of glassy polycarbonate.

Positron annihilation lifetime spectroscopy (PALS) provides a measurement of the time it takes for a positron to enter the sample material and annihilate with an electron from the surrounding molecular environment. The polycarbonate spectra can be modelled as comprising three positron lifetime components: 0.125 nsec attributed to para-positronium self-annihilation, 0.3 to 0.4 nsec attributed to free particle annihilation and 2 to 3 nsec attributed to ortho-positronium (oPs) pick-off annihilation. In the present study, as in previous similar studies of polycarbonate, only the oPs pick-off annihilation lifetime component (τ_3, I_3) exhibits a systematic dependence on time and temperature [8, 9] where τ_3 is its lifetime and I_3 its intensity. Because of its size, oPs is thought to localize only in regions of reduced electron density, including free volume sites in polymers. The free volume model used to interpret the results of this study depicts the free volume cavities in glassy polymers as spherical packets, which provide the space necessary for limited molecular mobility [10]. When oPs is trapped at these free volume sites, its lifetime (τ_3) is determined primarily by the local electron density and, therefore reflects the free volume cavity size. The relative intensity (I_3) of the oPs lifetime component gives an indication of the relative concentration of free volume cavities which serve as sites for oPs pick-off annihilation [9, 10]. A comprehensive description of the positron annihilation lifetime technique as applied to polymers has been provided elsewhere by Stevens [11].

2. Experimental procedure

The polycarbonate studied using PALS was a commercial sample of Calibre supplied by Dow Chemical Company. The unannealed polymer had a weight-average molecular weight of 30 000, and details of the compression moulding technique are presented elsewhere [12]. Polycarbonate samples, in the form of

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12 mm diameter discs for use in the PALS experiments, were annealed for 20 min at 165° C in an argon atmosphere at 1 torr and furnace cooled. The density of the samples was measured by the displacement method using distilled water as the displacement medium. Differential scanning calorimetry (DSC) measurements of the glass transition temperature were performed on a Dupont Model 900 thermal analyser equipped with a pressure DSC cell. The measurements were made at a pressure of 1 torr (1 torr = 133.322 Pa) in an argon atmosphere. The temperature scale was calibrated with the melting transitions of gallium, indium, and tin. Tests were run on 10 mg samples using a scanning rate of 5° C min^{-1}. The glass transition temperature was taken as the temperature at which the specific heat begins the transition from the glassy to the fluid state [13].

Positron lifetime measurements were performed using a standard fast–fast coincidence system with a timing resolution of 260 psec as determined from a ^{60}Co source with the energy windows set for ^{22}Na events. Two identically prepared samples were placed on opposite sides of 20 μCi (1 Ci = 3.7 × 10^{10} Bq) ^{22}Na–Ti foil source and subsequently sealed in a vacuum chamber maintained below 0.1 mtorr for the duration of the experiments. Each positron lifetime spectrum was collected to a peak height of 30 000 counts, corresponding to an integrated intensity of approximately 1 × 10^{6} counts. Thermal response and isothermal relaxation experiments were performed using a circulating bath with a temperature stability of ± 0.1° C. The temperature of the samples was monitored by a thermocouple in contact with one of the sample discs in the vacuum chamber. One set of annealed samples was used in the experiments. The annealed material was furnace cooled from 165 to 22° C at 1° C min^{-1} and allowed to stabilize at 22° C for over 600 h. The samples then were cooled to 4° C, and a spectrum was collected over a period of approximately 13 h. Next the samples were heated in 5° C increments, and the measurements were repeated at every stage up to 50° C. Thermal response measurements were made over a temperature range from 4 to 50° C both before and after completion of the isothermal relaxation experiments. The heating and cooling rate of the samples was 1° C min^{-1}. Isothermal relaxation experiments were performed by thermally inducing and monitoring the free volume relaxation process. The relaxation experiments followed a temperature programme that heated the samples to 50° C, held them at 50° C for 60 to 90 h and then cooled them to the relaxation temperature. Individual isothermal relaxation spectra subsequently were collected continuously until sufficient data were obtained for the relaxation analysis. The resulting spectra were modelled as a three-component exponential using the computer program PFPOSFIT [14]. A diagram of the heat treatment used in the positron experiments is shown in Fig. 1.

Fracture tests were conducted on compact tension specimens (CTS) machined from both unannealed and annealed Lexan polycarbonate. This material was supplied by General Electric Co. as 12.7 mm thick sheets of approximate size 1.2 m × 2.4 m. The polycarbonate was cut into smaller sheets and annealed at 155° C for 20 min using an Instron convective heat furnace. The annealing was followed by furnace cooling to 22° C. Using the procedures described earlier for Calibre, the density and glass transition temperature of the Lexan were measured both before and after the annealing.

Compact tension specimens were machined and tested in accordance with ASTM standard E399-83. A non-fatigue technique developed earlier was used to introduce precracks in the specimen [15]. This technique was used in order to avoid the heat generation and plastic deformation problems associated with fatigue-precracking techniques in polymers [16]. The fracture tests were conducted in an Instron tensile testing machine using a machine cross-head speed of 25.4 mm min^{-1}.

The fracture tests described above were conducted as a supplement to the PALS experiments on Calibre. Owing to the unavailability of Calibre at the time of the tests in the size and quantity required for valid fracture toughness measurements, Lexan was used as a surrogate material. However, it is unlikely that the response to annealing and the relaxations kinetics would be markedly different for these two polycarbonates. The kinetics are related to molecular mobility and thus to mechanical properties. A comparison of the known properties of the two materials (Table I) shows the high degree of similarity between them. In addition, the thermal response of these materials as measured by PALS has been shown to be similar by

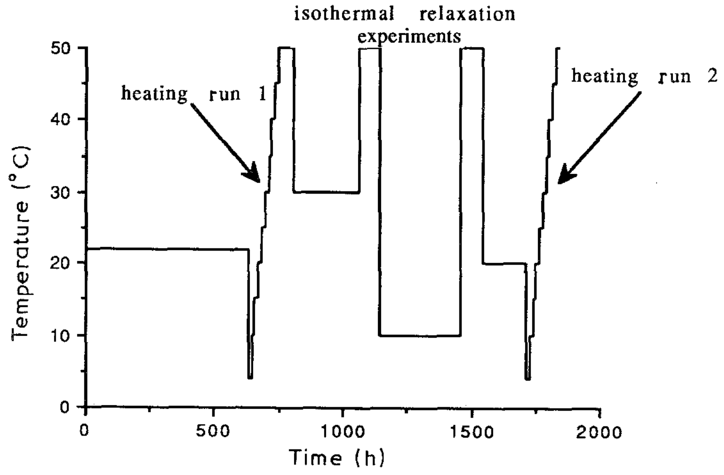

Figure 1 Schematic representation of the post-annealing heat treatment during the positron experiments.

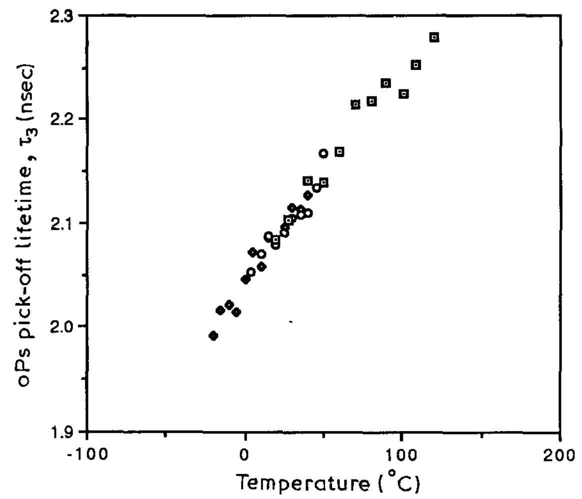

Figure 2 A comparison of the oPs component lifetime (τ_3) for Calibre and Lexan [20]. (◇) As-received Calibre, (○) annealed Calibre, (□) as-received Lexan.

Hill [20]. The variation of τ_3 with temperature for both Lexan and Calibre as determined by Hill [20], and reproduced here in Fig. 2, is indicative of this similarity. Thus, it is expected that relating the PALS studies to the results obtained by fracture tests is valid.

3. Results

3.1. Material characterization

Differential scanning calorimetry and density measurements were performed on the polycarbonate samples. Table II indicates that the glass transition temperature and the density are not changed appreciably by the annealing and the positron experiment thermal programme. A lack of crystallization, independent of thermal history, was inferred from the lack of a melting transition below 320° C.

3.2. Thermal response studies

The thermal response of the oPs pick-off annihilation lifetime (τ_3) is shown in Fig. 3 for both unannealed [17] and annealed samples of polycarbonate. The linear increase in τ_3 with temperature implies an increase in the free volume cavity size sampled by the oPs. The similarity in the τ_3 values and free volume cavity size expansion between the annealed and unannealed samples suggests that neither the thermal cycling of the positron experiments nor the short-term anneal above T_g alters the mean free volume cavity size in the temperature range studied. The τ_3 variation with temperature is statistically similar for the unannealed and annealed samples as determined by correlation coefficients of linear regression fits of the data. The error bars in Fig. 3 are representative of the component standard deviation calculated by the PFPOSFIT program [14] and are not the population standard deviation for the linear regression fits.

TABLE I Physical properties of polycarbonates

Properties	Calibre	Lexan
Yield strength (MPa)	62 000	62 000
Izod impact (kJ m^{-1})	0.85–0.90	0.64–0.85
Density (g cm^{-3})	1.1942 ± 0.0021	1.2009 ± 0.0001
T_g (° C)	150	144
M_w	30 000–32 000	≥ 30 000

TABLE II Density and glass transition values

Polycarbonate	Condition	T_g (° C)	Density (g cm^{-3})
Calibre	unannealed	150	1.1942 ± 0.0021
	annealed	151	1.1932 ± 0.0003
	post-relaxation	150	1.1935 ± 0.0025
Lexan	unannealed	144	1.2009 ± 0.0001
	annealed	143	1.2008 ± 0.0007

The thermal response of the intensity of the oPs pick-off component (I_3) for the annealed samples is shown in Fig. 4. The values of I_3 for the second heating (Run 2) indicate that upon cooling from 20° C after the final isothermal relaxation, the concentration of free volume sites available for oPs localization has decreased. This decrease is indicative of some physical ageing of the polycarbonate during isothermal relaxation experiments [9]. The I_3 values and thermal response for the annealed polycarbonate are similar to those reported previously for the unannealed polymer over the same temperature range [17].

3.3. Isothermal relaxation studies

The contraction experiment as described by Aklonis [18] consists of subjecting the material, previously at equilibrium at a temperature above the experimental temperature, to a rapid temperature decrease after which the free volume is monitored as a function of time. In the present study the annealed polycarbonate samples were held at 50° C and subsequently quenched to relaxation temperatures of 30, 10 and 20° C. The changes in τ_3 and I_3 as a function of time at constant temperature are shown in Figs 5a and b, respectively. The lifetime values (τ_3) exhibited no systematic change with time. The intensity values (I_3), however, decreased as a function of time. Because oPs is thought to localize in regions of reduced electron density such as free volume sites in polymers, a decrease in the intensity of the oPs pick-off component (I_3) indicates a decrease in the concentration of free volume sites available for localization.

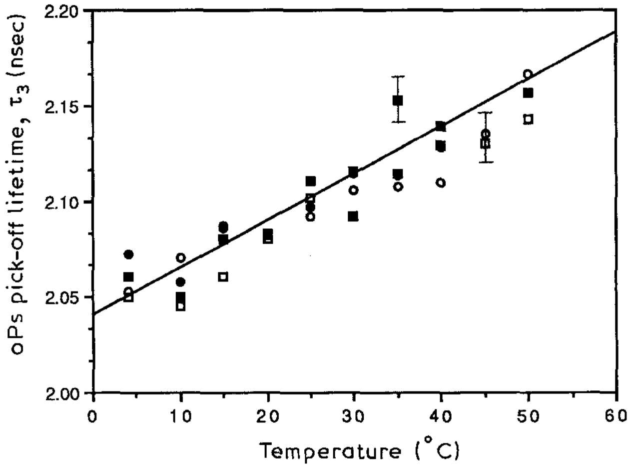

Figure 3 Variation of the oPs pick-off lifetime as a function of temperature upon heating for the (○, □) annealed and (●, ■) unannealed polycarbonate. (○, ●) Run 1, (□, ■) run 2.

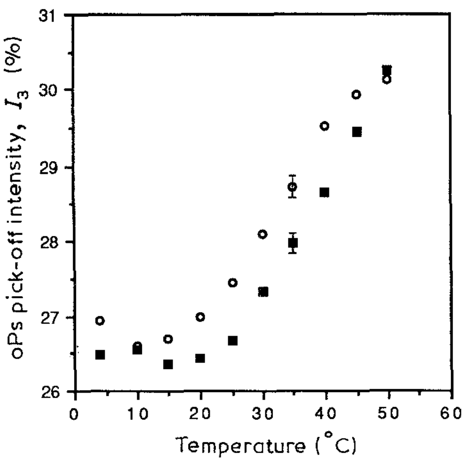

Figure 4 Variation of the oPs pick-off intensity as a function of temperature upon heating for the unannealed polycarbonate. (○) Run 1, (■) run 2.

3.4. Fracture tests

The average fracture toughness of the annealed specimens was not significantly different from the average fracture toughness of the unannealed material (Table III). Also, no significant difference was observed in the fracture morphology for these conditions. Both the annealed and unannealed specimens failed in a brittle fashion and exhibited a fracture morphology characteristic of brittle fracture in CTS of polycarbonate [9, 15, 16, 19].

4. Discussion

TABLE III Fracture toughness of Lexan

Condition	K_{Ic} (MPa m$^{1/2}$)
Unannealed	2.69 ± 0.09
Annealed	2.65 ± 0.10

The thermal response behaviour and the isothermal relaxation behaviour of the oPs pick-off component intensity can be interpreted in a manner that is consistent with the anticipated free volume behaviour in a glassy polymer. Fig. 6 shows a schematic illustration of the free volume concentration variation with temperature for a liquid cooled below T_g into the glassy state. The free volume concentration departure from the equilibrium liquid curve will be a function of cooling rate through the glass transition region. The non-equilibrium glassy state is time dependent: therefore as a function of departure from equilibrium and as a function of time, a glassy polymer subjected to a temperature step will display a free volume relaxation toward an equilibrium or more appropriately a quasi-equilibrium state. Observation of this relaxation depends on the time scale of the measurement. In the present study, free volume relaxations occurring over a 13 h period were combined into one datum point in the positron measurements.

As mentioned previously, some ageing of the polycarbonate occurs during the positron experiments. For Runs 1 and 2, ageing occurred at approximately 20° C because the material was held at that temperature for a substantial time period to further cooling (see Fig. 1). Partial erasure of this ageing will occur at temperatures greater than the ageing temperature. This erasure is reflected in the slope increase at approximately 20° C in Fig. 4 which is indicative of an increase in expansivity.

After the relaxation experiments, the free volume concentration appears to reach a lower quasi-equilibrium state as shown by the data points from

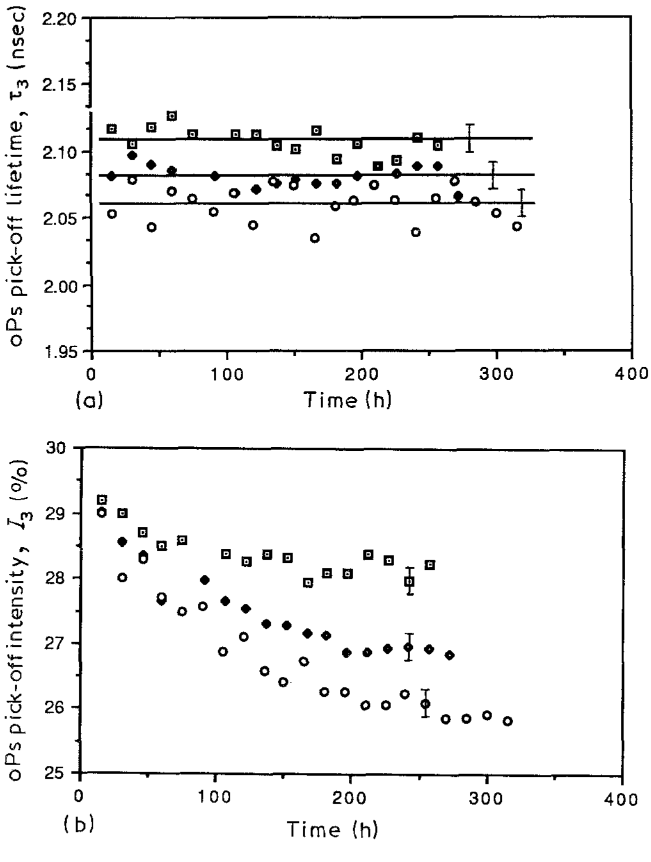

Figure 5 Variation of (a) the oPs pick-off lifetime and (b) intensity as a function of time at (□) 30° C, (◆) 20° C, (○) 10° C.

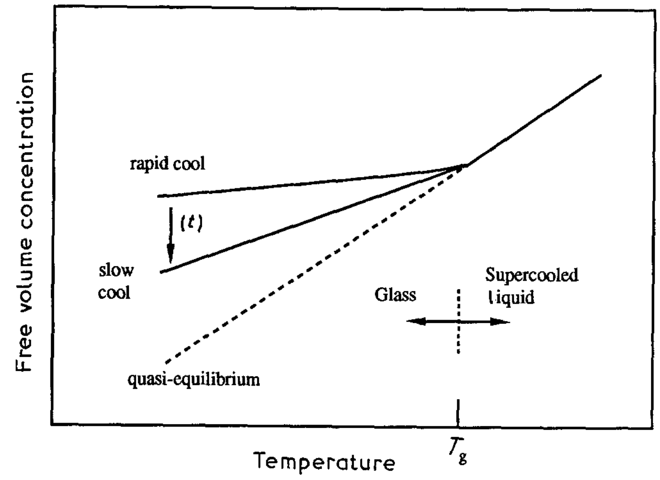

Figure 6 Schematic curves relating free volume concentration as a function of cooling rate through T_g.

Run 2. The lower state of quasi-equilibrium in Run 2 also is indicative of physical ageing and can be attributed in part to the repetitive ageing at 50° C during the isothermal experiments.

The dependence of the I_3 relaxation rate on the initial departure from equilibrium, as indicated by the first, second and final relaxation data points, is displayed in Fig 7. The arrows and dotted lines are drawn to indicate this dependence. The non-linear relaxation behaviour of glassy polymers has been modelled using the concept of fictive temperature. T_f, which describes the structural state of the polymer [21]. The fictive temperature for these relaxation experiments was 50° C, where the polymer was stabilized prior to the rapid temperature decrease. Fig. 8 is a schematic illustration of the free volume approach to a quasi-equilibrium state based on the relaxation data. An equilibrium relaxation function, $M_v(t)$ can be calculated using the values of free volume concentration derived from Fig. 8.

The equilibrium relaxation function is

$$M_v(t) = \frac{I_{3T_1}(t) - I_{3T_1}(\text{eq.})}{I_{3T_f}(\text{eq.}) - I_{3T_1}(\text{eq.})} \qquad (1)$$

which is an adaptation of the Narayanaswamy equilibrium density function for relaxation in glasses, where T_f is the fictive temperature and T_1 is the relaxation temperature [22, 23]. The expression

$$M_v(t) = \exp\left[-\left(\frac{t}{\tau_0}\right)^{\beta}\right] \qquad 0 < \beta \leqslant 1 \qquad (2)$$

has been shown to provide an excellent fit to nonlinear relaxation processes in glasses [24, 25]. The relaxation time constant is represented by τ_0. The value of β specifies both the deviation of the relaxation from exponential decay and also the distribution of relaxation times associated with the data. Figs 9a to c contain the experimental data points along with the best fit curves and the parameters derived for each relaxation temperature. The relaxation times increase as the relaxation temperature is lowered. If the relaxation times are modelled as the Arrhenius expression

$$\tau_0 = A \exp\left(\frac{\Delta E_a}{RT}\right) \qquad (3)$$

the calculated activation energy for the relaxation process is $\Delta E_a = 16.5\,\text{kJ}\,\text{mol}^{-1}$.

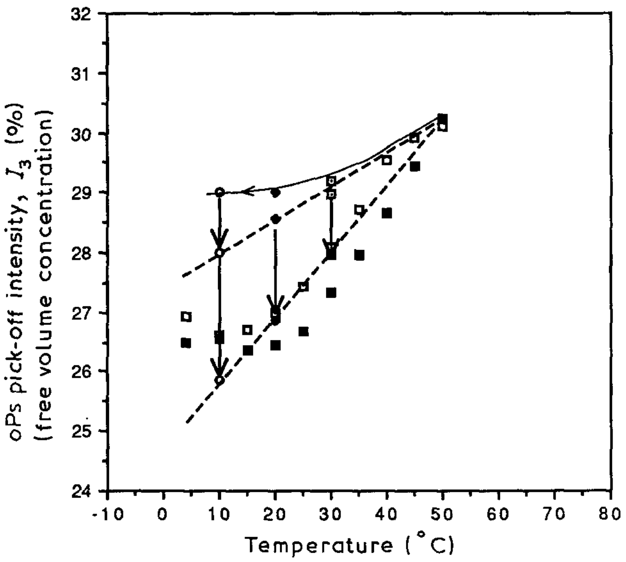

Figure 7 The oPs pick-off intensity thermal response and relaxation data related to a schematic curve of free volume concentration as a function of temperature and time. (□) Run 1, (■) run 2. (□) 30° C, (◆) 20° C, (o) 10° C.

The observed relaxation of the oPs pick-off intensity is consistent with the free volume concentration–temperature behaviour for a glassy amorphous polymer presented in Fig. 6. As indicated by the results, the activation energy for the relaxation process is in the approximate range of 12 to 17 kJ mol^{-1}. At temperatures this far below T_g, the molecular motions contributing to the relaxation are expected to be local motions of chain segments as opposed to the main chain motions expected near T_g [26, 27]. The activation energy of 12 to 17 kJ mol^{-1} is in the same range reported for secondary relaxations occurring below T_g in polycarbonate. These secondary transitions have been attributed to local motions of specific molecular groups. Measurement techniques such as dielectric loss spectroscopy, dynamic mechanical loss spectroscopy and nuclear resonance have identified the methyl group rotation with an activation energy range of 6.6 to 22.0 kJ mol^{-1} [28–31], and the carbonate group relaxation and the phenylene group motion with an activation energy range of 5.9 to 54.3 kJ mol^{-1} [27, 30, 32–39]. In light of the overlap of the activation energy ranges, attempts at identification of specific molecular features in polycarbonate responsible for the free volume relaxations are inconclusive [8]. Nonetheless, the relaxation times are representative of

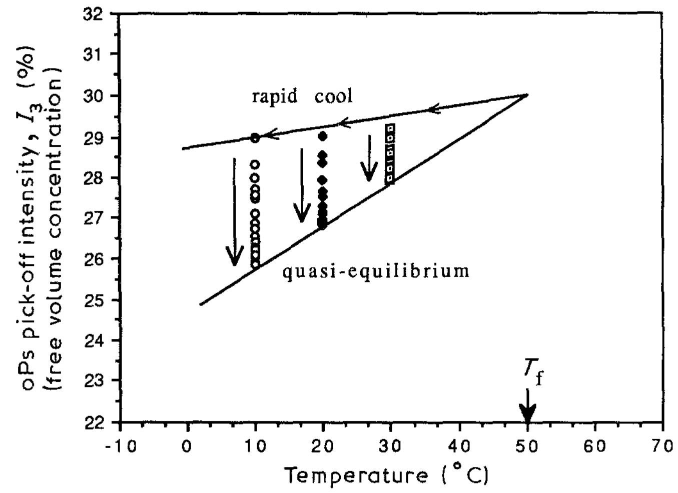

Figure 8 Schematic curves relating oPs pick-off intensity to the recovery of free volume in the glassy state. (□) 30° C, (◆) 20° C, (○) 10° C.

the molecular motions of the polymer and can be used to characterize the nonequilibrium nature of the glassy state [18, 40].

As Lindenmeyer [41] has stated, the structure and properties of glassy polymers are dependent not only on the temperature, pressure and composition but also on the history or path by which the polymer reaches its present state. The present study indicates that the free volume response to temperature in polycarbonate is not altered significantly by a short-term anneal above T_g. The activation energy of 16.5 kJ mol^{-1} calculated for free volume relaxations in the annealed polycarbonate compares well with the activation energy of 12.3 kJ mol^{-1} calculated in a similar manner, in a study for unannealed polycarbonate [8]. Struik [42] also observed no difference in the secondary relaxations of some glassy polymers which were studied both in the as-received condition and after annealing above T_g.

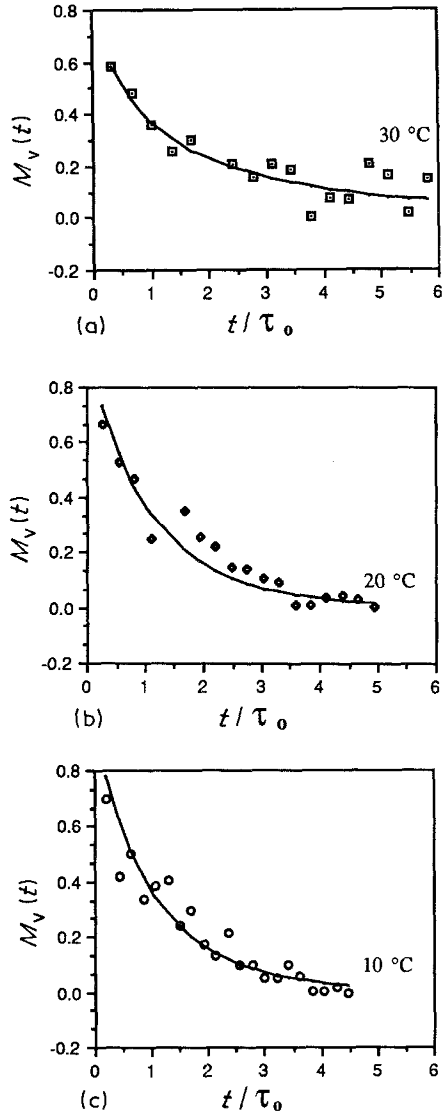

Figure 9 The oPs pick-off intensity relaxation data modelled using the Narayanaswamy model of structural relaxation. (a) τ = 44.26 h, β = 0.5732; (b) τ = 55.25 h, β = 0.8358; (c) τ = 70.32 h, β = 0.8921.

The results of the fracture tests in this study indicate that there is no significant difference in the fracture toughness of the as-received and annealed poly carbonate. Also, the fracture morphology of brittle fracture was determined to be similar for the polycarbonate in both conditions. In a polymeric material the ability to deform and absorb energy is contingent upon the ease with which its molecular chains can slide past each other, or change conformations via in-chain rotations. Because this ease would depend to a degree on the free volume available for facilitating molecular movement, it would be expected that any changes in the free volume would be reflected in the fracture toughness measurements. This was exemplified by the findings of an earlier study by Hill *et al.* [9], which demonstrated that the rapid physical ageing of polycarbonate at a temperature approximately 30° C less than T_g is accompanied by a subsequent decrease in the free volume cavity size and concentration, and a decrease in fracture toughness. In addition, the activation energy for isothermal relaxations of this aged polycarbonate, calculated in a manner similar to that of the present study, was 34.3 kJ mol^{-1}. In the present study both the lack of change in the fracture toughness and in the free volume characteristics measured by PALS indicate that a short-term anneal above T_g does not significantly change the structural or mechanical properties of glassy polycarbonate.

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