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The effect of gamma irradiation on the pressure dependence of the room temperature transition in PTFE

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Abstract

Some of the effect of gamma irradiation on the pneumatic pressure dependence of the well established room temperature transition (ca. 19 °C) in polytetra(fluoroethylene) are described. The experiments, conducted up to a maximum gamma dosage of 60 Mrad and a superimposed nitrogen pressure of 48.3 MPa indicate a significant reduction in the room temperature transition as well as its pressure dependence with the increasing of the gamma dosage. These data, combined with the observed and reported reduction in the free volume (actually net volume) are consistent with the proposition that irradiation process results in a reduction in the 'effective internal pressure' due to extensive bond scission. The latter process is manifested in an observed dramatic decrease in the molecular weight. Data on the compressibility and coefficient of thermal expansion, accompanied by thermodynamic arguments, indicate that the room temperature transition more closely resembles a second order transition as gamma dosage increases. This is consistent with a change in system behaviour progressing from a viscoelastic to that of a brittle glassy polymer as confirmed by monitoring the polymer creep behaviour following rapid pressurisation. Data for the 'freshly' irradiated specimens indicate highly transient post-irradiation induced changes in the polymer morphology.

Keywords: Gamma irradiation; Polytetra(fluoroethylene); Transition temperature

1. Introduction

Poly(tetrafluoroethylene) (PTFE) possesses an outstanding combination of chemical and physical properties comprising excellent chemical resistance [1], high temperature stability [2], excellent dielectric properties [3] and exceptionally low coefficient of friction [4]. The powder has a crystalline melting point of 327 °C [5], an unusually high value for an organic material. The useful monolithic polymer will not flow above its crystalline melting point due to its extremely high melt viscosity, and hence conventional, and attractive fabrication techniques such as injection moulding are not applicable to PTFE. The normal fabrication processes are therefore limited to compaction followed by sintering of the powder. This restriction makes PTFE an expensive polymer to manufacture. Various attempts [6] to develop a modified fluorinated polymer or copolymer, which may be utilised by conventional techniques, have either failed or produced a polymer which is far inferior to PTFE.

Despite these difficulties, the superior properties of PTFE have sustained a continued and considerable interest in providing a better understanding of its characteristics and ways of modifying them both at microscopic and macroscopic levels.

Studies on the crystal structure and chain conformation of PTFE have been extensively reviewed [7]. These studies indicate that this polymer undergoes two, reversible, transitions at 19 and 30 °C, which together involve a change of approximately 1% in density; the main change (ca. 80%) being at 19 °C [8].

A comprehensive study of the molecular motions that may occur as a result of these transitions was explored by McCrum [31] using a torsion pendulum and PTFE samples with widely different degrees of crystallinities; the 19 and 30 °C transitions were attributed to the crystalline domains.

Externally induced changes in the temperature range at which the two transitions may occur can be used as a useful tool to aid understanding as to how various factors, in particular applications of pressure and gamma irradiation may affect the polymer mechanical behaviour. One of the problems associated with the 'virgin' polymer is that its

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constitution, molecular weight and crystallinity are normally rather invariant. Irradiation of PTFE has often attracted special attention, since it can readily produce large reductions in molecular weight and increasing density leading to an increase in effective crystallinity [9]. Studies of the infrared spectra [9] indicate that most of this change is confined to the amorphous domains. Similar observations have also been made [10,11] following gamma irradiation of other polymers such as ultra high molecular weight poly(ethylene oxide) where an increase in crystallinity has been obtained based on positron annihilation measurements.

Interestingly, as for many other polymers [12], the friction and wear characteristics of PTFE may be greatly affected by subtle changes in chain mobility, migration or the molecular architecture both at the surface and in the bulk. Irradiation induces all of the above changes [4].

The effects of an external pressure on the transition temperatures in PTFE has been extensively studied [13–16, 25]. These studies indicate that the higher the external pressure, the higher is the transition temperature. This general outcome may be rationalised as follows. Relaxation processes in the polymer involve the rotation or displacement of side groups or chain segments requiring sufficient local space (free volume) and vibration energy to overcome the intra-molecular forces. Hydrostatic pressure reduces the available volume and hence restricts the mobility of the chains. This means that for a relaxation to occur at a higher pressure more thermal energy is required.

However, other data given by Briscoe and Mahgerefteh [17,18], indicate that this interpretation may not be valid in cases where the polymer is permeable to the pressure transmitting medium. In these cases, the specific intermolecular interactions of the permeated species with the polymeric chains may play an important role in affecting the transitions. Shifts in the transition temperatures for PTFE using N_2, He and Ar pressure media of 0.19, 0.20 and 0.16 °C/MPa were, respectively, reported. These values may be compared to a higher, but universally constant value of 0.21 °C/MPa in the case of impermeable pressure media such as an hydraulic oil. Briscoe and Mahgerefteh [17,18] concluded that sorbed gases, under high pressure, modify the intermolecular relaxations within PTFE by not only compressing the polymer but also 'lubricating' the polymeric chains.

These various studies indicate several interesting effects and have introduced a number of conceptional problems associated with describing how gas pressure can influence the internal state within a polymer. Most notable is the fact that the polymer absorbs large quantities of gas but yet sustains compressive stress.

The purpose of this paper is to report a study to examine whether the changes in the morphology and molecular weight brought about as a result of gamma irradiation may reveal any information on the way in which various levels of gas pressure may influence the polymer's properties. The study has been restricted to the monitoring of volumetric changes associated with the room temperature transition at various gas pressures using a specially developed capacitance transducer for several gamma irradiated modified PTFEs.

The data reported have been used to obtain a number of theoretical predictions and these have been compared with the experimental results. Three approaches are used; the Clapeyron equation [19] for entropy change, the Gee [20] equation for predicting the pressure dependence of the transition temperature and the computation of the 'internal pressures'. The comparison of theory and experiment enables a number of suggestions to be made regarding the influence of the gas pressure media, in particular a proposed mechanism by which gamma irradiation modifies the pressure dependence of the room transition temperature in PFTE.

2. Experimental

2.1. The high pressure apparatus

Fig. 1 shows a schematic layout of the high-pressure apparatus used for pressurising the polymer specimens. The unit consisted of a gas booster pump (1) (Charles Madan, Altrincham; 1:85 compression ratio) driven by an hydrovane air compressor (2.6 kW, 1450 rpm; Whittaker Hall, Manchester) (2), a supply gas cylinder (3), an intermediate gas receiver (4) and a main pressure vessel (5) containing the polymer specimen enveloped in a heat exchanger (6). The main pressure vessel, charged up to a maximum pressure of 48.3 MPa using the gas booster pump was contained in a blast box (7) for safety requirements. An important feature was the pump's ability to maintain a fixed pressure by simply adjusting the driving air pressure using a regulator. This compensated for small leaks or thermal fluctuations.

The intermediate gas receiver (4), designed to contain approximately five times the volume of gas in the main pressure vessel (5) acted as a pressure stabiliser or 'buffer'. The main stainless steel pressure vessel (5) was 61 cm in length with an OD and ID of 12.7 and 5.08 cm, respectively. The unit was assembled using two mushroom-shaped caps

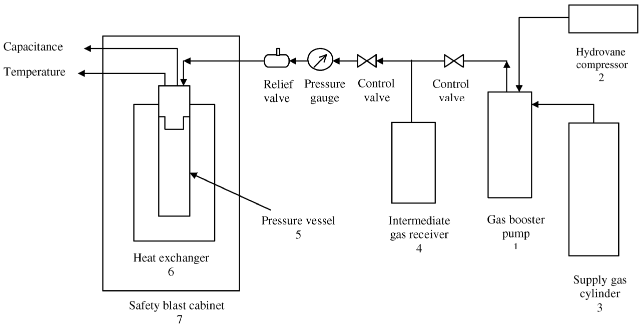

Fig. 1. A schematic representation of the high pressure apparatus used for pressurising the polymer specimens.

each secured to the body of the pressure vessel via 6 high tensile bolts. The safe working pressure was 258 MPa. The top cap contained 6 insulated electrical connections, two of which were used for measuring capacitance (see later), and another two served as connections for a platinum resistance thermometer (type 158-328, Radio Spare).

The heat exchanger used for controlling the polymer temperature contained heating oil (Type NS41; British Petroleum) heated by two thermostatically controlled 0.8 kW heaters. It was cooled by circulating a coolant (water and ethyleneglycol mixture) through a copper coil wound around the inner wall of the heat exchanger. The coolant temperature was lowered by a 0.6 kW thermostatically controlled cryostat.

The above arrangement allowed the polymer temperature, inside the pressure chamber, to be raised at a maximum rate of 15 °C/h with ±0.2 °C stability.

2.2. Materials and gamma irradiation procedure

PTFE was supplied by ICI PLC, with a crystallinity of ca. 70% (as determined by infrared absorption) corresponding to a density of ca. 2220 $\mathrm{kgm^{-3}}$ at 23 °C. Nitrogen gas was supplied as white spot oxygen free (BOC, UK).

PTFE specimens were evacuated in glass tubes using a high vacuum diffusion pump (Edwards High Vacuum, Ltd) up to ca. 9×10^{-5} Torr vacuum for approximately 6 h. These vials were then flame sealed. Evacuation avoided complications associated with decarboxylation due to combination of oxygen with the $\mathrm{CF2^{\cdot}}$ radicals generated as a result of gamma irradiation [9,21]. The specimens were irradiated at 26 °C up to a maximum dosage of 60 Mrad using a $\mathrm{Co^{60}}$ Gamma source at a rate of 1.3 Mrad/h. The glass tubes, containing the specimens were equally spaced near the gamma source to ensure uniform irradiation. Five samples were prepared with the various dosages; 2.5, 5, 10, 20, and 60 Mrad.

All of the samples were aged conditioned. This involved leaving the irradiated specimens in the sealed glass tubes for approximately 2 weeks prior to use. The 20 Mrad specimen was however tested soon (ca. 1 h) after irradiation in order to investigate the influence of residual post-irradiation effects [22,23] on the polymer behaviour.

2.3. The capacitance transducer

Fig. 2 shows a schematic representation of the capacitance cell used for measuring transition temperatures and polymer volume, mounted inside the pressure vessel. Briefly, the technique was based upon measuring the electrical capacitance between two conductive brass plates incorporating the PTFE specimen. The latter (A) in the form of a cylindrical rod (ca. 16 mm in dia and 50 mm in long) was machined at one end to accommodated a brass ring (B) which acted as one of the capacitance plates. Brass was used as the material of construction for all metallic parts in the cell due to its very low thermal expansion coefficient (ca. $18\times10^{-6}\ \mathrm{C^{-1}}$; [5]). A 30 mm long support rod (C) passing along a clearance hole drilled through polymer's axis supported the polymer and also provided an electrical connection for the second element (D) of the capacitance probe. Three spring loaded 1.3 mm diameter screws (E) passing through the brass support plate (F) were used for adjusting the separation, *t* between the brass ring (B) and the brass tube (D). The brass support plate (F) sat in a tightly fit PTFE cap (G). This ensured electrical insulation of the capacitance assembly from the pressure vessel cap (H) and its cylindrical chamber (I). A measurement of the capacitance between the members (B) and (D) allows the precise measurement of the gap, *t* and hence to polymer linear expansion. However, in practice the gaseous electrical capacitance is both pressure and temperature dependent and a calibration is therefore essential in order to infer the polymer volume. This data was previously provided by Briscoe and Mahgerefteh [24] using a capacitance cell identical to that used in the present work with the exception of the polymer specimen being replaced by quartz. The latter was assumed to be incompressible with a negligible coefficient of thermal expansion.

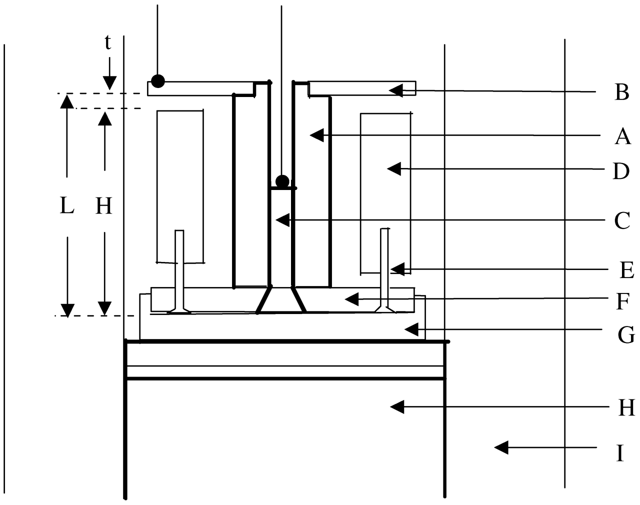

Fig. 2. A schematic representation of the capacitance probe used for measuring transition temperatures and polymer volume. PTFE rod (A), top capacitance plate (B), central support rod (C), housing brass tube (D), adjusting support screws (E), base support plate (F), PTFE insulation cap (G), pressure vessel top cap (H) and pressure vessel chamber (I).

Transition temperatures were manifested in a marked change in electrical capacitance as a result of an abrupt change in the polymer volume.

A capacitance measuring assembly (type 1620-A, General Radio) was used for the measurement of electrical capacitance. The system consisted of a transformer-ratio-arm bridge, an audio-oscillator, a tuned amplifier and a null detector. A typical oscillator frequency of approximately 1 kHz was used. Temperature was monitored using a platinum resistance film (type 158-328; Radio Spares, UK) with typical response time and accuracy of 0.1 s and

± 0.1 °C, respectively. The probe was placed close to the PTFE specimen in the capacitance cell.

2.4. Molecular weight measurement

Molecular weights of irradiated specimens were measured using a differential scanning calorimeter. The number average molecular weight, M_n was calculated from a previously obtained (ICI; private communication) calibration equation which related the height of the crystallisation peak, H_m in mm to the sample's molecular weight. The relation is given by

$$M_n = 1.172 \times l0^6 H_m^{-0.1313} \quad (1)$$

2.5. Experimental procedure

The polymer cell was placed at the base of the gas pressure vessel. The specimen was then maintained at ca. 0 °C for 8 h using the heat exchange system prior to pressurisation in order to ensure thermal equilibration. Experiments were carried out at the pressures of 0, 1, 13.8, 20.7, 27.6, 34.5 and 48.3 MPa using nitrogen gas. The polymer sample temperature was raised at a maximum rate of 0.1 °C/min. This ensured thermal equilibration between the ambient and the polymer at all pressures [25]. The electrical capacitance signal was monitored at 0.2 °C intervals.

A slow pressurisation rate of 3 MPa/min avoided complications associated with the quasi-adiabatic heating of the polymer [25]. A typical experiment at each isobar lasted approximately 9 h.

3. Data analysis

3.1. Polymer volumetric strain measurement

The electrical capacitance, C between two parallel plates separated at a distance, t is given by [26]

$$C = [K_0 K(P,T) A]/t \quad (2)$$

where K_0 is the permittivity of free space and $K(P,T)$ is the relative permittivity or the dielectric constant of the medium separating the two plates. The latter is a function of both ambient temperature and pressure. A, is the effective area of the plates and, t is the plate separation (see Fig. 2).

Considering the glass calibration and the polymer capacitance cells having the same area, A at the same temperature and pressure, the capacitance plate separation, t_p using Eq. (2) for the polymer cell is therefore given by

$$t_p = (C_r/C_p)t_r \quad (3)$$

where the subscripts, r and p refer to the glass calibration reference and the polymer cells, respectively. In the case of the polymer cell, assuming that the thermal expansion coefficient of brass is negligible, the length, L (see Fig. 2) of the polymer is given by

$$L = H + t = H_p + (C_r/C_p)t_r \quad (4)$$

where H is the distance between the base plate (F) and top of the brass housing cylinder (D) (see Fig. 2). Based on previous work by Briscoe and Mahgerefteh [27], the influence of pressure on the calibrated electrical capacitance for nitrogen at 0 and 45 °C are presented by the following second order polynomials

$$C_r = 9.2515 + (571 \times 10^{-10} P) - (402 \times 10^{-18} P^2) \quad (5)$$

at 0 °C

$$C_r = 9.2536 + (477 \times 10^{-10} P) - (297 \times 10^{-18} P^2) \quad (6)$$

at 45 °C

where P is pressure in Pa and C_r is the calibrated capacitance in pF. Unfortunately, Briscoe and Mahgerefteh [27] did not provide data for, C_r at intermediate temperatures between 0 and 45 °C. In this work these data are obtained based on linear interpolation as the variation of calibration capacitance with temperature is very small as compared to that obtained in conjunction with the polymer specimens. Assuming that the polymer expands isotropically, the volumetric strain, ΔV during transition is given by

$$\Delta V = 3\Delta L = 3(L_1 - L_0)/L_1 \quad (7)$$

or substituting the above in Eq. (4) and rearranging, we have

$$\Delta V = 3C_{p0}t_r(C_{r1}/C_{p1} - C_{r0}/C_{p0})/(C_{r0}t_r + C_{p0}H_p) \quad (8)$$

The subscripts, 0 and 1, respectively, refer to the beginning and the termination of transition at the corresponding capacitance (C_p or C_r) and polymer lengths (L_p).

3.2. Coefficient of linear thermal expansion

The coefficient of linear thermal expansion is defined as

$$\alpha = \frac{\Delta L}{L_s \Delta T} = \frac{(L_1 - L_0)}{L_s(T_1 - T_0)} \quad (9)$$

or using Eq. (4), we have

$$\alpha = \frac{(C_{r1}/C_{p1} - C_{r0}/C_{p0})t_r}{(T_1 - T_0)L_s} \quad (10)$$

where L_s is the polymer length at a reference temperature (10 °C).

4. Results and discussion

4.1. Transition temperatures

Figs. 3 and 4 show the results of capacitance measurements using the polymer cell incorporating the irradiated PTFE specimens. The data show the variations of the capacitance with temperature at various gamma doses and pressures using nitrogen gas as the pressure transmitting medium. Although the experiments were carried out at 5, 10, 20 and 60 Mrad radiation doses, only the results for the 5 and 60 Mrad specimens are shown here to conserve space.

Some of the salient features of the data presented in the figures may be summarised as follows. The drop in capacitance with increasing temperature at each isobar is consistent with the polymer's expansion. The rapid discontinuity on the other hand is associated with a sudden expansion of the polymer at the 20 °C atmospheric transition. The subsequent much less pronounced discontinuity is associated with the 30 °C transition.

The rate of change in capacitance with temperature, dC/dT is directly governed by the coefficient of thermal expansion, α of the polymer. Also, the change in capacitance during the transition is directly related to the change in the volume, ΔV.

Remarkably, it was found that the freshly irradiated 20 Mrad sample exhibited a much less marked transition as compared to the conditioned specimens, which were tested some time (120 h) after irradiation. This is tantamount to suggesting that the structural changes within the polymer matrix following irradiation are highly time dependent. The origin and the manifestation of this phenomenon on other characteristics of the polymer will be discussed later.

Fig. 4 includes data for the 60 Mrad (curve G) specimen which had already been exposed to the full pressure cycle and then re-tested at atmospheric pressure. The negligible change in capacitance compared to the unpressurised specimen (curve A) indicates no permanent densification of the polymer matrix due to pressurisation. This is in contrast to the data previously reported [18] for the unirradiated PTFE specimen where a 1% permanent densification was observed following exposure to the same pressure cycle.

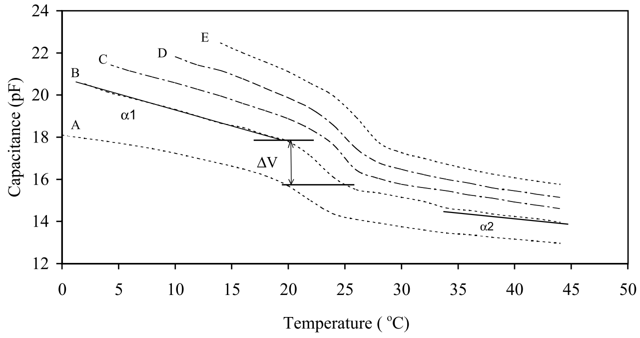

Fig. 3. The variation of electrical capacitance with temperature for 5 Mrad irradiated PTFE specimen at various ambient (nitrogen gas) pressures. Curve A: 0.1 MPa; Curve B: 13.8 MPa; Curve C: 20.7 MPa; Curve D: 27.6 MPa; Curve E: 34.5 MPa.

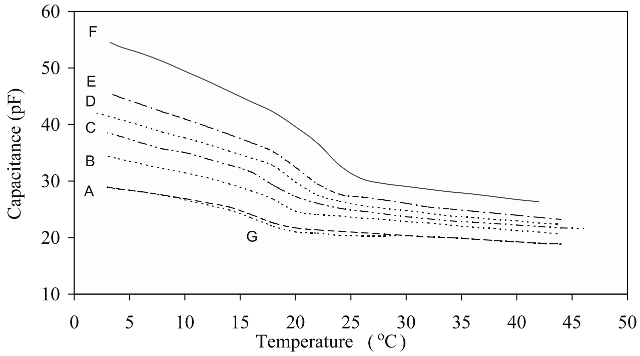

Fig. 4. The variation of electrical capacitance with temperature for 60 Mrad irradiated PTFE specimen at various ambient (N2) pressures. Curve A: 0.1 MPa; Curve B: 13.8 MPa; Curve C: 20.7 MPa; Curve D: 27.6 MPa; Curve E: 34.5 MPa; Curve F: 48.3 MPa; Curve G: 0.1 MPa (pre-pressurised to 48.3 MPa).

The capacitance/temperature data were differentiated to locate the position of the transition temperatures. These results, plotted in terms of the variation of the rate of change in capacitance with temperature, dC/dT against temperature for 5 Mrad specimen are presented in Fig. 5. The dC/dT values were calculated at 0.2 °C intervals and averaged at every 4 consecutive points. This procedure greatly reduced the amount of scatter in the data.

The data show two peaks at each isobar. The first is associated with the atmospheric room temperature transition. The second peak, broader and shallower is a consequence of the 30 °C transition. The observed systematic increase in the height of the peaks indicates that the reorganisation in the polymer's structural conformation, during the transition occurs over a smaller temperature range, or becomes 'more rapid', when either the ambient pressure or gamma dosage are increased. This point will be discussed later.

The variation in the location of the room temperature transition with increasing pressure at various irradiation doses, as extracted from the data in Fig. 5 as well as those for the other radiation doses are plotted in Fig. 6. The

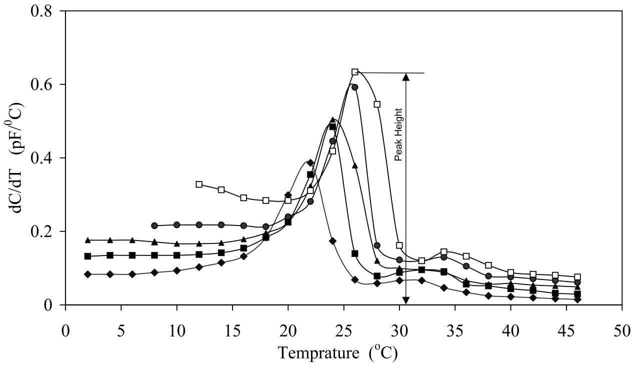

Fig. 5. The variation of the temperature dependence of capacitance (dC/dT) with temperature at various pressures for 5 Mrad irradiated PTFE specimen. ◆: 0.1 MPa; ■: 13.8 MPa; ▲: 20.7 MPa; ●: 27.6 MPa; □: 34.5 MPa.

corresponding data [18] for the virgin polymer are also presented for comparison. The location of the 30 °C transition is less precise.

These data indicate two important points. First, as expected, the room temperature transition increases with rising of the pressure and the dependence is also linear. The introduction of the gamma irradiation reduces the transition temperature and the magnitude of the decrease increases with the dose level. Thermally induced transitions involve the cooperative motion of polymeric chains [7]. These processes require sufficient thermal energy whose magnitude is directly related to the chain length, temperature and available free space. A decrease in the transition temperature, following irradiation, is therefore consistent with either a reduction in chain length due to bond-scission or an increase in free volume. The latter is at first sight unlikely as it is known [4] that irradiation of PTFE results in its densification. Notably, experiments by Zhang and Cameron [28] have indicated a modest increase in the glass transition temperature of polypropylene following gamma irradiation. This apparent anomaly may be due to the interaction of oxygen atoms with the polymeric chains as for these tests, the polypropylene specimen was irradiated in air.

The data in Fig. 6 were fitted to straight line using the method of least squares. The corresponding variation of the transition temperature, T_α with pressure, P is given by

$$T_\alpha = AP + B \tag{11}$$

where A is the pressure dependence of the transition temperature, $\mathrm{d}T_\alpha/\mathrm{d}P$ (°C/MPa) and B, the intercept. Fig. 7 shows the variation of $\mathrm{d}T_\alpha/\mathrm{d}P$ plotted against irradiation dosage. As it may be observed, the pressure dependence of the room temperature transition decreases, albeit at a small rate with increasing gamma dosage.

Based upon the Clapeyron equation, the pressure dependence of the transition temperature for a phase change is given by is given by [19]

$$\mathrm{d}T_\alpha/\mathrm{d}P = \Delta V/\Delta S \tag{12}$$

where ΔV and ΔS are, respectively, the accompanying changes in volume and entropy which occur during the transition. Assuming that the room temperature transition is sufficiently rapid so that thermodynamic principles may be applied, the observed reduction in the value of $\mathrm{d}T_\alpha/\mathrm{d}P$, as a result of irradiation is therefore consistent with either an increase in ΔS and/or a decrease in the ΔV parameter.

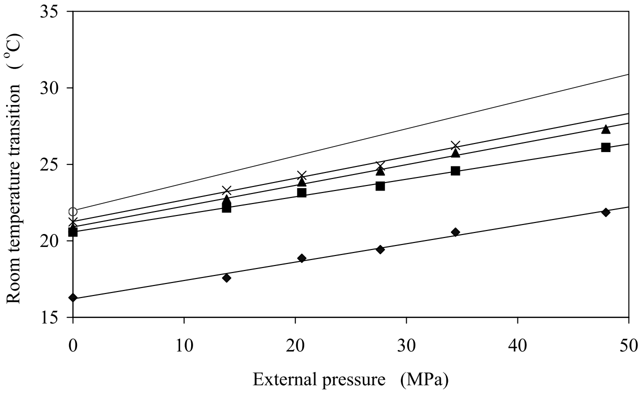

Fig. 6. The variation of the room temperature transition with applied pressure for different dose gamma irradiated PTFE samples. ◆: 60 Mrad; ■: 20 Mrad; ▲: 10 Mrad; ×: 5 Mrad; ○: Virgin [17].

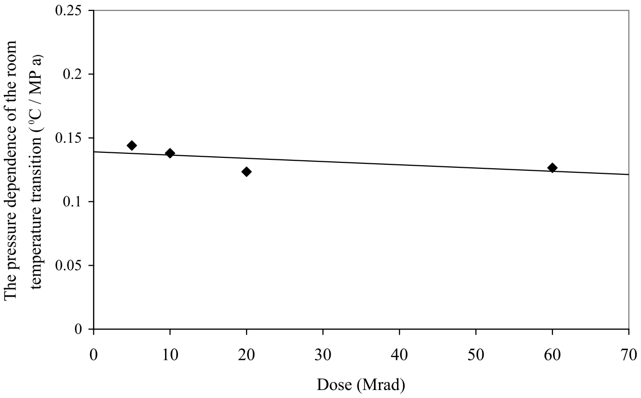

Fig. 7. The effect of gamma irradiation dosage on the pressure dependence of the room temperature transition in PTFE.

Fig. 8 shows the variation of the computed volumetric strain, ΔV which evolves during the transition with pressure at various gamma doses. ΔV is calculated based upon the data given in Fig. 3 as well as those for other radiation doses and using Eq. (8). With the exception of the 20 Mrad ‘freshly’ irradiated sample, the data indicate a linear increase in the value of ΔV with both irradiation dose and pressure. Thus, based upon the Clapeyron equation, the observed reduction in $\mathrm{d}T_\alpha/\mathrm{d}P$ with irradiation dosage is consistent with an increase in ΔS, and hence the degree of disorder associated with the transition. This implies that the reduction in structural order, or crystallinity, as a result of the room temperature transition becomes more pronounced with the increasing gamma dosage.

However, the data for the ‘freshly’ irradiated 20 Mrad specimen are consistent with a lower crystallinity than expected. This is probably due to an evolving increase in the crystallinity of the freshly irradiated specimen with time as

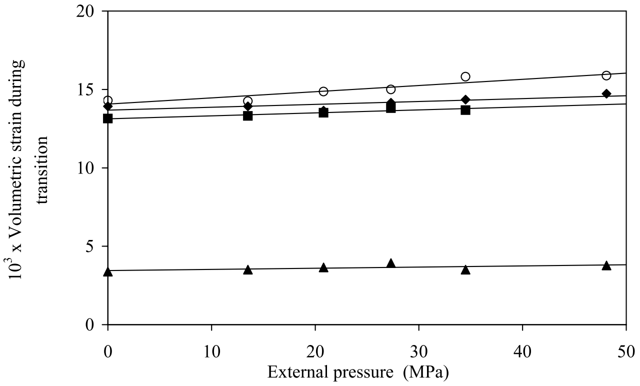

Fig. 8. The effect of pressure on the volumetric strain during the room temperature transition for various dose gamma irradiated PTFE samples. ◆: 5 Mrad; ■: 10 Mrad; ▲: 20 Mrad; ○: 60 Mrad.

the free radical species are quenched. The above is further evidence of post-irradiation effects associated with the combining of the secondary free radicals following irradiation together with the volumetric relaxation of the polymer matrix.

Assuming that molecular weight decreases with crystallinity, it is then reasonable to expect that for the freshly irradiated specimen, the above would be manifested in a higher molecular weight than expected as compared to the ‘conditioned’ sample irradiated at the same dosage.

Unfortunately, however, the molecular weight of the 20 Mrad specimen was measured some two weeks after irradiation and no such observation was made. The data presented in Fig. 9 for the conditioned samples however indicate a significant drop in molecular weight following irradiation. Notably, most of the effect is completed after 5 Mrad. This probably explains the relatively small effect of irradiation on the room temperature transition in PTFE (Fig. 7).

4.2. Polymer creep experiments

The effect of rapid pressurisation upon the volumetric creep behaviour of the conditioned 10 and the 20 Mrad specimens are shown in Fig. 10. The experiments were performed by exposing the polymers to a rapid pressure ramp of 34.5 MPa in 15 s at 40 °C and then measuring the corresponding change in capacitance immediately after pressurisation. Linear compressive strains were then calculated by inserting the capacitance values into Eq. (7). The data indicate that, for both irradiation doses, a rapid compression of the polymer is followed by a prolonged recovery period. However, there are some subtle differences in behaviour. The initial expansion rate is noticeably reduced (by a factor of 5) at the higher irradiation dose. Also, the long-term creep rate decreases with irradiation dose. This is in agreement with the data reported by Briscoe and Ni [4] and later by Oshima et al. [29] for PTFE where the ultimate creep rates were greatly suppressed with the increasing of the irradiation dose. These experiments were however performed by exposing the polymer to a tensile load in one direction only.

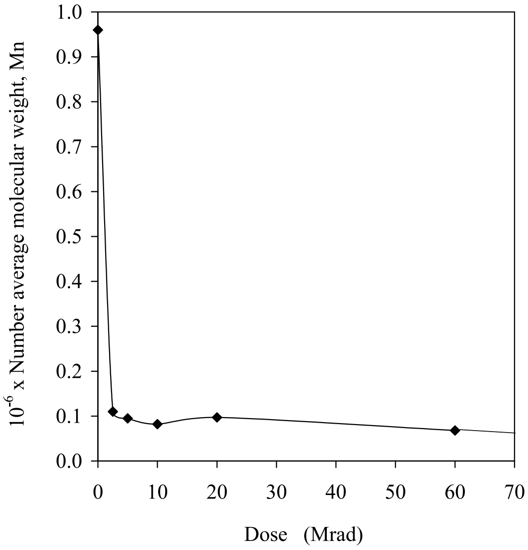

Fig. 9. The effect of gamma irradiation on the number average molecular weight of PTFE.

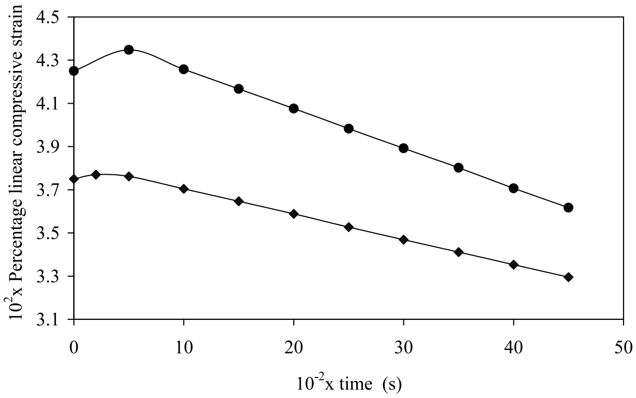

Fig. 10. The effect of rapid pressurisation on the creep behaviour of gamma irradiated PTFE. ◆: 10 Mrad; ●: 20 Mrad.

It is also interesting to note that the 10 Mrad specimen is more compressible than the 20 Mrad specimen at all times. This is consistent with a larger initial density of the 20 Mrad which would in turn make the polymer ultimately less compressible.

Returning to the data in Fig. 6, it is clear that an excess pressure is required in order to bring about a transition temperature for the irradiated specimens which is at the same location as that for the virgin specimen at atmospheric pressure. It is therefore reasonable, as a basis for argument, to assume that the virgin specimen possesses an effective ‘internal pressure’, ΔP which is reduced as a result of irradiation. Irradiation of PTFE can therefore be regarded as a process, which causes a loss in the ‘internal pressure’.

Fig. 11 shows the variation of this loss in the computed ‘effective’ internal pressure, ΔP as a function of gamma dosage, G. The data indicate a linear relationship between the two variables. The variation may be expressed accurately in terms of the following equation

$$\Delta P = KG \tag{13}$$

where K is a constant of proportionality (ca. 0.75 MPa/Mrad). It is interesting to note that the loss in the internal pressure for the 20 Mrad (freshly irradiated) specimen is lower than expected. Once again, the freshly irradiated specimen behaves as though it has been irradiated at a lower gamma dosage.

At this stage we may invoke the modification of the Calpeyron equation introduced by Gee [20] for a second order transition in order to predict the pressure dependence of the transition and hence provide an insight to the way in

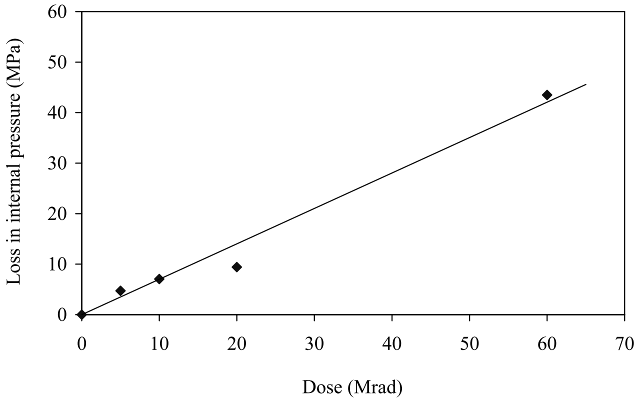

Fig. 11. The variation of the loss in the effective internal pressure in PTFE as a function of gamma dosage.

which transitions are modified by the process of irradiation. This is given by

$$dT_\alpha/dP = \Delta\alpha_p/\Delta\beta_T \tag{14}$$

where $\Delta\alpha_p$ and $\Delta\beta_T$ are the changes in coefficient of thermal expansion and compressibility during the transition and constant temperature, T and pressure, P, respectively.

We take note that the room temperature transition in PTFE is a consequence of specific relaxation times associated with characteristically similar molecular motions within the polymer matrix. Nevertheless, previous work by Passaglia and Martin [14] has shown that the thermodynamic principles, for which time is an irrelevant parameter, can be successfully employed to predict the pressure dependence of the relatively abrupt second order glass transition temperature in poly(propylene).

Table 1 shows the variation of dT_α/dP, as calculated from the above equation, at various dose levels together with the derived experimentally measured values. The necessary values of $\Delta\alpha_p$ and $\Delta\beta_T$ were obtained from Figs. 3–6 in conjunction with Eqs. (8) and (10). These data indicate comparatively large deviations between the calculated and the measured values of dT_α/dP parameter. However, an improvement in agreement is seen at higher doses. This implies that transitions at higher radiation doses become more rapid and hence thermodynamic considerations become more appropriate.

Indeed, the above observation is in agreement with the data in Figs. 7–10 where a marked increase in the rate or the ‘rapidity’ or ‘sharpness’ of the room temperature transition is obtained with the increasing of the gamma dosage.

5. Conclusion

This paper indicates that the gamma irradiation of PTFE results in a number of important changes in its morphology and related properties.

The room temperature transition, together with its pneumatic pressure dependence are both reduced although the rate of reduction in the latter in response to increasing gamma dosage is relatively small. The volumetric strain which occurs during transition increases with both pressure and gamma irradiation dosage. The above, together with a plausible increase in the entropy change during transition based on the Clapeyron equation, suggest that the reduction in structural order or crystallinity during the transition becomes more pronounced with the increasing of the level of gamma irradiation dosage.

Irradiation of the polymer results in a significant reduction in molecular weight with most of the change completed by a 5 Mrad dosage level. The data for a freshly irradiated specimen on the other hand indicate the presence of extensive post-irradiation effects in the polymer. This may be attributed to the existence of rather stable secondary free radicals in the freshly irradiated specimen. The above is manifested in time dependent changes in many of the properties of the polymer. The behaviour is consistent with that of a polymer, which has been irradiated at a lower gamma dosage.

The application of the Calpeyron equation produces a relatively poor prediction of the pressure dependence of the room temperature transition in PTFE. However, the degree of disagreement reduces with the increasing of gamma dosage. This is consistent with the observed increase in the rate of change in the transition temperature with increasing dosage thus indicating that thermodynamics arguments for which time is an essentially irrelevant parameter become more relevant.

The polymer volumetric creep rate, following a rapid pneumatic pressure loading, reduces with the increasing of the dosage which is an indication of a change from a viscoelastic behaviour to that of a brittle glassy response. Once again, this behaviour is further evidence of better applicability of thermodynamic arguments describing the

Table 1
A comparison of experimentally measured values of the pressures dependence of the room transition in PTFE with calculated values based on Gee’s [20] equation at various gamma doses

Dosage (Mrad)	$(dT_\alpha/dP)_{calculated}$	$(dT_\alpha/dP)_{measured}$	$(dT_\alpha/dP)_{calculated}/(dT_\alpha/dP)_{measured}$
5	0.740	0.147	0.199
10	0.497	0.142	0.286
20	0.309	0.123	0.398
60	0.297	0.128	0.431

pressure dependence of room temperature transition in PTFE with increasing gamma dosage; viscoelastic response is less evident.

The decrease in the value of the room transition temperature, with increase in the irradiation dosage, was somewhat unexpected as irradiation naturally results in the densification of the polymer. Previous work [30] suggests that any loss in the free volume would be manifested in an increase in transition temperature. Since the density increases, one would expect a reduction in the free volume and hence a higher transition temperature. However, extensive chain scission occurs as confirmed from molecular weight measurements. The shorter chains will require less vibrational energy leading to a lower transition temperature. It seems therefore, that while free volume may decrease as a result of irradiation, the total activation energy required to induce the transition is reduced.

Although in all cases, the application of pressure to the irradiated samples resulted in a compressive strain, it was found that this effect was essentially reversible with the polymer reverting back to its original volume upon the removal of the superimposed pressure. This was in contrast to the behaviour of the virgin specimen where a permanent densification was observed. Such effect may be partly attributed to the different gas transport characteristics of the irradiated compared to the virgin polymer.

Clearly a useful extension of this study would be to monitor the gas sorption as a function of pressure and gamma dose. This is particularly the case in view of our previous work indicating the effect of the molecular type of the gaseous pressure medium has a significant effect on the pressure dependence of the transition temperature. This is not taken into account when applying simple thermodynamic arguments for predicting the pressure dependence of the room temperature transition of irradiated PTFE and could partly explain the disagreement between theory and experiment. A comparison of such data with the current results would elaborate some of the effects induced by the presence of gas in the irradiated polymer matrix.

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