PII: S0032-3861(97)00622-8

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Effect of stress on the free volume content of poly(chlorotrifluoroethylene)

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(Revised 28 July 1997)

The effect of stress (hydrostatic compression) on the free volume of poly(chlorotrifluoroethylene) has been investigated using the positron annihilation lifetime (PAL) technique in the pressure range of 0–14 kbar at room temperature. The variation of the annihilation parameters indicates that the free volume compression occurs at a higher pressure (>8 kbar) compared to molecular compression (4 kbar). The measured free volume size decreases from 95 to 73 $\overset{\circ}{A}{}^3$ under the influence of compression. The results also indicate a crystalline–amorphous transformation. The free volume compressibility (β_f) is found to be maximum around 9 kbar (10^{-3} atm^{-1}). © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(chlorotrifluoroethylene); free volume; compression)

Introduction

Studies on the microscopic free volume properties at atomic and molecular scales can provide a basic understanding of the mechanical and physical properties of polymers. Finding a correlation between microstructure and the macroscopic properties of polymers has been of interest for many years[1,2]. In the amorphous regions of a polymer, structural changes can be characterized in statistical terms, such as density fluctuation or concentration and average size of the free-volume holes[3]. Experimental studies have shown that these randomly distributed holes are relevant in the context of macroscopic properties of polymers, e.g. the glass transition[4,5], pressure response[6], physical aging[7,8], etc. Studies on the deformation-induced changes in the microstructure of polymers are of great interest in understanding their behavior under stress. For a polymer, its ability to deform and absorb energy under a stress depends to a large extent on the ease with which its chains slide past each other. This also depends on the conformational changes due to chain rotation. In a way, this ability of the polymer to deform determines its mechanical properties. Furthermore, the applied stress can significantly alter the physical properties of the polymer. Increased stress (pressure) even leads to collapse of free volume holes and thereby increases the glass transition temperature (T_g)[9]. In comparison to temperature effects, the stress has an opposite effect on the free volume hole properties[1].

Of all the available techniques, the positron annihilation lifetime (PAL) technique is a versatile tool for measuring the changes in average free volume hole sizes and their concentration[10,11]. This is based on the fact that positronium (Ps) preferentially scans the free volume holes existing mainly in the amorphous domains of the polymer system[12]. In the present study, we have measured the o-Ps pick-off lifetime (τ_3) and its intensity (I_3) as a function of external pressure on poly(chlorotrifluoro ethylene) (PCTFE). Since Ps samples atom-size holes, we are able to observe the effect of stress at a microscopic level as a function of compressive stress. A qualitative explanation of these variations are

reported in this paper. For details of positron and positronium decay in polymers, one can refer to the articles by Stevens[13] and Jean[11].

Experimental

PCTFE film used in this study is marketed by Allied Signal Inc., (USA) as Aclar, type 22A. These films contain about 3.0% of vinylidene fluoride (VF$_2$) as a comonomer and the weight average molecular weights of these films are about 250 000. The films were cast on a cold roll so as to obtain a film of low crystallinity (around 30%). These films were compressed to various pressures using the Electronic Compression Testing Machine CTE-300 (GDR type) available at National Institute of Rock Mechanics (NIRM), Kolar Gold Fields, India. This machine is hydraulically operated, driven by an electric motor and equipped with a digital display for directly reading the load deflection. Film samples of an area of 2700 mm^2 (90 × 30 mm) and of 0.076 mm in thickness were placed between anvils of diameter 110 mm for 1 min under different loads to achieve the required stress. These films were then cut into two equal parts and 12 pieces from each made in order to stack them together to form two identical samples. A 15-μCi source (^{22}Na), deposited and sealed on a Kapton foil of 0.0127 mm thickness, was sandwiched between the above-mentioned two identical stacked samples and placed in between the two detectors of the lifetime spectrometer. The positron lifetime spectrometer consists of a fast–fast coincidence system with a time resolution of 340 ps measured from the prompt curve of a ^{60}Co source. The details of the spectrometer can be found elsewhere[14,15]. More than one million counts were collected for each spectrum at room temperature. The experiment was repeated at each compressive stress to check the reproducibility of the measurements, and consistently reproducible spectra were used in the final analysis. The source correction term was obtained from a metal spectrum of known lifetime (well-annealed aluminum) using the program RESOLUTION[16]. The measured lifetime spectra were analyzed using the program PATFIT-88[16].

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Results and discussion

All the positron lifetime spectra were analyzed into two, three and four components. The three-component fit gave better χ^2 values and standard deviations than the two- and four-component fits. In the three-component fit, the intensity of the third component I_3, though small (4–5%), is considered, because the four-component fit gave negative intensities and higher χ^2 values, whereas the two-component fit invariably gave very large χ^2 values. Hence, the three-component fit lifetime results are presented and discussed here. Generally, the fluoro polymers are known to have lower o-Ps intensity compared to other polymers[17]. This suggests that, in this material, the free volume distribution is composed of a small number of large holes. The source correction term was carefully measured and it was found that it never contained a term having a lifetime around the τ_3 value reported here because of the low I_3 value.

The attribution of three lifetimes to various states of positron annihilation are as follows: the fist short-lived component τ_1 with intensity I_1 is attributed to p-Ps and free annihilations. With regard to the attribution of the second or the intermediate lifetime component (τ_2) and its intensity (I_2), there is some ambiguity, since different research groups follow slightly different approaches. We follow the prescription outlined by Goldanskii et al.[18] according to which the intermediate lifetime component τ_2 with intensity I_2 is considered to be caused due to the annihilation of positrons trapped at the defects present in the crystalline regions or trapped at the crystalline–amorphous (c–a) interfaces. The longest-lived component τ_3 with intensity I_3 is attributed to pick-off annihilation of the o-Ps in the free volume sites present in the amorphous regions of polymer matrix [12].

The free volume hole radius R and the o-Ps lifetime τ_3 are related through a simple relationship[12], which is based on a model developed by Tao for molecular liquids[19]. This is given as

$$\tau_3^{-1} = 2[(1 - R/R_0) + 0.159\{\sin(2\pi R/R_0)\}] \text{ ns}^{-1} \quad (1)$$

where $R_0 = R + \delta R$ and $\delta R = 0.1656$ nm. δR is the thickness of the electron layer in the free volume cavity[20]. Using this value of R, the free volume size (V_{f3}) is calculated as $V_{f3} = 4/3(\pi R^3)$. Once V_{f3} and the o-Ps intensity, I_3, are known, then we can calculate the fractional free volume (F_v) using the relation

$$F_v = CV_{f3}I_3 \quad (2)$$

Here C is the structural constant which can be derived[6], if the coefficient of thermal expansion (α) of the free volume of the polymer is known. For this polymer, α has been measured and the value of C turns out to be 0.0065 Å^{-3}.

The variation of o-Ps lifetime and its intensity as a function of applied pressure are as shown in *Figure 1*. It is clear from *Figure 1* that the o-Ps lifetime remains almost constant up to 8 kbar, and thereafter decreases suddenly and remains constant after 10 kbar. On the other hand, its intensity I_3 shows an increase over the same range of pressure. The possible explanation for this is that, when pressure is applied to a polymer, the molecular chains begin to move. The movement of molecular chains leads to the movement of free volume holes. The compressibility of polymers is generally considered as the sum of the molecular compressibility and free volume compressibility. Since the molecular compressibility occurs only at high
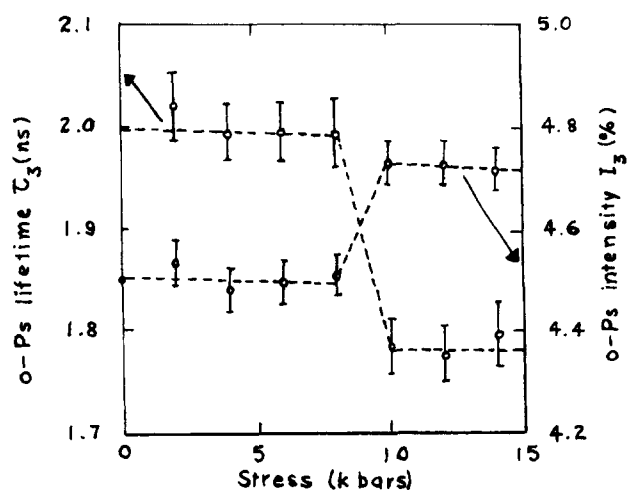

Figure 1 Variation of o-Ps lifetime and its intensity as a function of applied pressure. Dotted lines are provided as a visual guide.

pressures (>3 kbar)[21], this indicates that the molecular chain movement is possible only at pressures above 3 kbar. As the molecular chain movement leads to the movement of free volume holes, we feel the free volume compression is possible only after the molecular compression has started. As a result, we expect a constancy in the values of both the o-Ps lifetime and its intensity at the initial values of applied stress (up to 8 kbar). The present results support this.

This polymer contains about 3.0% of vinylidene fluoride (VF_2) as a comonomer, which occupies the amorphous regions of the polymer matrix[22,23]. Further application of pressure causes squeezing of free volume holes[24]. This results in splitting up of the free volume holes into small-sized holes leading to a decrease in their size and an increase in their number density. This is evident from *Figure 1*. After the collapse of the free volume holes, further application of pressure (> 10 kbar) does not seems to alter the size of the free volume holes as it reduces the segmental mobility. Hence beyond this pressure, the free volume compression is not possible as evidenced by the constancy of both the aforesaid parameters. The estimated free volume size (from Eq. (1)) decreases from 95 to 73 Å^3 (nearly 26% change) under the influence of compression. The physical state of the sample appears to indicate embrittlement. It has been observed in earlier investigations that reduction in free volume results in embrittlement of the polymer[25,26].

From the present data, the free volume compressibility (β_f) is calculated in the following way: The compressibility of free volume, β_f, is defined as

$$\beta_f = -(1/V)(\delta V_{f3}/\delta P) = -(\delta F_v/\delta P)_T = -(dF_v/dP) \quad (3)$$

where V is the total volume of the polymer. We took the derivatives numerically from the F_v data shown in *Figure 2* and this is plotted as a function of pressure in *Figure 2*. It varies from 10^{-5} to 10^{-6} atm^{-1} at low pressures to 10^{-3} atm^{-1} at 8–10 kbar pressure and shows a maximum around 9 kbar suggesting maximum free volume compression. The fractional free volume (F_v) estimated using Eq. (2) is shown in *Figure 2*. At room temperature this polymer is in the glassy state ($T_g = 52°C$)[15], its fractional free volume is around 2.5% and this decreases with pressure to a value of 2.2% (nearly 13% change) which clearly indicates the compression of free volume holes as well as squeezing out of some holes.

The variation of second lifetime τ_2 and its intensity I_2 are represented in *Figure 3*. The second lifetime corresponds to
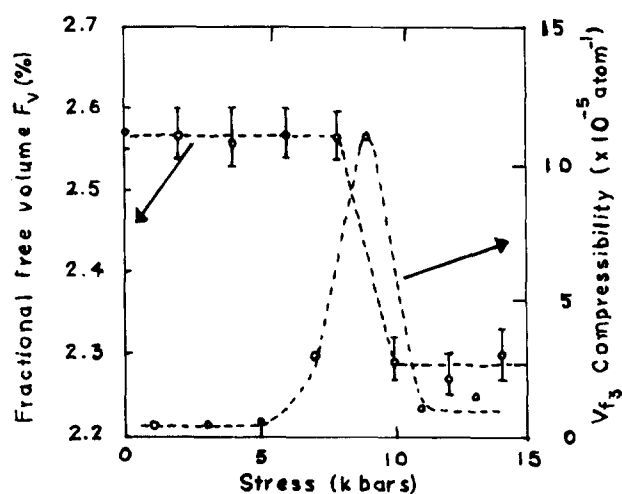
Figure 2 Variation of fractional free volume and free volume compressibility as a function of applied pressure. Dotted lines are provided as a visual guide.
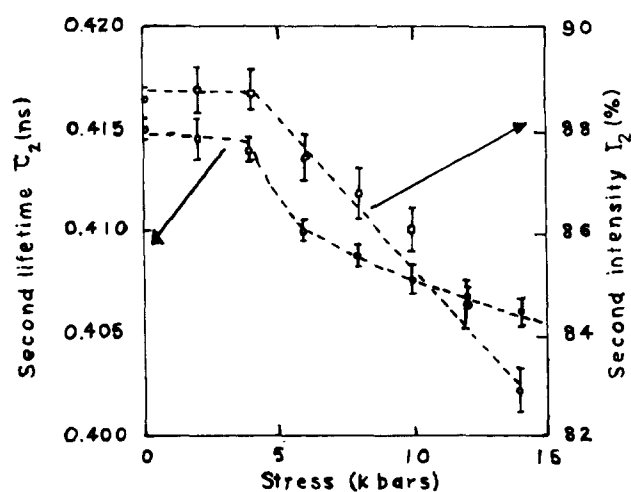

Figure 3 Variation of second lifetime and its intensity as a function of applied pressure. Dotted lines are provided as a visual guide.

the annihilation of positrons in the crystalline and crystalline amorphous interfaces in accordance with Goldanskii et al.'s treatment[18]. This second lifetime and its intensity remains almost constant up to 4 kbar and then decreases with increase in pressure. As mentioned earlier[21], the molecular compressibility can occur only at pressures greater than 3 kbar and, as such, we find constancy in the values of both τ_2 and I_2 up to 4 kbar pressure. Beyond this pressure, there is a decrease in both τ_2 and I_2. In our previous investigation on this sample (PCTFE) under annealing treatment, the observed increase in I_2 was interpreted as being due to an increase in crystallinity, which was supported by XRD measurements[15]. In the present investigation, I_2 is decreasing, indicating a decrease in crystallinity. It is shown that a number of crystalline materials become amorphous when subjected to a pressure of the order of 10 GPa (around 100 kbar)[27]. But it has been observed, in the case of polystyrene[28], that there is no crystallization with the application of pressure. In the light of these findings, although the pressure applied in the present case is only up to 14 kbar, which should be around one order lower to bring about c–a transformation, we are of the opinion that this c–a transformation is possible because plastics can be more easily compressed compared to crystalline solids. In general, c–a transformation is a

consequence of poor kinetics preventing an equilibrium phase being reached[29]. In fact, the basic concept is that pressure promotes the close packing of materials and if a c–c transformation cannot attain this close packed equilibrium structure due to very poor rates of transformation, then the material compacts to a disordered phase; even a variation of I_3 which is small, it is significant and supports this correlation.

Conclusions

Positron lifetimes in compressed PCTFE have been measured as a function of applied stress in the range 0–14 kbar. From the variations of positron and positronium lifetimes and their intensities, the compression of a polymer can be divided into two parts; molecular compression and the free volume compression. The free volume compression occurs at higher pressures, in comparison to molecular compression. Our present investigation supports the observation that certain crystalline materials transform from crystalline to amorphous phase on compression; this occurs at a smaller rate in the present material.

References

1. Ferry, J. D., *Viscoelastic Properties of Polymers*, 3rd edn. Wiley, New York, 1980.
2. Samuels, R. J., *Structured Polymer Properties*, Wiley, New York, 1974.
3. Liu, L.B., Gidley, D. and Yee, A.F., *J. Polym. Sci. B.*, 1992, **30**, 231.
4. Lin, D., Wang, B., Li, X.H. and Wang, S., *J. Mater. Sci. Forum.*, 1992, **105-110**, 1637.
5. Lin, D. and Wang, S.J., *J. Phys. Condens. Matter.*, 1992, **4**, 3331.
6. Deng, Q., Sundar, C.S. and Jean, Y.C., *J. Phys. Chem.*, 1992, **96**, 492.
7. Milan, S., Sanchez, V., Fucugauchi, L.A., Ito, Y. and Tabata, Y., *J. Polym. Sci. B.*, 1992, **30**, 1.
8. Ramachandra, P., Ramani, R., Ramgopal, G. and Ranganathaiah, C., *Eur. Polym. J.* (In press).
9. Penwell, R.C. and Porter, R.S., *J. Appl. Polym. Sci.*, 1969, **13**, 2427.
10. Brandt, W., Berko, S. and Walker, W.W., *Phys. Rev.*, 1960, **120**, 1289.
11. Jean, Y.C., *Michrochem. J.*, 1990, **42**, 72.
12. Nakanishi, H., Jean, Y.C., Smith, E.G. and Sandreczki, T.C., *J. Polym. Sci. B.*, 1989, **27**, 1419.
13. Stevens, J. R., in *Methods of Experimental Physics*, Vol. 16, ed. R. A. Fava. Academic Press, New York, 1980, p. 371.
14. Ramani, R., Ramachandra, P., Ravichandran, T.S.G., Ramgopal, G., Ranganathaiah, C. and Gopal, S., *Appl. Phys. A.*, 1995, **60**, 481.
15. Ramachandra, P., Ramani, R., Ravichandran, T.S.G., Ramgopal, G., Gopal, S., Raganathaiah, C. and Murthy, N.S., *Polymer*, 1996, **37**, 3233.
16. Kirkegaard, P., Pederson, N. J. and Eldrup, M., in *Report of Riso Natl. Lab*, Denmark, 1989, M-2740.
17. Davies, W.J. and Pethrick, R.A., *Eur. Polym. J.*, 1994, **30**, 1289.
18. Goldanskii, A.V., Onishuk, V.A. and Shantarovich, V.P., *Phys. Stat. Sol. (a)*, 1987, **102**, 559.

19. Tao, S.J., *J. Chem. Phys.*, 1972, **56**, 5499.
20. Nakanishi, H. and Jean, Y. C., in *Positron and Positronium Chemistry*, Chapter 5, ed. D. M. Schrader and Y. C. Jean. Elsevier, Amsterdam, 1988.
21. Haward, R.N., *J. Polym. Sci. A-2*, 1969, **7**, 219.
22. Murthy, N.S., Khanna, Y.P. and Signorelli, A.J., *J. Polym. Sci. Eng.*, 1994, **36**, 1254.
23. Moggi, G. and Bonardelli, P., *J. Polym Sci. Part B Polym. Phys.*, 1984, **22**, 357.

24. Wilson, R.K., Johnson, P.O. and Stump, R., *Phys. Rev.*, 1963, **129**. 2091.
25. Mininni, R.M., Moore, R.S., Flick, F.R. and Petrie, S.E.B., *J. Macromol. Sci. Phys. B*, 1972, **8**, 343.
26. Hutchison, J.M. and Bucknall, C.B., *Polym. Eng. Sci.*, 1980, **20**, 1973.
27. Sharma, S.M., *Indian J. Pure Appl. Phys.*, 1995, **33**, 562.
28. Matsuoka, S. and Maxwell, B., *J. Polym. Sci.*, 1958, **32**, 131.
29. Ramachandran, G.N. and Sasisekharan, V., *Adv. Protein Chem.*, 1968, **23**, 283.