Polymer Bulletin 28, 481–487 (1992)

Polymer Bulletin

Thermal expansion of irradiated polyvinyl chloride from 10 K to 340 K

H. S. Jayanna and S. V. Subramanyam

Department of Physics, Indian Institute of Science, Bangalore 560 012, India

Summary

The coefficient of thermal expansion is measured for irradiated Polyvinyl Chloride (PVC) from 10K to 340K. The samples of PVC are irradiated, up to 500 Mrad in steps of 100 Mrad, in air at room temperature by using Co^{60} gamma rays with a dose rate of 0.3 Mrad/h. The PVC is an amorphous sample which is confirmed by X-ray diffraction. The coefficient of thermal expansion is found to decrease with radiation dose from 10K to 110K and it increaseswith radiation dose from 110K to 340K. The results are explained on the basis of radiation induced degradation of the sample.

Introduction

Study of thermal properties of irradiated polymers is very important from both scientific and technological points of view. Very little information is available on thermal properties like thermal conductivity, specific heat and thermal expansion of irradiated polymers. Thermal expansion of some of the technologically important polymers has been studied by Subrahmanyam and Subramanyam (1,2).

Polyvinyl Chloride is a common polymer of great practical interest. Lawton et al (3) reported that Polyvinyl Chloride undergoes degradation during irradiation, whereas Karpov (4) and Charlesby (5) reported that PVC undergoes crosslinking during irradiation. Subsequent work has shown that crosslinking or degradation can occur depending on the conditions and on the type of additives present in the polymer. The crosslinking in Polyvinyl Chloride predominates over degradation when the samples are irradiated in vacuum, whereas the degradation predominates over crosslinking when the samples are irradiated in the presence of air.

Irradiation in air causes a steady degradation of the polymer as demonstrated by the lowering of the melting temperature of the fiber by Chapiro (6), whereas Hiroshi sobue et al (7) found that crosslinking increases with dose in PVC films of thickness 0.1 mm and crosslinking decreases when the thickness exceeds 0.1mm when PVC was exposed to ultra violet radiation.

Radiation chemistry of PVC has been extensively reviewed in the literature (6,8,9,10,). For the first time we made an attempt to measure the thermal expansion coefficient for gamma-ray irradiated PVC.

Experimental Procedure

Sample

Samples as received from POLYPENCO LTD., (UK). are in the form of solid cylinders with diameter 1cm. They are of grey colour, probably due to additives and plasticisers. Samples are cut into 1cm in length and the two surfaces are polished and made parallel.

Irradiation Procedure

Commercial grade Polyvinyl Chloride (Supplied by POLYPENCO Ltd., UK) is used in the present investigation. Samples were irradiated in air at room temperature with gamma radiation from Co^{60} source at a dose rate of 0.3 Mrad/h at Indira Gandhi Center for Atomic Research (IGCAR),Kalpakkam, INDIA. The samples were irradiated to various integral dosages like 100, 200, 300, 400 and 500 Mrad. After irradiation samples were kept in a box which are exposed to air constantly.

Infrared spectrum

Infrared (IR) spectrum has been obtained for unirradiated and for the sample irradiated to 200 Mrad. The samples are dissolved in tetra hydro furan. The IR spectrum has been recorded for the solution by using Perkin-Elmer IR spectrometer.

Thermal Expansion Apparatus

The co-efficient of thermal expansion of samples of PVC are measured by the three terminal capacitance technique, which has been described in detail elsewhere (11). In this technique the changes in length of the sample are converted into changes in electrical capacitance, which is measured by using a ratio transformer bridge to a resolution of 1 ppm (12).

Measuring Procedure

The samples were cut into required size and shape and the two surfaces were made flat and parallel. Sample was mounted in the capacitance cell and cooled down to liquid helium temperature over a period of 15 hours. The sample was heated in steps of 5K by using the temperature controller. For every stabilised temperature, measurements were taken only when the gradients in temperature across the sample and any two sections of the cell were less than 0.25K. The ratio transformer bridge was balanced and the readings giving 1/C directly were taken. Thus a set of values of T and 1/C were recorded in the temperature range 10K to 340K for PVC samples irradiated to 0, 200, and 500 Mrad. The thermal expansion co-efficient was then calculated by using the relation

$$\alpha_s = \frac{L_c}{L_s}\alpha_c - \frac{0.15625}{L_s}\frac{d}{dT}\left(\frac{1}{C}\right)$$

where L_s is the length of the sample and L_c is the corresponding length of the cell. α_c is the expansivity of the cell which is determined by a calibration of the capacitance cell by using two NBS standard reference materials, viz. Aluminium and Germanium.

Numerical differentiation and graphical methods of finding $\frac{d}{dT}\left(\frac{1}{C}\right)$ generates a lot of scatter. An accurate method is to fit the data into a suitable polynomial and differentiate it to get the derivative. We have used the spline approximation because of its distinct advantages (13). By using NAGLIB subroutines E02BAF, E02BBF, E02BCF, the data of 1/C vs T is fitted into least square cubic splines and the derivative $\frac{d}{dT}\left(\frac{1}{C}\right)$ is determined at the experimental temperatures.

RESULTS AND DISCUSSION

The variation of thermal expansion coefficient, α , with temperature for PVC irradiated to 0 , 300 and 500 Mrad are plotted in fig. 1.

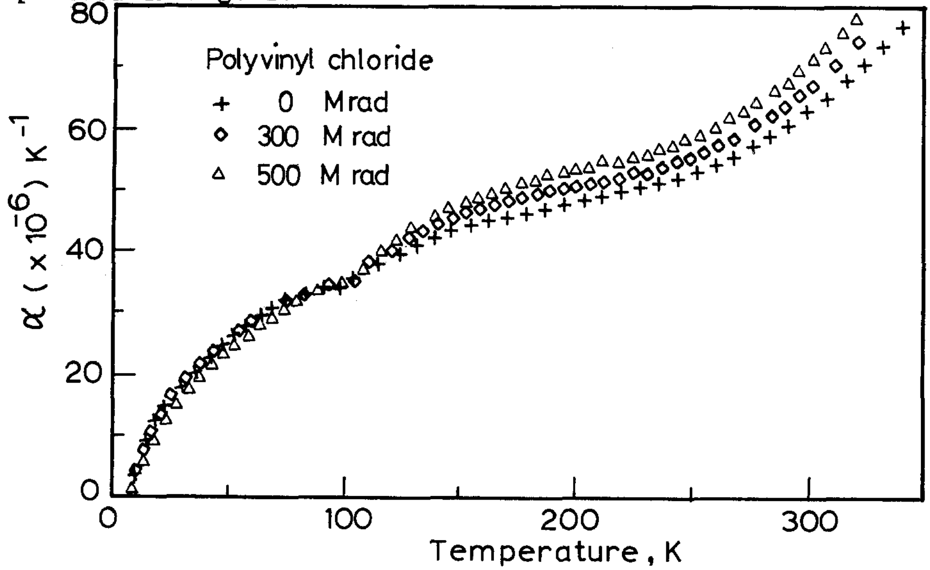

Fig. 1. Variation of α with temperature

The variation of ($\Delta l/l$) with temperature is shown in fig.2.

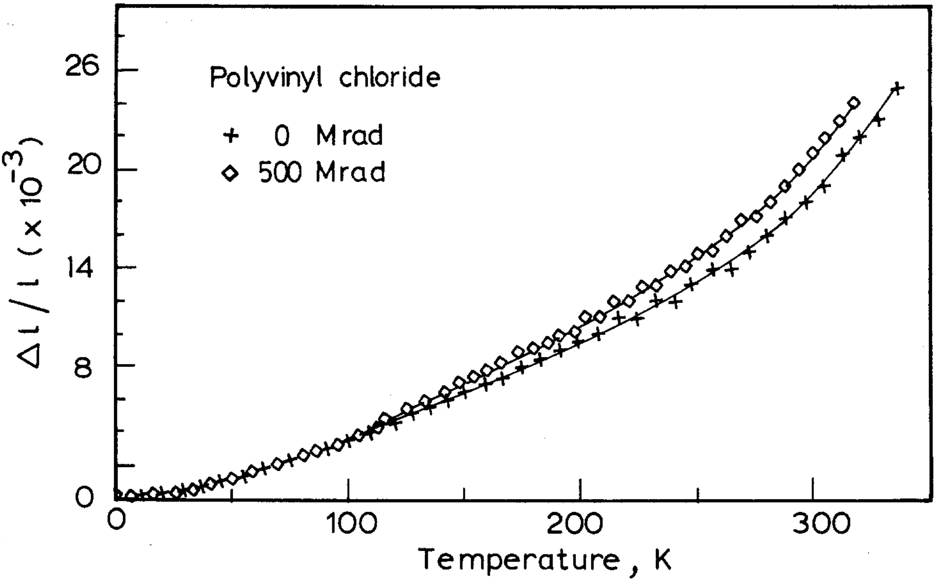

Fig. 2. Variation of $\Delta l/l$ with temperature

The variation of α with radiation dose at some distinct temperatures is shown in fig.3.

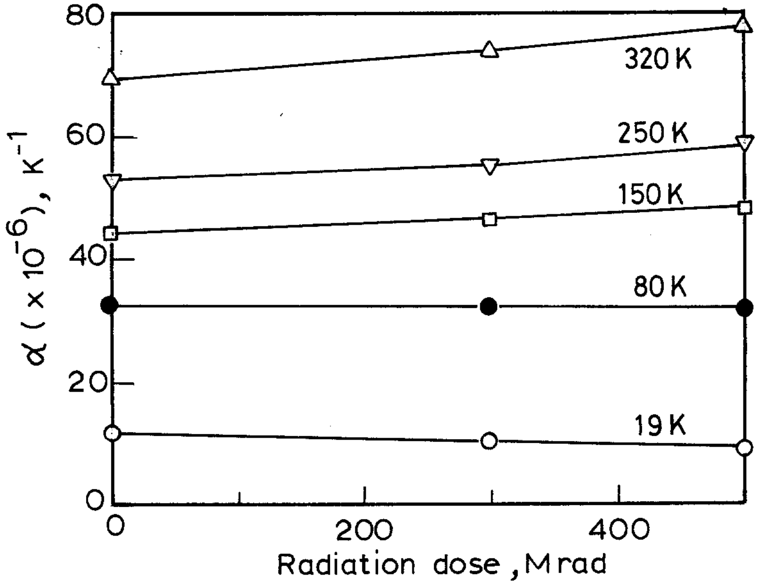

Fig. 3. Variation of α with radiation dose

From fig.1 we observe that α decreases with radiation dose from 10 K to 110K. After 110K the trend is reversed i.e., α increases with radiation dose from 110K to 340K. The decrease in α at 19K is about 1.2% between 0 and 500 Mrad, the increase in α at 155K is about 9.5% between 0 and 500 Mrad and at 320K it is about 12.5% between 0 and 500 Mrad.

Polyvinyl Chloride undergoes both crosslinking and degradation when it is exposed to high energy radiation. But the degradation is predominant over crosslinking when the samples are irradiated in air. The degradation is confirmed by the IR spectra as shown in fig. 4. In the IR spectra the absorption peaks at 1722 cm^{-1} is due to carbonyl group (C=O) caused by radiation induced oxidative degradation of the sample.

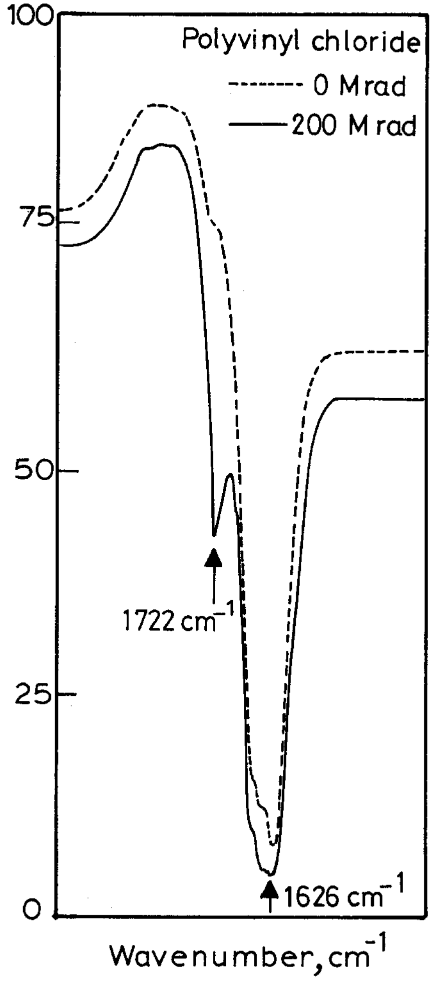

Fig. 4. Infrared spectrum of unirradiated and irradiated to 200 Mrad PVC samples.

The decrease in α with radiation dose from 10K to 110K is due to the simultaneous crosslinking of PVC when it is exposed to radiation. The increase in α with radiation dose from 110K to 340K is due to the main chain degradation of the polymer. With every chain scission a covalent bond in a polymer chain is broken and the two stable end groups that are formed at the scission point will have vander waal's interaction (14). The thermal expansion coefficient α depends on the strength of the interaction of the constituent units. The thermal expansion of the solid whose atoms /molecules are held by vander waal's force is about two orders of magnitude greater than that of a covalently bonded solid. Thus the relative increase in the vander waal bonds caused by the scissioning of the polymer chain by irradiation is responsible for an increase in α with radiation dose.This conclusion is supported by the work of Wang et.al (15).

The decrease in the thermal expansion with radiation dose from 10K to 110K is due to the simultaneous crosslinking of polymeric chains when sample is exposed to high energy radiation in air. The molecular crosslinks together from a covalent bond. Thermal expansion decreases with the number of covalent bonds. When both the crosslinking and degradation occurs simultaneously, the effect of one on the thermal expansion is opposed by the effect of the other. Further, crosslinking and degradation may have different temperature dependences so that they predominate in different temperature regions. The thermal expansion results indicate that crosslinking predominates in the low temperature region from 10K to 110K; when above 110K, degradation seems to dominate.

The thermal expansion studies on oriented amorphous polymers seem to support this conclusion (15,16). When the amorphous polymer is drawn, the decrease in $\alpha_{\perp}$ is much more than the corresponding increase in $\alpha_{\parallel}$. Hence by analogy, crosslinking should have much dominant effect on thermal expansion than degradation, so that the net effect of both is to decrease the thermal expansion coefficient. Further, $\alpha_{\parallel}$ has been found to have a weaker temperature dependence than $\alpha_{\perp}$, so that the anisotropy parameter $\alpha_{\perp}/\alpha_{\parallel}$ is larger at higher temperature. The anisotropy parameter $\alpha_{\perp}/\alpha_{\parallel}$ is quite significant for PVC (17). Again, by analogy, crosslinking has a weaker temperature dependence than degradation, so that crosslinking predominates at lower temperatures while degradation dominates at higher temperatures.

Acknowledgements

The authors are thankful to IGCAR, Kalpakkam for providing the radiation facility and also to ISRO-IISc Space Technology Cell for financial assistance.

REFERENCES

1. Subrahmanyam H.N. and Subramanyam S.V.,(1987) J.Polym.Sci.Polym.Phys., 25: 1549
2. Subrahmanyam H.N.and Subramanyam S.V., (1987) Polymer (GB) 20:1331
3. Lawton E.J., Bueche A.M. and Balwit J.S.,(1953) Nature 172:76
4. Karpov V.L., (1955)Sessiya Akad. Nauk. SSSR Po. Mirnomu Ispolzovaniyu Atomnoi Energii, Moscow pp 1.
5. Charlesby A., (1953) Plastics 18: 142
6. Chapiro A.(1962) `Radiation chemistry of polymeric systems´ Interscience, NY., pp 464.
7. Hiroshi Sobue, Yoneho Tabata and Yoshio Tajima (1958) J. Polym. Sci. 115: 596
8. Chapiro A.(1956) J. Chim. Physique, 53: 895
9. Charlesby A.(1960) `Atomic radiation and polymers´, Pergamon Press, Oxford, pp 312.
10. Miller A.A, (1959) J. Phy. Chem., 63:1755
11. Subrahmanyam H.N.and Subramanyam S.V., (1986) Pramana 27:647
12. Krishnapur P.P.,Subramanyam S.V.and Rajagopal E.S., (1979) Ind. J. Technol., 17: 165
13. Pott R. and Schefzyk, (1983) J.Phys.E., 16: 444
14. Subrahmanyam H.N., (1985) Ph.D., Thesis, Indian Institute of Science, Bangalore India.
15. Wang L.H., Choy C.L.and Porter R.S., J.Polym.Sci. (1982) Polym.Phys., 20:633
16. Wang L.H., Choy C.L. and Porter R.S., (1983) J.Polym.Sci. Polym.Phys., 21: 657
17. Hellwege K.H., Hennig J. and Knappe W.,(1963) Kolloid-Z., 188 : 121

Accepted April 2, 1992 Shi