Accelerated Failure of Bisphenol-A Polysulfone during Electron Beam Irradiation under an Applied Stress

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SYNOPSIS

Bisphenol-A polysulfone, poly(oxy-1,4-phenylene-sulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene), PSF (I) showed greatly reduced resistance to electron beam irradiation when subjected simultaneously to an applied tensile stress. The creep rate increased, and the time (dose) to failure of the sample decreased with increasing stress. The failure strain was constant for different applied stresses. Air, oxygen, and moisture caused decreases in radiation resistance compared with a dry nitrogen atmosphere. Increasing the irradiation temperature from 0 to 90°C resulted in substantially decreased radiation resistance.

INTRODUCTION

The behavior of polymer materials in radiation environments is of considerable interest for a variety of applications, including aerospace structures,[1] especially as carbon fiber composites, in nuclear facilities, where radiation resistance is necessary for long service life, and in the electronics industry. Aromatic polymers would be expected to show high resistance to radiation. This has been confirmed for irradiation of poly(arylene sulfones) in vacuum,[2,3] although the radiation resistance is decreased for irradiation in air.[2-4]

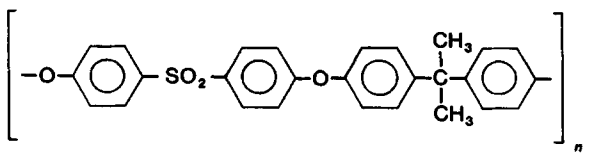
Polysulfones are an important class of aromatic polymers having excellent mechanical properties (including high modulus and strength) at service temperatures above 100°C and are finding increasing use in engineering applications.

However, there have been few investigations of the effect of stress during irradiation of these polymers, although high localized stresses can be expected when polymers are used as construction materials. Mechanical stress induced by thermal expansion is particularly important in some applications.

Some early studies of the effects of applied stress during UV, reactor, and electron irradiation of natural and synthetic polymers, including silk, cotton, nylon, polystyrene, poly(methyl methacrylate), polycarbonate, PTFE, cellulose triacetate, polyethylene and poly(ethylene terephthalate),[5-20] showed that radiation increased the rate of creep and decreased the time to failure in these polymers under tensile stress.

Changes in the properties of polymer materials resulting from irradiation are due to the chemical reactions that follow energy absorption. In particular, scission and crosslinking of the polymer molecules cause changes in molecular weight, which affect mechanical properties such as modulus, strength, and strain to failure.

Bisphenol-A polysulfone, poly(oxy-1,4-phenylene-sulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene), PSF (I) comprises alternating units of bisphenol-A and diphenyl sulfone.



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Brown and O'Donnell[3] found that the flexural strength of PSF was largely unaffected by doses of γ radiation up to 6 MGy in vacuum at 35 and 125°C,

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Journal of Applied Polymer Science, Vol. 44, 115–120 (1992)
 CCC 0021-8995/92/010115-06$04.00

although it was reduced by 50% after approximately 2 MGy in air at both temperatures. Davis et al.[21] found that gel formation due to crosslinking occurred during electron irradiation of PSF in vacuum, and they derived yields of scission and crosslinking, $G(S)$ and $G(X)$, from the variation in gel content with dose. The temperature dependence of $G(S)$ and $G(X)$ for γ irradiation of PSF was investigated by Brown and O'Donnell[3] and by Lewis.[22]

The marked effect of stress in reducing the radiation resistance of PSF was first observed in the present work when strips of film were wound around 5-mm-diameter glass tubes and subjected to γ irradiation in vacuum; transverse cracking caused the samples to break into small pieces after about 0.5 MGy at 30°C.

Sykes[23] subsequently reported unexpected early failure of strips of PSF irradiated with 120-keV electrons in vacuum while under low tensile stress.

In this article we report the dependence of creep rate and dose to failure on stress level, irradiation temperature, atmospheric environment, and dose rate for PSF during electron beam irradiation under tensile stress.

EXPERIMENTAL

Polymer Samples

The bisphenol-A polysulfone was obtained from Union Carbide (Udel P1700). The pellets were dried by heating to 150°C in a vacuum oven and compression moulded at 220°C and 5 MPa in a nitrogen atmosphere to produce films about 0.3 mm thick. The films were cut into 5 × 50 mm strips, which were annealed at 170°C in vacuum for 6 h to remove stress, and equilibrated in air for 1 week.

Irradiations and Dosimetry

A van de Graaff accelerator operating at 0.7 MeV in pulse mode (2 μ-s pulse length at 1 kHz) was used for the electron irradiations with dose rates of 0.8, 2.7, and 6.0 MGy/h. The electron beam was found to spread with a solid angle of 45° after exit from the flight tube, and doses could be varied by adjustment of the distance between the accelerator window and the polymer sample.

Film dosimeters produced by Far West Technologies (California) were used to measure the electron beam dose rates. These dosimeters contain a radiochromic dye in a nylon matrix. Hansen and Wille[24] have shown that the optical density of the films has the same wavelength and dose responses for ^{60}Co and 10-MeV electron radiation. The films were calibrated in the present work by Fricke dosimetry using ^{60}Co radiation. The depth–dose profile in PSF was determined by using alternate layers of dosimeter films and PSF films; it was found to be consistent with the profile calculated for an electron energy of 700 keV.[25]

An irradiation cell was constructed to enable samples of polymer film to be irradiated by the electron beam at a controlled temperature (0–100°C) and selected dose rate (0.8–6 MGy/h) in a chosen atmosphere (N_2, O_2, air). The cell consisted of a hollow, rectangular, aluminium block frame with removable, aluminium plates fitted to the front and back, and a thin aluminium window for entrance of the electron beam.

The film was mounted between stainless steel clamps with a gauge length of 30 mm. The upper clamp was attached to the top of the frame and the lower clamp to a vertical rod that could move freely through a hole in the bottom of the frame. Appropriate weights were loaded into a pan on the bottom of the rod. The extension of the sample was monitored continuously by a potentiometric extensometer.

Two cartridge heaters were inserted into the sides of the block to provide heating, and low temperatures were achieved using a flow of cooled gas. The temperature near the sample was monitored continuously using a thermocouple and found to be constant within ±1.5°C.

RESULTS AND DISCUSSION

Creep, Elongation, and Failure

A typical experimental record of the time dependence of sample strain with tensile stress and irradiation is shown in Figure 1. The polymer was mounted in the apparatus at A and the load was applied at B, when there was an elastic extension with a small recovery, B–C, followed by creep at a low rate, C–D. Irradiation was commenced at D, which resulted in a significant increase in the creep rate, D–E. At E the sample failed by brittle fracture. Three quantities can be derived from each experiment: (i) irradiation time (or dose) to failure, (ii) radiation-induced creep rate, and (iii) elongation (extension or strain) to failure. The dose (or time) to failure, which is a convenient measure of the radiation resistance of the polymer, was studied in detail in this work.

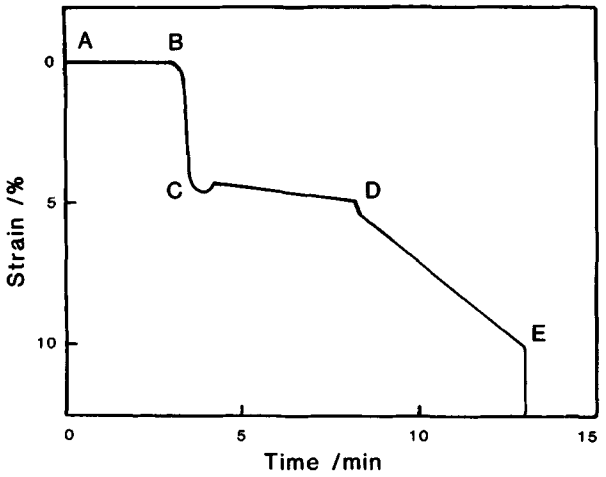

Figure 1 Representative variation in strain of PSF during an experiment. *A*, sample inserted; *B*, load applied; *CD*, extension under load; *D*, irradiation started; *E*, sample failure.

Effect of Stress

The plot of log(dose to failure) versus applied stress in Figure 2 shows two linear regions—for low and high stress with a transition at a critical stress, σ_c (point *F* in Figure 2)—in agreement with previous reports for other polymers.[9,10,12,13,18,19] It has been suggested that the linear relationship observed in the high stress region is the same with and without irradiation. Measurements of the time to failure made in the present apparatus without irradiation gave a linear relationship parallel to, but not coincident with, the data in the high stress region, as shown in Figure 2.

The deviation between the dotted line *FH* obtained by extrapolation of region 2 of Figure 2 and the experimental relationship *FE* in region 1 of Figure 2 is a measure of the decrease in radiation resistance due to the applied stress. The main feature is the great reduction in the service lifetime of this normally radiation-resistant polymer when it is subjected to even a low stress during irradiation.

The relationship between the time to failure, t_f, and the applied stress, σ, in region 1 can be described by Eq. (1):

$$\log(t_f) = a - b\sigma \qquad (1)$$

where a is the intercept of the plot at zero stress and b is the slope of the linear relationship between $\log(t_f)$ and σ.

If the radiation resistance of a polymer were not reduced by stress, there would be only a single linear relationship *GH* between log (t_f) and stress. Therefore, the smaller the intercept, a, and the slope, b,

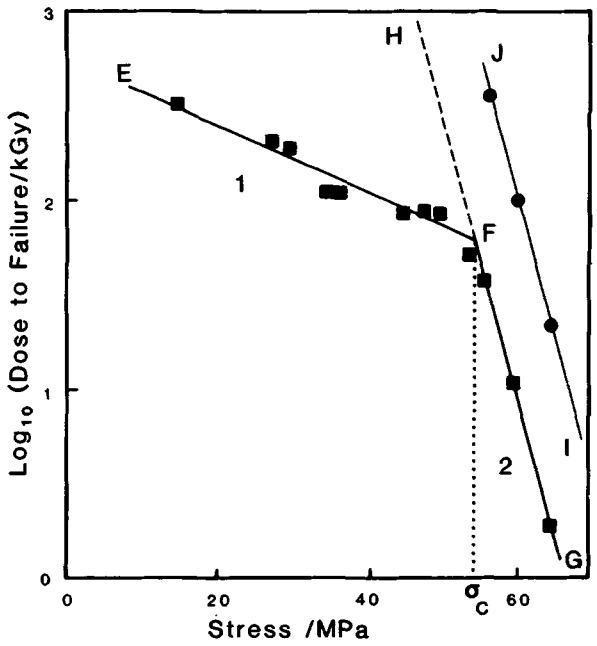

Figure 2 Relationship between log(dose to failure) and applied stress for irradiation in air at 20°C. (●) measurements without irradiation.

the lower the resistance of the polymer to radiation while subjected to an applied stress. The relative values of the intercept and slope for region 1, compared with the values for region 2, are indices of the enhancement of degradation by stress.

Effect of Environment

The degradation of unstressed PSF has been shown by Brown and O'Donnell[3] to be greatly enhanced by γ irradiation in air compared with vacuum, and this is true for many polymers. Experiments were carried out in the present work in dry nitrogen, wet nitrogen, and in dry oxygen; the values of a and b decreased in that order, as shown in Table I. The effect of oxygen may be reduced by depletion of oxygen in the sample, due to its relatively slow rate of diffusion into the specimen compared to its rate of

Table I Effect of Environment on log(Time to Failure) versus Applied Stress Relationship for Irradiation of PSF at 6 MGy/h at 20°C

Environment	a	b
Dry N_2	2.45	0.32
Wet N_2	2.14	0.28
Dry O_2	1.89	0.23

consumption in radiation-induced oxidation reactions.

The mechanical properties of PSF are known to be affected by absorbed water, and therefore experiments were performed to investigate the effect of water on the resistance of PSF to irradiation under stress. When the flowing nitrogen atmosphere was saturated with water, there was a reduction in a and b, although less than the effect of oxygen. If the polysulfone samples were thoroughly dried in an oven and stored in a desiccator before irradiation in dry nitrogen, i.e., the samples were not allowed to equilibrate with atmospheric moisture, then higher values were obtained for a and b.

All subsequent experiments were carried out in flowing dry nitrogen.

Effect of Irradiation Temperature

The effect of irradiation temperature on the time to failure is shown in Figure 3 for irradiations at 0, 20, and 90°C. Linear relationships between $\log(t_f)$ and stress were obtained at all three temperatures for region 1 (below σ_c). The values of a and b both decreased with increasing temperature, indicating a marked temperature dependence for radiation resistance, although the temperature range is well below the T_g of 190°C for PSF.

This marked effect of irradiation temperature for electron beam irradiation of stressed samples contrasts with the absence of any significant effect of irradiation temperature on the flexural strength and modulus for irradiation of unstressed samples in vacuum in the studies of Brown and O'Donnell.[3] However, these authors showed that the yields of scission and crosslinking increased with increasing irradiation temperature.

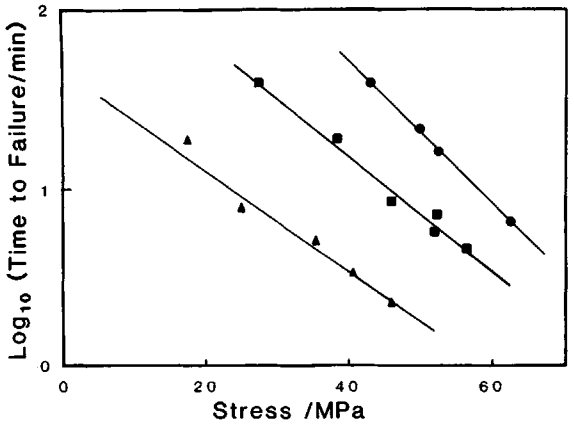

Figure 3 The relationship between log(time to failure) and applied stress for irradiation at different temperatures in nitrogen. (●) 0°C; (■) 20°C; (▲) 90°C.

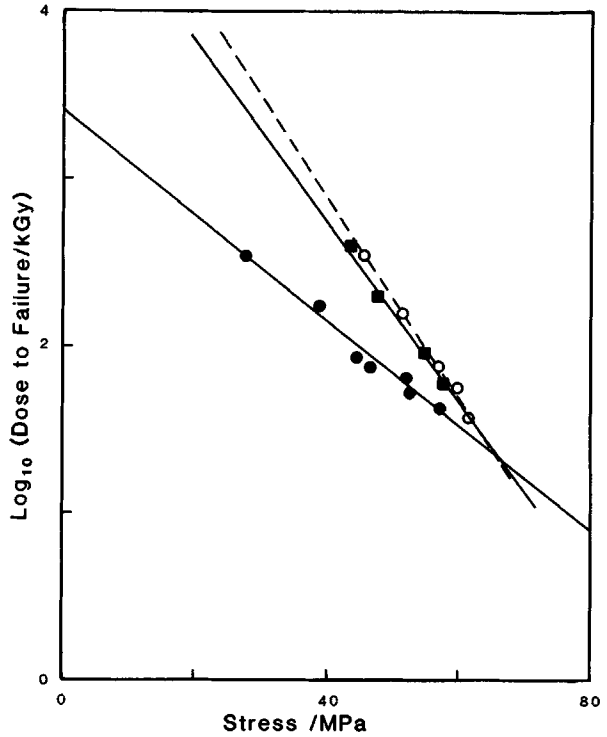

Figure 4 Effect of dose rate on the dose to failure for irradiation in nitrogen at 20°C. (○) 0.8 MGy/h; (■) 2.7 MGy/h; (●) 6 MGy/h.

The time to failure decreased approximately 50-fold over the temperature range from 0 to 90°C at an applied stress of 40 MPa. The slopes of the plots in Figure 3 decreased with increasing temperature. This is similar to the observations of Regel,[12] but Stepanov et al.[13] apparently found no temperature dependence for a polyamide.

Effect of Dose Rate

The variation in the dose to failure, D_f (= dose rate $\times t_f$), with applied stress for irradiation at different dose rates at 20°C is shown in Figure 4. The relationships between $\log(D_f)$ and stress are similar for dose rates of 0.8 and 2.7 MGy/h, but the values of both a and b decreased for a dose rate of 6 MGy/h.

The different behavior at 6 MGy/h could be due to a temperature rise in the polymer at the high dose rate. This would be consistent with the effect of irradiation temperature shown in Figure 3. Also, the parallel displacement between the linear relationships FG and IJ in region 2 of Figure 2 for an applied stress at high strain with and without irradiation

could be explained by a temperature rise due to absorbed radiation energy.

The possibility of a temperature rise in the sample during irradiation at 6 MGy/h was investigated by using periods of irradiation of 2 min separated by periods without irradiation of 4 min to allow cooling. The dose to failure was the same as for continuous irradiation for a series of stresses. This result suggests that heating of the polymer may not be the cause of the dose rate effect at 6 MGy/h, and hence there may be a real dose rate effect.

The dose rate effect observed at 6 MGy/h could occur because diffusion of small, volatile molecular products within the polymer to relieve internal stresses is less efficient at high dose rates, or because localized heating is greater at high dose rates due to decreased heat conduction, leading to greater bond cleavage.

Strain to Failure

Irradiation of PSF samples under tensile stress has been shown to result in an increase in creep rate and a decrease in the time to failure, both quantities being related to the applied stress. At each irradiation temperature, the strain to failure was independent of the applied stress. However, the failure strain did increase with increasing irradiation temperature; average values of 3, 10, and 15% were observed at 0, 20, and 90°C. The failure strain was also unaffected by the environment of the sample.

Mechanism of Stress-Enhanced Radiation Degradation

Three hypotheses have been proposed to explain the increased creep rate and decreased time to failure of a polymer under stress when simultaneously irradiated:

1. Local heating at the site of absorption of the radiation[26] and especially at the end of electron tracks causes a thermally induced increase in creep rate.[27]
2. Small, volatile radiolysis products act as local stress centres.[20,28] The increase in creep rate has been correlated by Mayer and Hoffman[20] and Bell et al.[28] with G(volatile products) to support this hypothesis.
3. Enhanced scission of stressed bonds,[15,29,30] which occurs either because part of the energy necessary to break the bond is supplied by the stress or because recombination of the chain fragments is decreased, i.e., the efficiency of the cage effect is reduced.

The local heating seems the least likely mechanism. Similarly enhanced creep and reduced lifetime to failure has been observed for reactor and UV radiation in some previous studies, but the UV cannot produce the same heating effect. Also, degradation due to local heating should not be markedly affected by the bulk temperature of the polymer (although the conduction of heat away from the sites of radiation absorption will be reduced), whereas the irradiation temperature was found to have a major effect in the present work (Fig. 3).

Yields of gaseous products from bisphenol-A polysulfone increase with irradiation temperature and, combined with the reduction in viscosity of the polymer, would lead to increased creep rates. If the apparent dose rate effect in Figure 4 is at least partly real—and the slope of the log(dose to failure) versus stress plots shows a much greater variation than observed for temperature alone (Fig. 3)—then the trapped gas theory is supported. Diffusion of gaseous products will be unaffected by dose rate, and the development of localized stresses will be greater at higher dose rates.

It is difficult to confirm or refute the theory of enhanced scission of stressed bonds, which is also consistent with the present experimental results.

CONCLUSIONS

Stress on bisphenol-A polysulfone greatly enhances the rate of creep during irradiation and decreases the lifetime to failure. The effect is relatively greater at low stresses and at higher temperatures. These observations have serious implications for the use of high-performance polymer materials in radiation environments.

The authors thank the Australian Research Committee, the NASA Langley Research Center, and the Australian Institute of Nuclear Science and Engineering (AINSE) for supporting their research; the CSIRO Division of Chemicals and Polymers for providing the Van de Graaff accelerator; the Australian Nuclear Science and Technology Organization (ANSTO) for facilities; and D. F. Sangster for assistance with the electron irradiation and much useful advice.

REFERENCES

1. E. Reichmanis and J. H. O'Donnell, *The Effects of Radiation on High-Technology Polymers*, ACS Symposium Series, Vol. 381, American Chemical Society, Washington, 1989.

2. J. R. Brown and J. H. O'Donnell, *J. Appl. Polym. Sci.*, **19,** 405 (1975).
3. J. R. Brown and J. H. O'Donnell, *J. Appl. Polym. Sci.*, **23,** 2763 (1979).
4. T. Sasuga, N. Hayakawa, K. Yoshida, and M. Hagiwara, *Polymer,* **26,** 1039 (1985).
5. V. R. Regel and N. N. Chernyi, *Vysokomol. Soed.,* **5,** 925 (1963).
6. M. P. Vershinina, V. R. Regel, and N. N. Chernyi, *Vysokomol. Soed.,* **6,** 1450 (1964).
7. V. R. Regel and N. N. Chernyi, *Khim. Volokna,* **6,** 50 (1965).
8. V. R. Regel, N. N. Chernyi, V. G. Kryzhanovskii, and T. B. Boboev, *Mekh. Polim.,* **3,** 404 (1967).
9. T. B. Boboev, V. R. Regel, T. P. Sanfirova, and N. N. Chernyi, *Mekh. Polim.,* **4,** 661 (1968).
10. V. R. Regel, T. B. Boboev, and N. N. Chernyi, *Mekh. Polim.,* **5,** 442 (1969).
11. V. R. Regel and N. N. Chernyi, *Mekh. Polim.,* **5,** 636 (1969).
12. V. R. Regel, *Mekh. Polim.,* **7,** 98 (1971).
13. V. F. Stepanov, S. E. Vaisberg, and V. L. Karpov, *Fiz.-Khim. Mekh. Mater.,* **5,** 306 (1969).
14. V. F. Stepanov, S. E. Vaisberg, and V. L. Karpov, *Fiz.-Khim. Mekh. Mater.,* **7,** 65 (1971).
15. S. E. Vaisberg, V. F. Stepanov, V. P. Sichkar, and V. L. Karpov, *Vysokomol. Soed.,* **A14,** 899, 1972.
16. A. N. Tynnyi, S. I. Mikitishin, A. A. Velikovskii, Yu. N. Khomitskii, and Yu. A. Kolevatov, *Fiz.-Khim. Mekh. Mater.,* **3,** 42 (1967).
17. A. A. Velikovskii, A. N. Tynnyi, V. S. Karasev, and S. I. Mikitishin, *Fiz.-Khim. Mekh. Mater.,* **4,** 30 (1968).
18. A. A. Velikovskii, A. N. Tynnyi, and V. S. Karasev, *Fiz.-Khim. Mekh. Mater.,* **4,** 448 (1968).
19. A. A. Velikovskii, A. N. Tynnyi, and V. S. Karasev, *Fiz.-Khim. Mekh. Mater.,* **5,** 374 (1969).
20. R. H. Mayer and A. S. Hoffman, *U.S. At. Energy Commission.,* **UCRL-13328,** (1967).
21. A. Davis, M. H. Gleaves, J. H. Golden, and M. B. Huglin, *Makromol. Chem.,* **129,** 63 (1969).
22. D. A. Lewis, The Radiation Degradation of Aromatic Polysulfones, Ph.D Thesis, University of Queensland, St. Lucia, Qld. Australia, 1988.
23. G. F. Sykes, personal communication, 1985.
24. J. W. Hansen and M. Wille, *Radiat. Phys. Chem.,* **23,** 455 (1984).
25. International Commission on Radiation Units and Measurements, *Stopping Powers for Electrons and Positrons,* Report No. 37, Bethesda, MD., 1984.
26. M. A. Mokulskii, Yu. S. Lazurkin, M. B. Fiveiski, and V. I. Kozin, *Doklady Akad. Nauk. SSSR,* **125,** 1007 (1959).
27. M. A. Mokulskii, *Vysokomol. Soed.,* **2,** 119 (1960).
28. J. P. Bell, A. S. Michaels, A. S. Hoffman, and E. A. Mason, *Adv. Chem. Ser.,* **66,** 79 (1967).
29. G. G. Samoilov and E. E. Tomashevskii, *Fiz. Tverd. Tela,* **10,** 1729, 3039 (1968).
30. S. E. Vaisberg, V. P. Sichkar, V. F. Stepanov, and V. L. Karpov, *Vysokomol. Soed.,* **A11,** 2577 (1969).

Received April 3, 1990
Accepted January 29, 1991