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Mechanical Behavior of Ultra High Molecular Weight Polyethylene

Fourth Annual Report for the Period
October 1, 1982 - September 30, 1983

Task 80-01, NBS-Bureau of Medical Devices Interagency Agreement

January 1984

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary
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MECHANICAL BEHAVIOR OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE

By

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Abstract

This report describes work done during FY 1983 under task 80-01, NBS-FDA/BMD (Bureau of Medical Devices) Interagency Agreement. The report covers the fourth year a a four year project concerned with the study of the morphology and mechanical properties of ultra high molecular weight polyethylene (UHMWPE). The work done during FY 1983 dealt principally with the following aspects of the mechanical behavior of UHMWPE, (1) the temperature dependence of the creep and recovery behavior in uniaxial extension and compression at small deformations, (2) longer term (>1 day) creep and recovery behavior in uniaxial extension and compression at small deformations, (3) the effect of γ-irradiation on the creep and recovery behavior, and (4) the effect of γ-irradiation on the environmental stress-crack resistance of UHMWPE.

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1. Introduction

This report describes work done during FY 1983 under task 80-01, NBS-BMD (Bureau of Medical Devices) Interagency Agreement. A summary of prior work done during fiscal years 1980 through 1982 is contained in references [1-3]*. Task 80-01 is concerned with a study of the morphology and time dependent mechanical properties of ultra high molecular weight polyethylene (UHMWPE), the polymer used in a variety of orthopedic implant devices. During FY 1983 the principal areas of investigation were:

1. the temperature dependence of the creep and recovery behavior at small deformations in uniaxial extension and compression.
2. the long time creep and recovery behavior at small deformations in uniaxial extension and compression.
3. the effect of γ-irradiation on the creep and recovery behavior.
4. the effect of γ irradiation on the environmental stress crack resistance of UHMWPE.

Before proceeding with the discussion of the work done during FY 1983 it will be useful to first review briefly certain aspects of the work contained in reference 3. Figures 1 and 2 (Figures 3 and 4 in reference 3) present creep and recovery data for specimens of the slowly cooled UH-1 UHMWPE ($M_w \approx 4.5 \times 10^6$, density = 0.935 g/cm^3) in uniaxial extension. Figure 1 shows the creep strain and strain during recovery for experiments carried out at constant t_1 (duration of the creep step) but varied applied stress. Figure 2 presents the strain during recovery from experiments done at constant applied stress (8 MPa), but varied t_1. In both figures the dashed lines represent the recovery predicted assuming a superposition principle of the form

$$\varepsilon_R(t) = \varepsilon_c(t+t_1) - \varepsilon_c(t), \qquad (1)$$

*Numbers in brackets indicate references found at the end of this report.

where $\varepsilon_R(t)$ is the strain during recovery at a time t after a creep experiment of duration t_1, and $\varepsilon_c(t+t_1)$ and $\varepsilon_c(t)$ are the strains at times $t+t_1$ and t during the creep experiment. It is clear from both sets of data that the observed recovery and the predicted recovery deviate significantly at the longer recovery times, and the actual recovery tends to plateau to a finite value. (See for example the curves corresponding to t_1's of 1 and 10 seconds in Figure 2). This result led to the introduction of a new one-dimensional constitutive equation of the form,

$$\varepsilon(t) = \int_0^t J_*(\sigma(\xi),t-\xi)d\xi + J(\sigma(t),0) + \phi(\int_0^t \hat{g}(\sigma(\xi))d\xi). \qquad (2)$$

In equation 2, $\varepsilon(t)$ is the strain observed at time t, $\sigma(\xi)$ is the applied stress at time ξ, $\phi(\int_0^t \hat{g}(\sigma(\xi))\,d\xi)$ is a functional which depends on the stress history, and $J(\sigma,t)$ is in the manner of a non-linear compliance multiplied by σ. $J_*(.,.)$ denotes the derivative of $J(.,.)$ with respect to the second argument, and $J(0,t) = J_*(0,t)=\hat{g}(0)=0$. For a two step creep and recovery experiment in which the duration of both the creep step and the recovery time is t_1, it was shown [3] that

$$\varepsilon_R(t_1;t_1) = \varepsilon_c(\sigma;2t_1) - \varepsilon_c(\sigma;t_1) + \Delta\varepsilon_{Rc}(t_1;t_1), \qquad (3)$$

where $\varepsilon_R(t_1;t_1)$ is the strain during recovery at a time t_1 after creep for a time t_1, and $\Delta\varepsilon_{Rc}(t_1;t_1)$ is given by

$$\Delta\varepsilon_{Rc}(t_1;t_1) = 2\phi(\hat{g}(\sigma)t_1)-\phi(\hat{g}(\sigma)2t_1). \qquad (4)$$

In Eqn. (4), $\Delta\varepsilon_{Rc}(t_1;t_1)$ represents the deviation of the actual recovery from that calculated using eqn. (1) (at a time t_1 after creep for a duration t_1). It was then assumed that in its simplest form $\phi(\hat{g}(\sigma)t_1)$ could be represented by

$$\phi(\hat{g}(\sigma)t_1) = g(\sigma)t_1^{\alpha}, \qquad (5)$$

where $g(\sigma) = (\hat{g}(\sigma))^{\alpha}$, then from equation 4 it followed that

$$\Delta\varepsilon_{RC}(t_1;t_1) = g(\sigma)(2-2^{\alpha})\, t_1^{\alpha}. \qquad (6)$$

For constant σ a plot of log $\Delta\varepsilon_{RC}(t_1;t_1)$ versus log t_1 should then yield a straight line with slope α. From such a plot it was found [3] that the data shown in Figure 2 could be represented to a very good approximation by a straight line having a slope of 1/3, or

$$\Delta\varepsilon_{RC}(t_1;t_1) = 0.74\ g(\sigma)\ t_1^{1/3}. \qquad (7)$$

2. Comparison of the Short Time Creep Behavior of UHMWPE in Extension and Compression

Figure 3 shows a comparison of the short time creep behavior of the slowly cooled UH-1 polymer in uniaxial extension and uniaxial compression at four different levels of applied stress. With the exception of the curves obtained at the highest stress of 15.6 MPa, there is no significant difference in behavior between extension and compression over the range of stress and time examined. At 15.6 MPa, where the strain approaches ten percent at 10^3 seconds, the true stress is significantly larger in extension than in compression and deviations in the creep behavior are observed.

3. Temperature Dependence of the Short Time Creep and Recovery at Small Deformation in Uniaxial Extension

Figures 4-6 present short time creep and recovery data obtained on specimens of the slowly cooled UH-1 polymer in uniaxial extension at temperatures of 23 $\pm$0.5 °C, 38 $\pm$0.5 °C, and 47 $\pm$0.5 °C. Only the 10^3 second creep data are shown in each figure. In each experiment the applied stress was 4 MPa. A comparison of the 10^3 second creep data at four different temperatures is shown in Figure 7. Comparison of the creep data obtained at constant stress but different temperatures with those obtained at constant temperature but varied stress indicate that the creep curve obtained at 23 °C and a stress of 4 MPa is roughly equivalent to that obtained at 38 °C and 2.5 MPa.

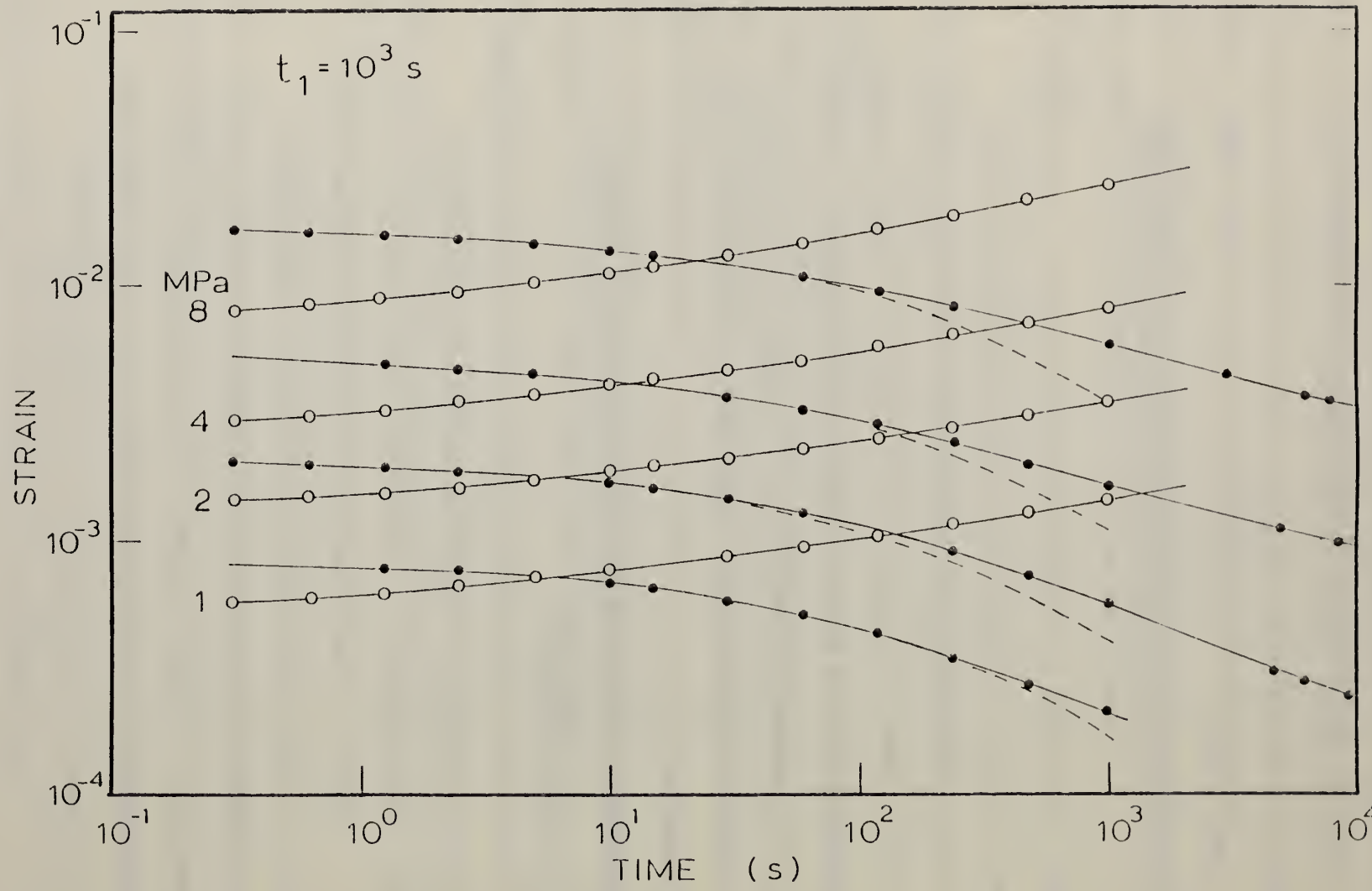


Figure 1. Creep strain (-O-) and strain during recovery (-●-) versus time (log-log) coordinates) from experiments carried out at constant t_1 but varied applied stress σ_A. The dashed lines represent the recovery predicted using equation 1.

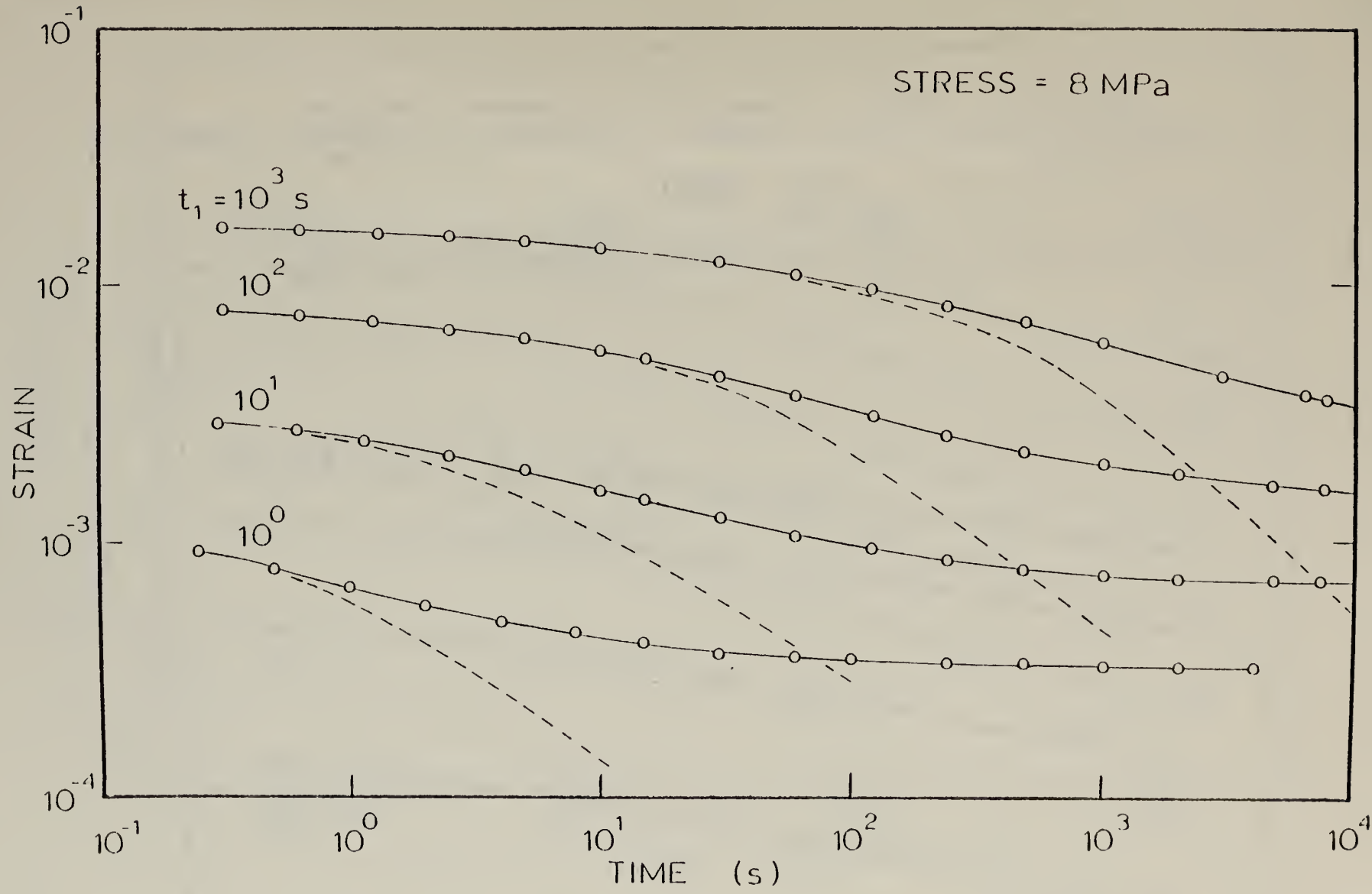


Figure 2. Strain during recovery (log-log coordinates) from experiments done at constant applied stress but varied t_1. The dashed lines represent the recovery predicted using equation 1.

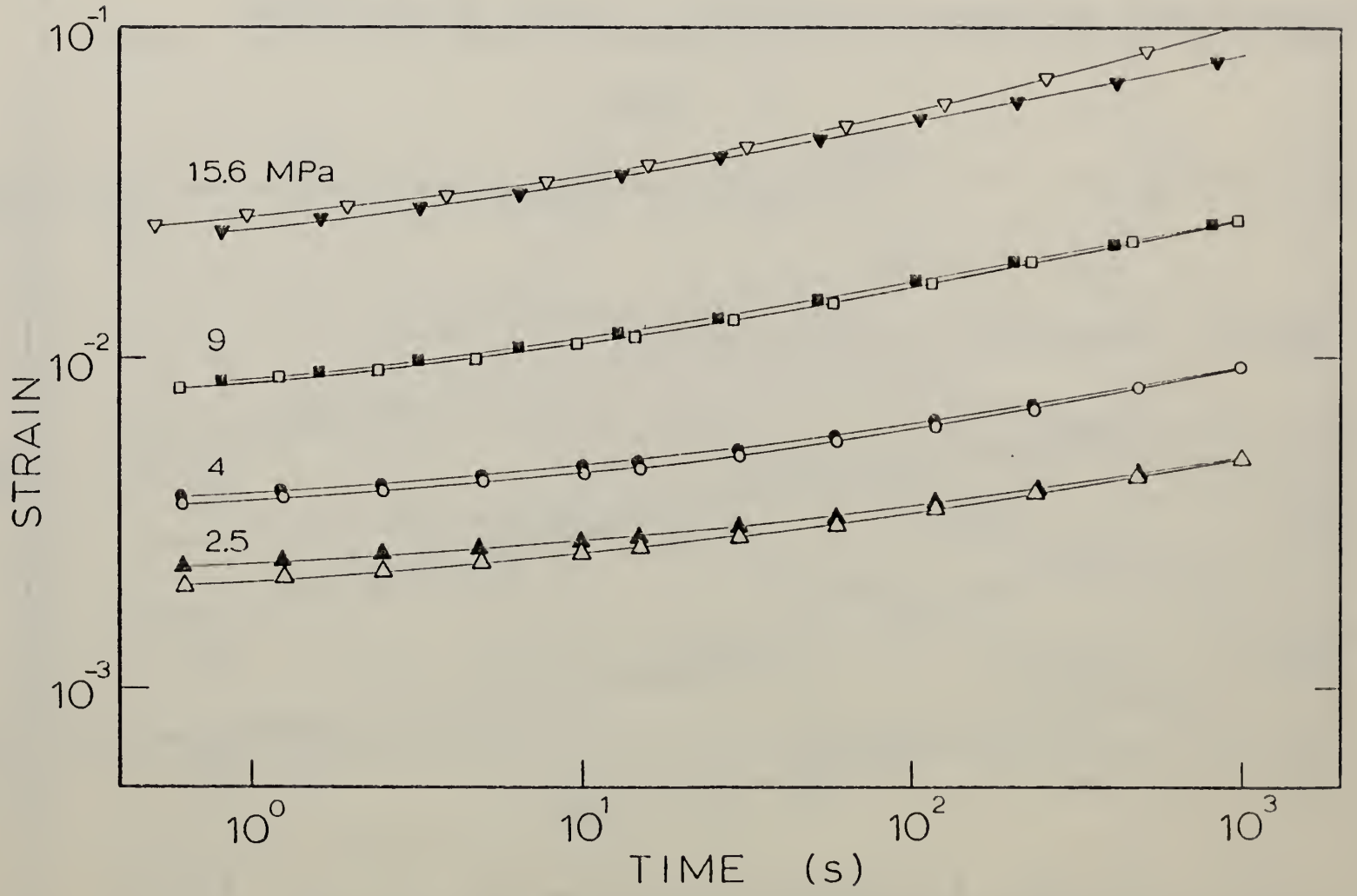


Figure 3. Comparison of creep behavior of UHMWPE in uniaxial extension (open symbols) and uniaxial compression (filled symbols). $M_w \tilde{\sim} 4 \times 10^6$, $\rho = 0.935$ g/cm^3.

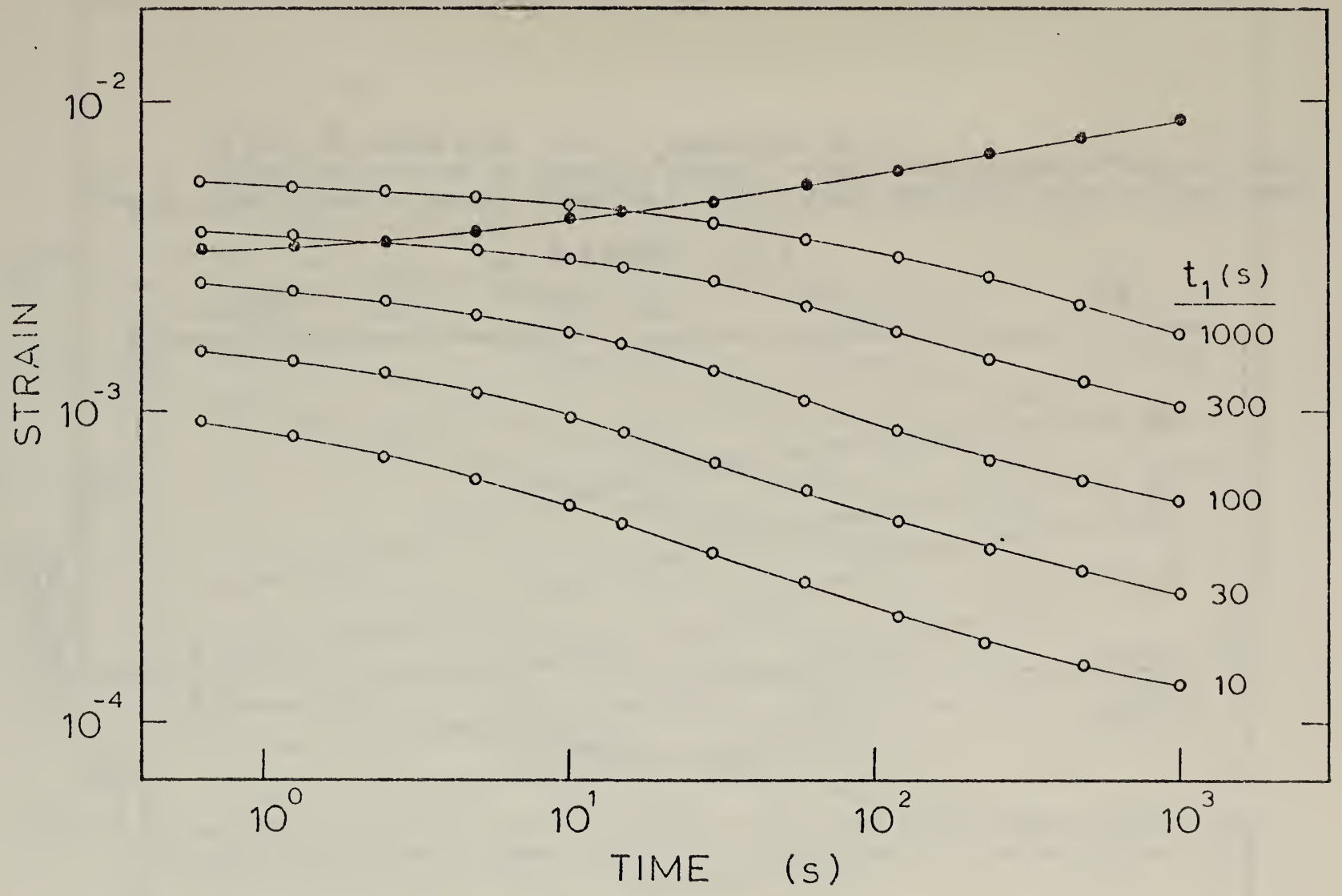


Figure 4. Creep strain in uniaxial extension (filled circles) and strain during recovery (open circles) versus time for UHMWPE ($M_w \approx 4 \times 10^6$, $\rho = 0.935$ g/cm^3) at constant applied stress (4 MPa) but varied creep time t_1. Temperature 23 °C.

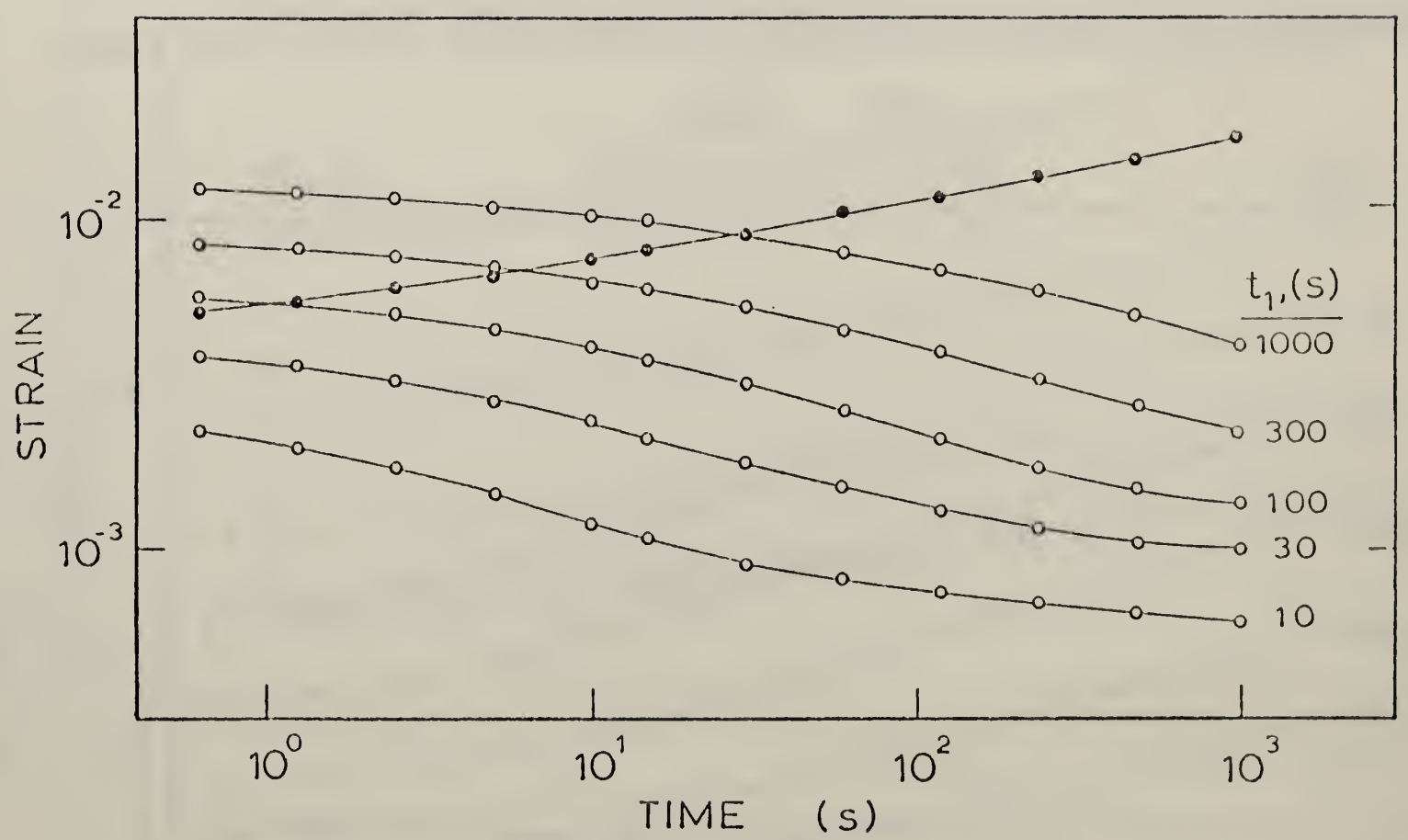


Figure 5. Creep strain in uniaxial extension (filled circles) and strain during recovery (open circles) versus time for UHMWPE ($M_w \tilde{\sim} 4 \times 10^6$, ρ=0.935 g/cm^3) at constant applied stress (4 MPa) but varied creep time t_1. Temperature 38 °C.

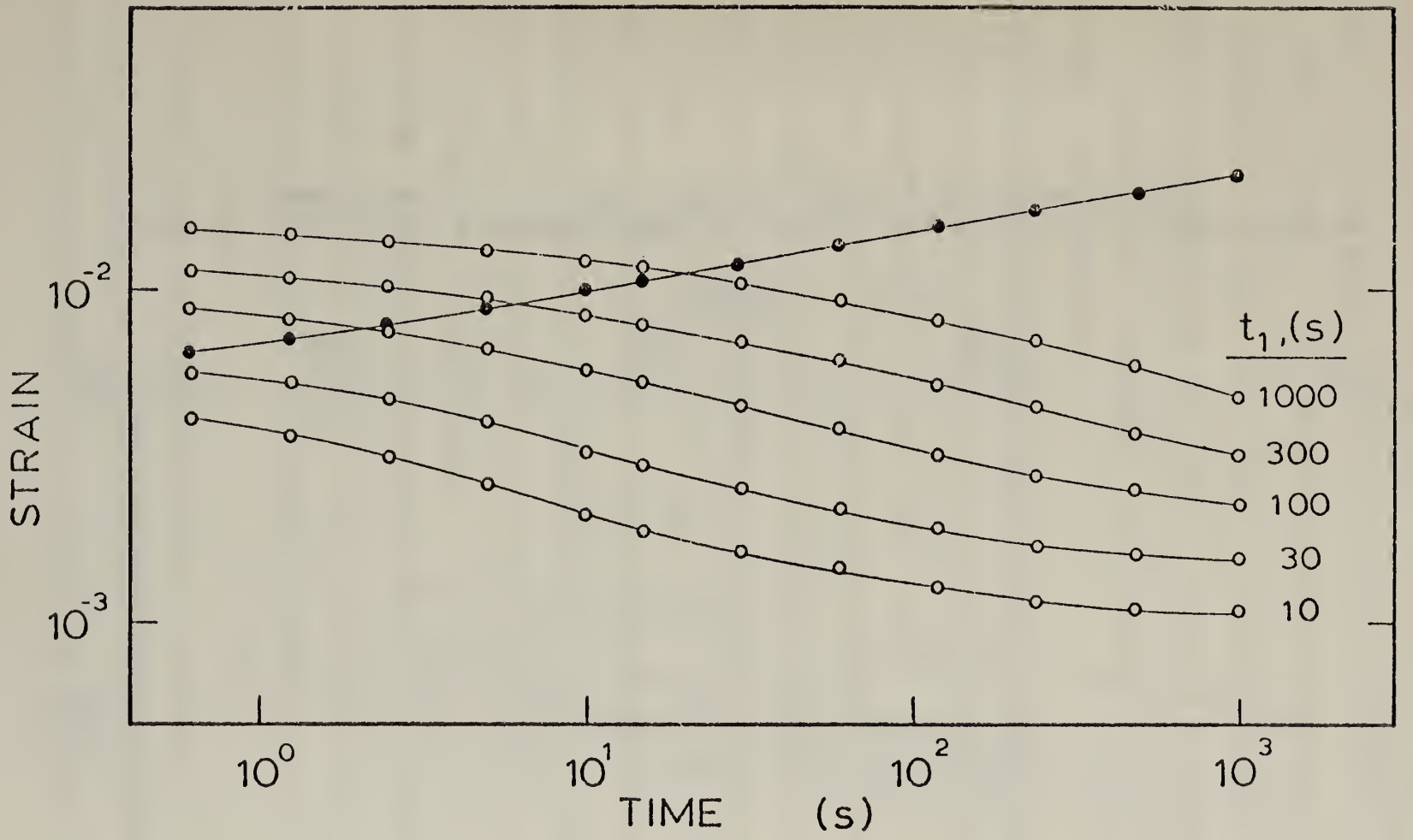


Figure 6. Creep strain in uniaxial extension (filled circles) and strain during recovery (open circles) versus time for UHMWPE ($M_w \tilde{\approx} 4 \times 10^6$, ρ=0.935 g/cm^3) at constant applied stress (4 MPa) but varied creep time t_1. Temperature 47 °C.

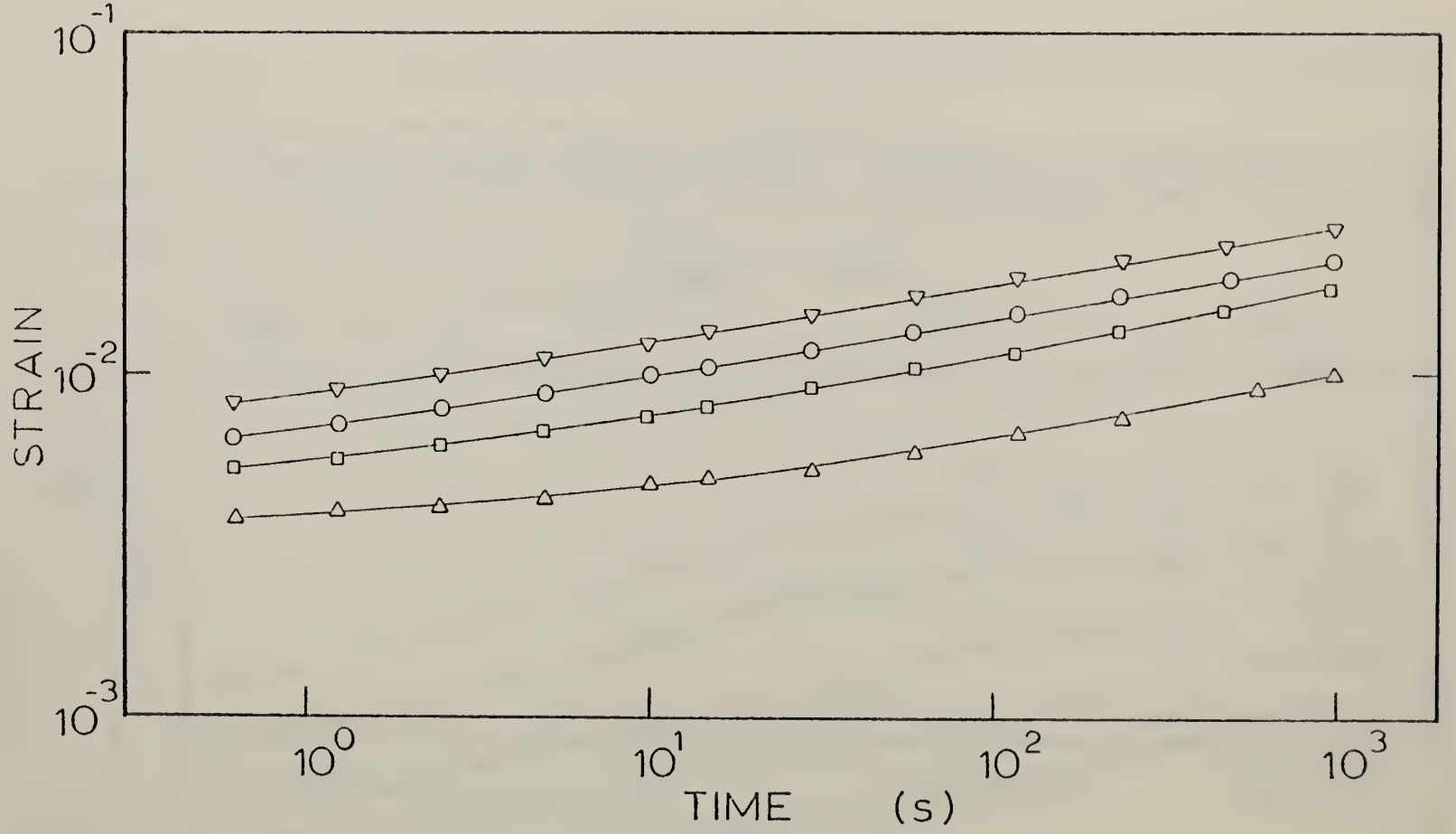


Figure 7. Creep curves in uniaxial extension for the slowly cooled UH-1 at four different temperatures. σ_A = 4 MPa. Δ 23 °C, 38 °C, O 47 °C, and ▽ 62 °C.

Following the same procedures outlined earlier, $\Delta\varepsilon_{RC}\ (t_1;t_1)$ was calculated for each of the recovery curves shown in Figures 4-6 and these results are presented in Figure 8. As was the case for an applied stress of 8 MPa (Figure 2) the room temperature data can still be represented by a straight line having a slope of 1/3. At the two higher temperatures the data can also be represented by straight lines, however the slope decreases with increased temperature, decreasing from 1/3 at 23 °C, to 0.271 at 38 °C, to 0.225 at 47 °C. This means that the exponent α and the term $(2\text{-}2^{\alpha})$ in equation 6 are dependent on the temperature.

4. Long Time Creep and Recovery Behavior at Small Deformations

Creep and recovery data are shown in Figure 9 for specimens of the slowly cooled UH-1 polymer which were under load for times up to 405 hours (approximately 17 days). The creep data were obtained in uniaxial extension at an applied engineering stress of 4 MPa and at room temperature (23 $\pm$0.5 °C). The one creep curve shown corresponds to the longest time under load (405 hours). It can be seen that after about 10^5 seconds under load (approximately 1 day) a "break point" occurs beyond which the creep proceeds more slowly, and on log-log coordinates the creep can be represented quite well by a straight line. In earlier work by Turner and Moore [4,5] on the creep behavior of lower molecular weight polyethylenes and polypropylene, it was found that the breakpoint or "discontinuity" depended on the processing conditions in the following ways.

1. The break point moves to longer times as the rate of cooling from above the melting point decreases. This movement corresponds to a horizontal shift only of the break point.

2. The break point moves from one strain to a smaller one in a vertical fashion as the storage time prior to testing increases. The vertical shift is large for the quenched polymer and undetectable for the fully annealed material.

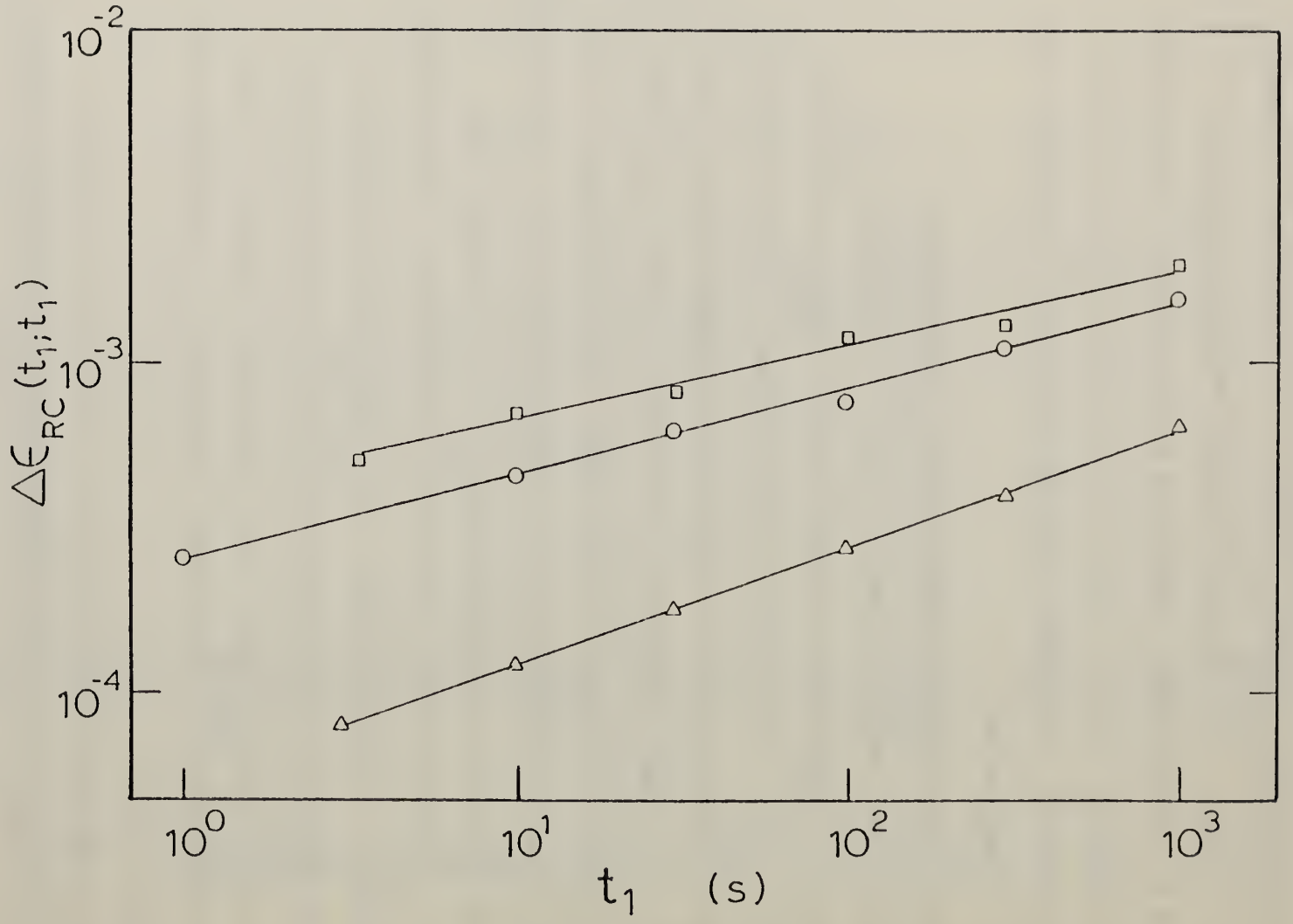


Figure 8. Values of $\Delta\varepsilon_{RC}(t_1;t_1)$ versus t_1 on log-log coordinates obtained at three different temperatures. Δ 23 °C, O 38 °C, and □ 47 °C.

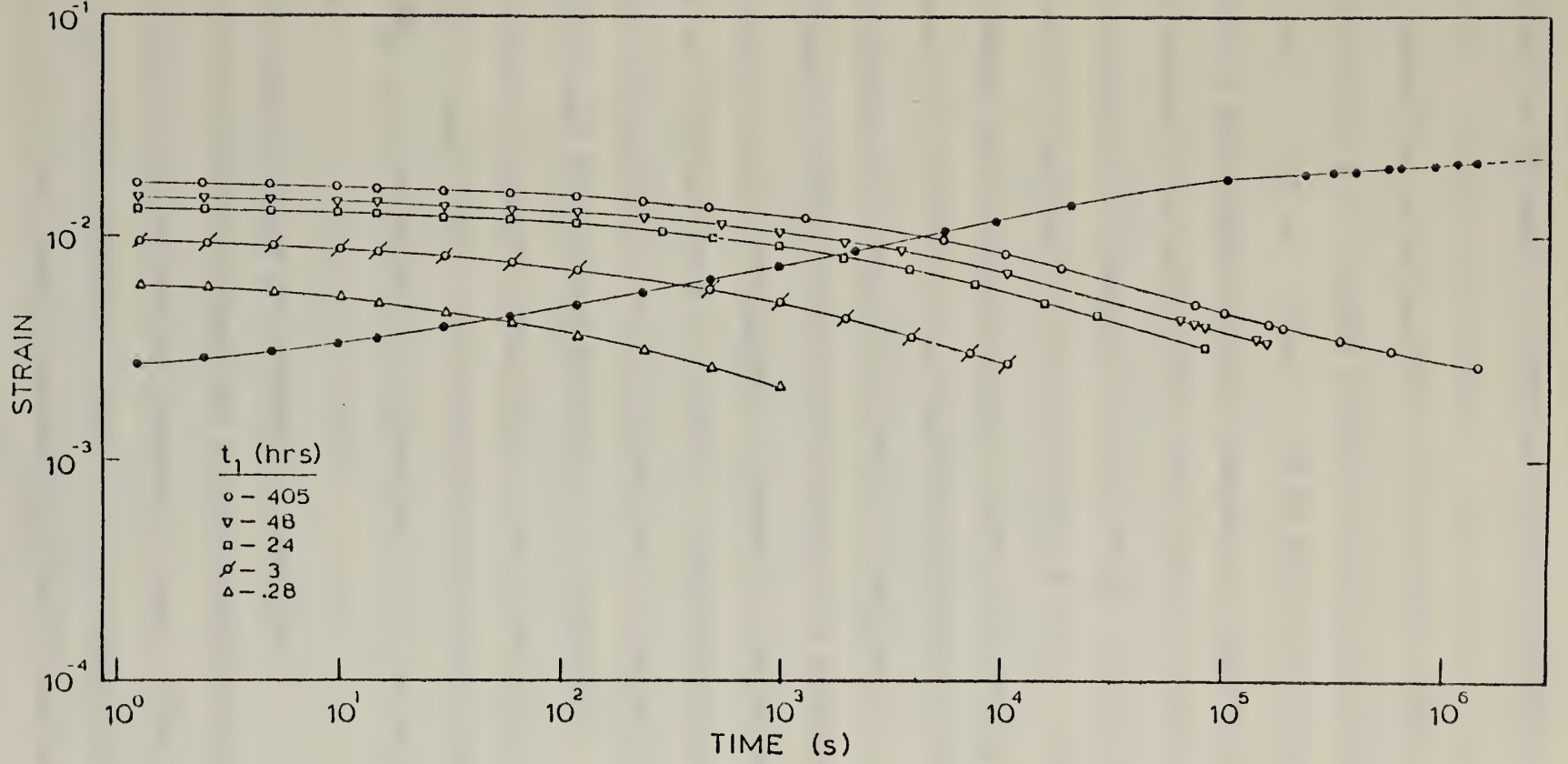


Figure 9. Creep and recovery of slowly cooled UH-1 in uniaxial extension at 23 °C. σ_A = 4 MPa and t_1 = duration of the creep step. Creep data are shown only for t_1 = 405 hours.

3. When plotted on log-log coordinates the creep curve maintains the same shape for a range of material states and therefore a range of coordinates of the break point.

4. Beyond the break point the slope of the creep curve is independent of the stress level and temperature for strains below about 3% in uniaxial extension and for temperatures up to at least 60 °C.

5. The break point decreases in time with increased temperature or applied stress.

Also shown in Figure 9 are the recovery data obtained from experiments in which the creep time, t_1, was varied from 0.28 to 405 hours. For each of the recovery curves shown in Figure 9 $\Delta\varepsilon_{RC}(t_1;t_1)$ was calculated, following the procedures outlined earlier, and these values are shown plotted versus t_1 in Figure 10. The two points corresponding to t_1's of 100 and 300 seconds are taken from Figure 4. Out to times of nearly 10^5 seconds (approximately 1 day) the data can be represented by the same function given earlier in equation (7). However, at times approaching 10^5 seconds a "breakpoint" also occurs in $\Delta\varepsilon_{RC}(t_1;t_1)$. From the results shown in Figure 10 it would appear that at the longer times the contribution of the plasticity term in equation (2) becomes essentially constant. Therefore, in its present form, either equation 5 or 7 is not applicable to situations in which creep occurs for times longer than about one day. It is also interesting that the break point in the $\Delta\varepsilon_{RC}(t_i;t_i)$ versus t_1 plot occurs at essentially the same time as it does in the creep curve (Figure 9).

Experiments were also performed to determine the extent to which the break point depends upon variables such as the magnitude of the applied stress and the temperature (points 4 and 5 cited earlier from the work of Turner and Moore [4,5]). For this purpose 0.75 cm diameter cylinders of the slowly cooled UH-1 polymer similar to those described in reference [2] were tested in uniaxial

compression. Results from experiments done at room temperatures (23 ±0.5 °C) in which the applied engineering stress was varied are shown in Figure 11. It can be seen that the break point does move toward earlier times as the stress is increased, although the dependence is not a strong one. Beyond the break point the creep curves form a set of parallel straight lines (on log-log coordinates). In compression even the specimen loaded to the 16 MPa shows the same behavior as that found at the smaller loads. At 10^6 second the strain in the specimen loaded to 16 MPa approaches 10 percent (λ=0.9), whereas in uniaxial extension at a stress of 16 MPa and a time of 10^6 seconds the material has already elongated to a stretch ratio of 5 (see Figure 3 in reference [2]).

The influence that temperature has on the position of the break point is demonstrated in Figure 12 where creep curves obtained at four different temperatures are shown. For these experiments the specimens were held at the operating temperature for one hour prior to loading in order to approach temperature equilibrium. With temperature, there is quite a strong shift in the position of the break point, more than two decades in time for an increase in temperature from 23 to 64 °C. To the right of the break point the creep curves have the same constant slope (on log-log coordinates) as those shown in figure 11. For the purpose of predicting the very long time creep behavior of UHMWPE (30-50 years), what is not known at this point is whether the creep curves continue indefinitely as straight lines on a log-log plot, or at yet longer times than those investigated whether the shape of the curves changes.

5. Effect of γ-Radiation on the Performance of UHMWPE

Sterilization of UHMWPE components in orthopedic prostheses is done using high energy radiation, most commonly gamma irradiation. The typical dose is in the 2-4 Mrad range. In addition to sterilization, high energy radiation also causes chemical crosslinking and/or degradation of the polymer [6-8]. In the absence of oxygen, radiation is said to produce a net crosslinking effect

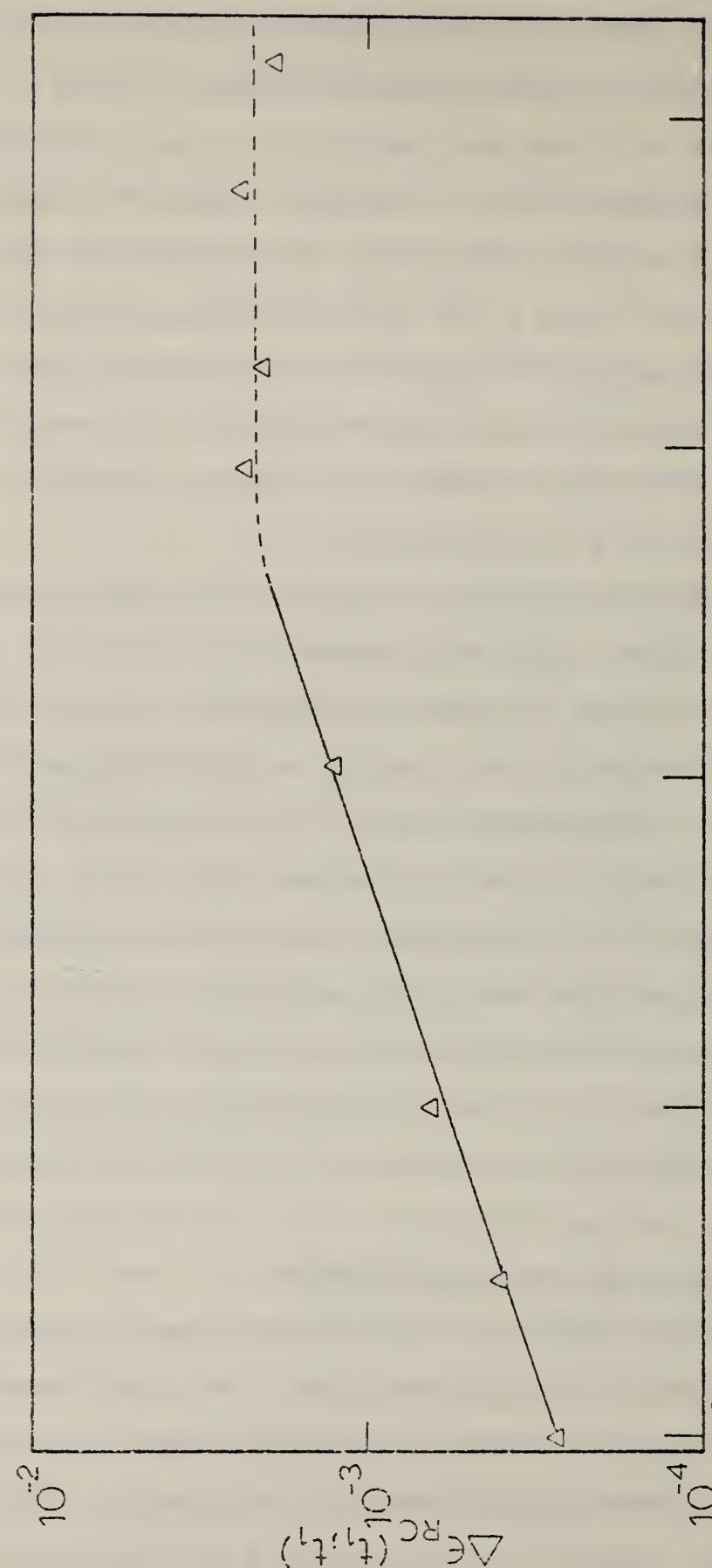


Figure 10. Values of $\Delta\epsilon_{RC}(t_1;t_1)$ versus t_1 on log-log coordinates for slowly cooled UH-1 at 23 °C.

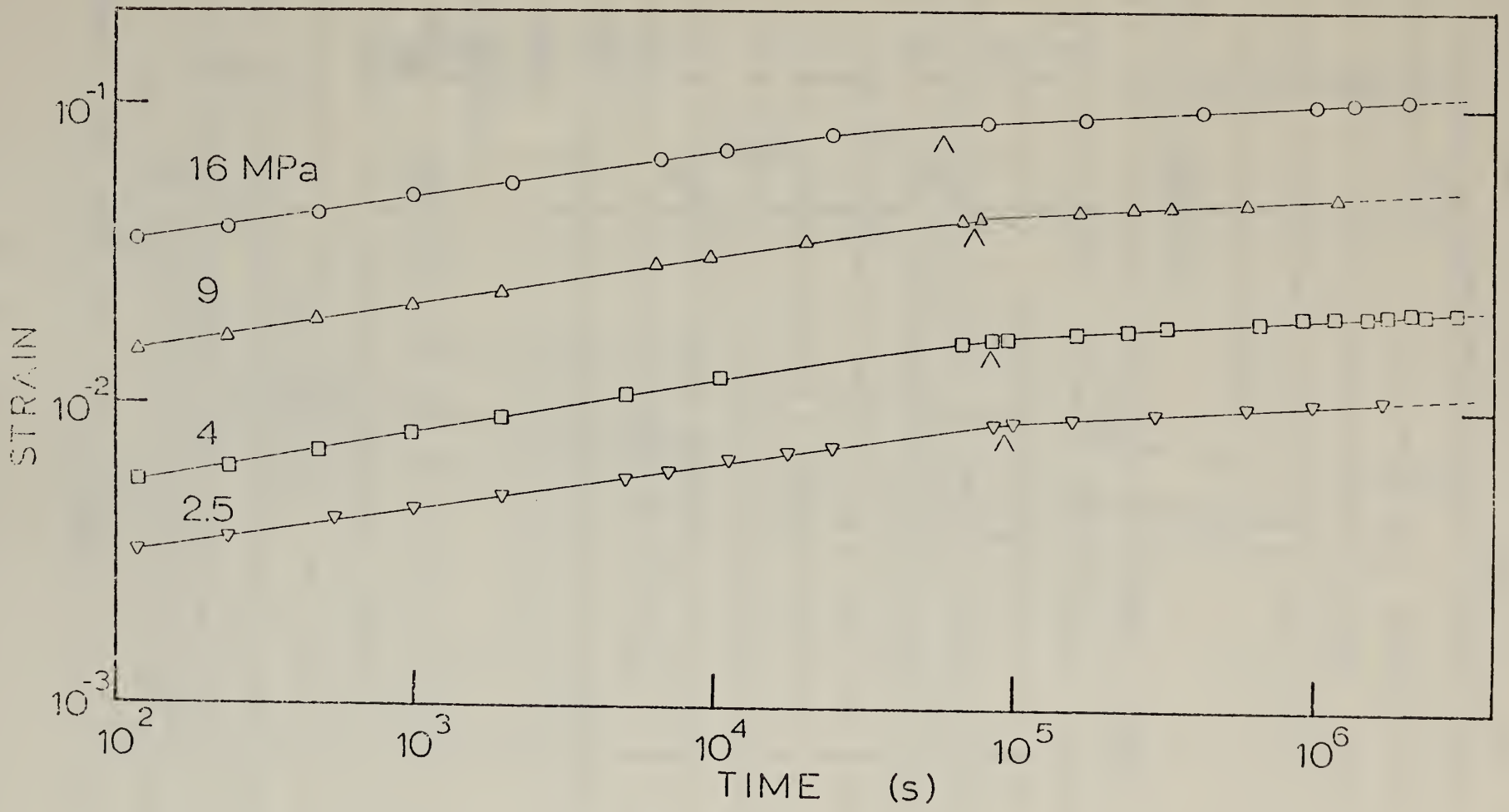


Figure 11. Creep of slowly cooled UH-1 in uniaxial compression at 4 levels of applied stress at 23 °C. Λ indicates the approximate location of the break point.

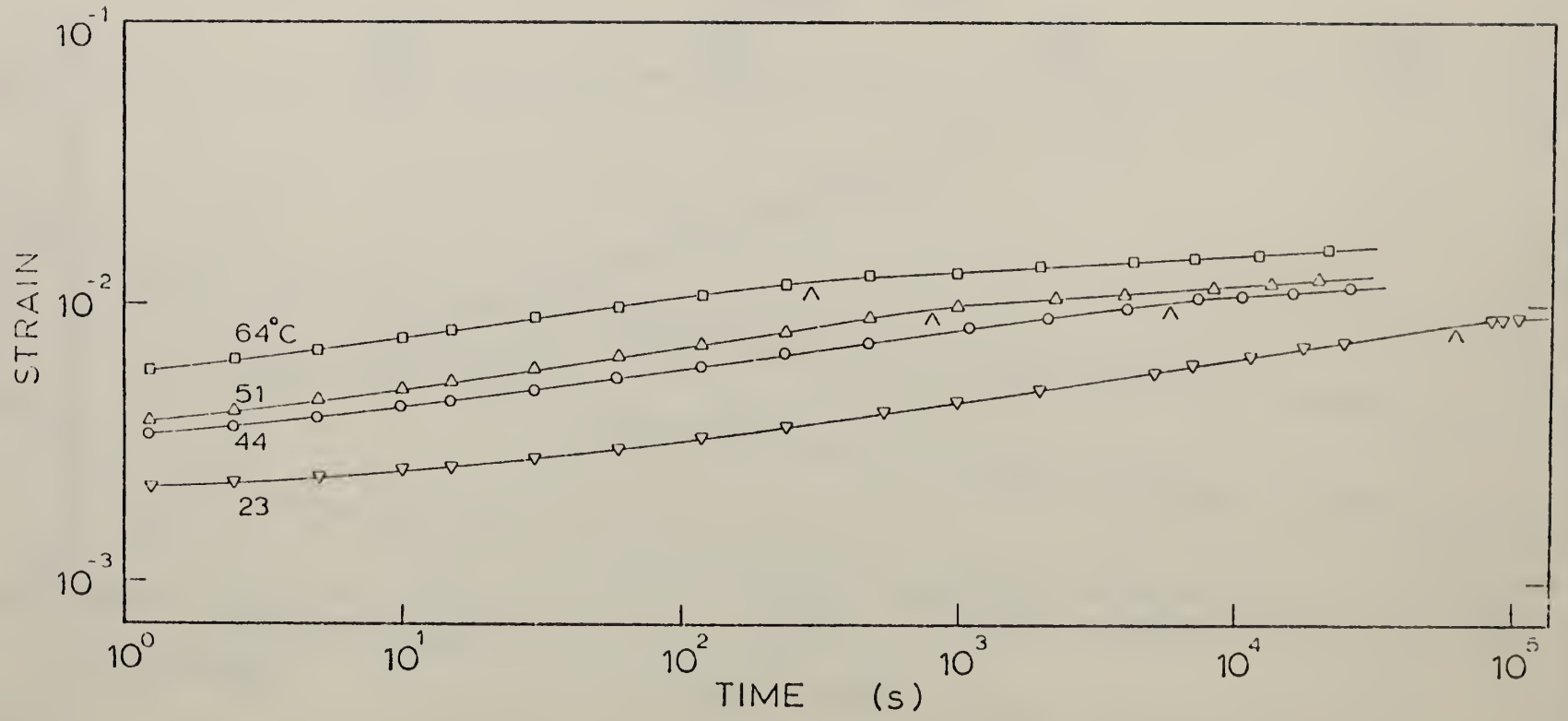


Figure 12. Creep of slowly cooled UH-1 in uniaxial compression at four different temperatures. Λ indicates the approximate location of the break point.

which occurs preferentially in the amorphous regions [9]. There is additional evidence that some crosslinking occurs within the crystals, possibly limited to the fold surfaces [10,11]. Crosslinking and/or degradation can alter the mechanical behavior from that of the unirradiated polymer. Section 5 describes various aspects of the changes in physical and mechanical behavior of UHMWPE brought about by high energy radiation.

5.1 Density and Crystallinity

One effect of high energy radiation is to increase the density, or percent crystallinity, of the UHMWPE. Figures 13 and 14 indicates how the percent crystallinity and density increase with increased irradiation dose.

Both sets of data indicate that the density increases with dose for doses up to at least 10 Mrad. Two explanations for the increase in density have been given; (1) highly constrained tie molecules are preferentially severed by the irradiation, thus removing hinderance to further crystallization [9]; and (2) greater localized chain mobility occurs due to energy absorption during irradiation, and the material tends to reorganize in the direction of higher crystallinity [12]. There is also evidence that subsequent to the irradiation aging of UHMWPE occurs, and the density continues to increase over a period of many months [13].

5.2 Melting Behavior

The effect of high energy radiation on the melting behavior of UHMWPE is less well defined than in the case of the density. Bhateja et. al [9] report that for an experimental sample of UHMWPE, which was subjected to β radiation, an increase in the temperature of the DSC melting peak of about 5-7°C occurred over the first 16 Mrad of radiation. These results are shown in Figure 15.

On the other hand, Roe et al. [12] compared the DSC curves for two specimens of a commercial grade UHMWPE, which were α irradiated to 0.0 and 10.0 Mrad,

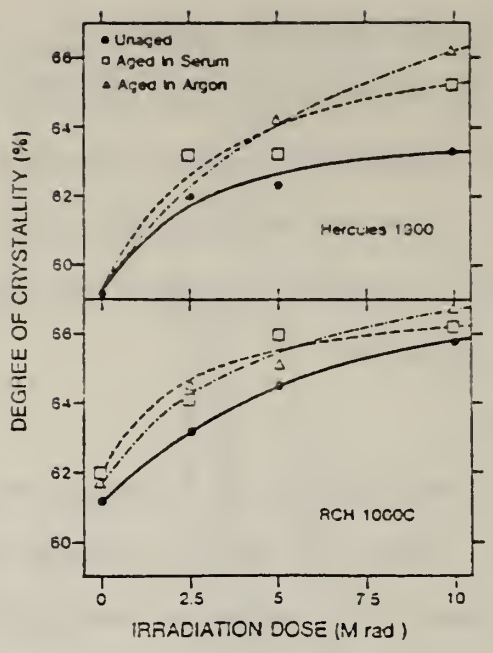


Figure 13. The degree of crystallinity, calculated from the density versus irradiation dose (gamma irradiation) for UHMWPE from two different commercial sources. (From reference 12).

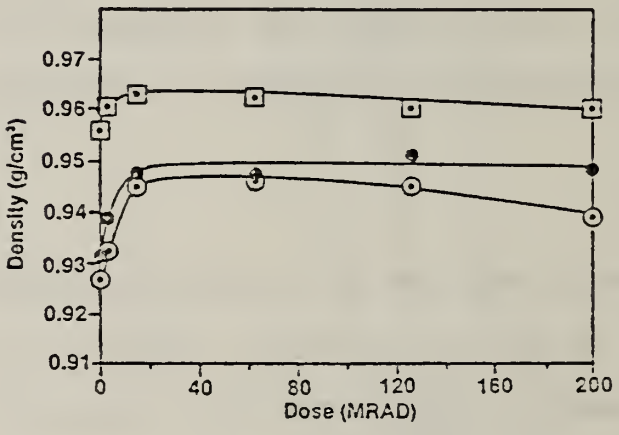


Figure 14. Density as a function of irradiation dose (β irradiation) for two different experimental samples of UHMWPE (⊖,•) and normal molecular weight polyethylene (⊡). (From reference 9).

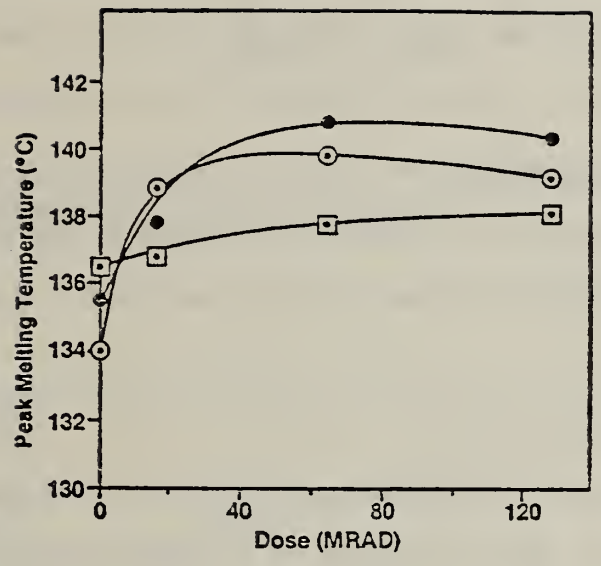


Figure 15. Effect of β radiation dose on the DSC (differential scanning calorimetry) peak melting temperature. ⊙,● - UHMWPE, ⊡ - normal molecular weight polyethylene. (From reference 9).

respectively, and found little or no change in position of the primary melting peak centered around 137 °C. A small secondary melting peak was observed at around 120 °C for the specimen irradiated to 10 Mrad.

5.3 Tensile Yield Stress

The tensile yield stress is defined as the peak engineering stress occurring at tensile yield. Several studies have been made of the effect of high energy radiation on the tensile yield stress of UHMWPE. Data showing tensile yield stress as a function of radiation dose, for doses up to 200 Mrad, are shown in Figure 16. The yield stress is found to increase with increased dose.

5.4 Tensile Yield Point Elongation

The effect of γ irradiation on UHMWPE is to decrease the elongation at yield [12]. Most of the reduction occurs during the first 5 Mrad of irradiation (Figure 17).

5.5 Tensile Modulus

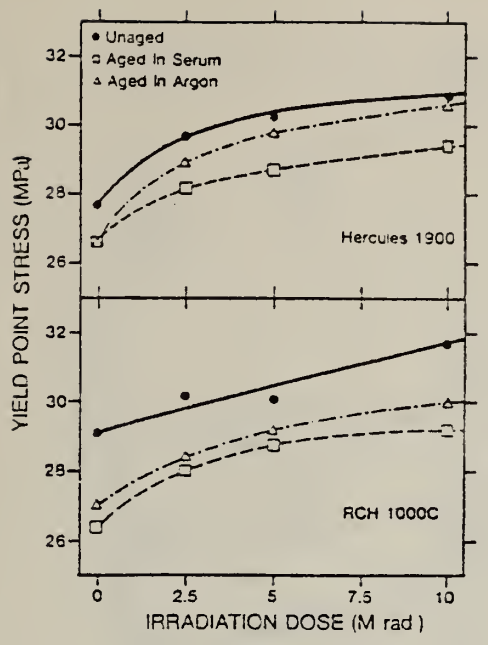
The effect of high energy irradiation on UHMWPE is to increase the tensile modulus with increased dose. Data are shown in Figure 18 for polymer subjected to β-irradiation [9] and γ-irradiation [12].

5.6 Impact Strength

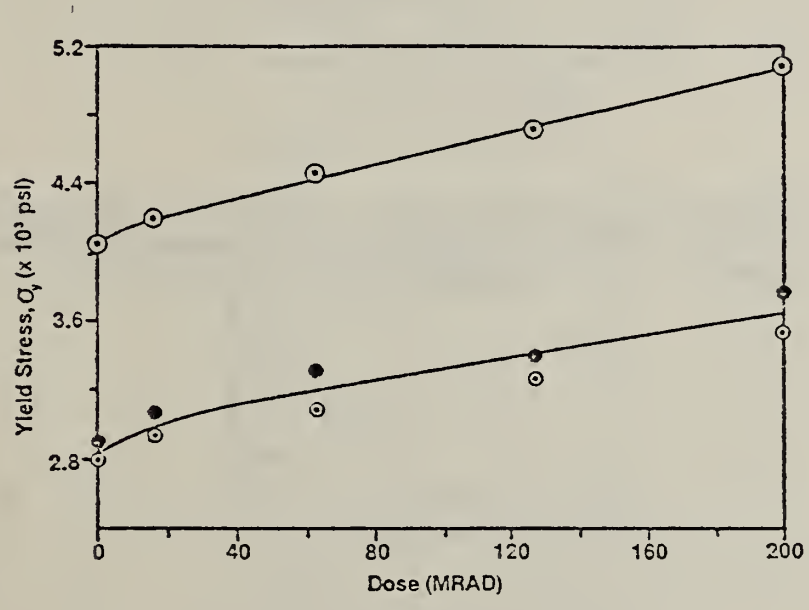
DuPlessis et al. [14] report that the impact strength of irradiated UHMWPE decreases significantly with an increase in irradiation dose. Their data are shown in Figure 19 for specimens irradiated in the presence of three different environments.

5.7 Surface Hardness

DuPlessis et al. [14] report that the surface hardness (Type D-Shore) of UHMWPE increases when the polymer is irradiated (γ rays) in the presence of crosslinking agents, but not so if irradiated in a nitrogen atmosphere (Figure 20).



(a) γ irradiated UHMWPE from two different commercial sources. Aging time 6-24 months. (from reference 12).



(b) β irradiated experimental UHMWPE. ⊙,● - UHMWPE, ⊙- normal molecular weight PE (From reference 9).

Figure 16. The effect of irradiation dose on the tensile yield stress of UHMWPE.

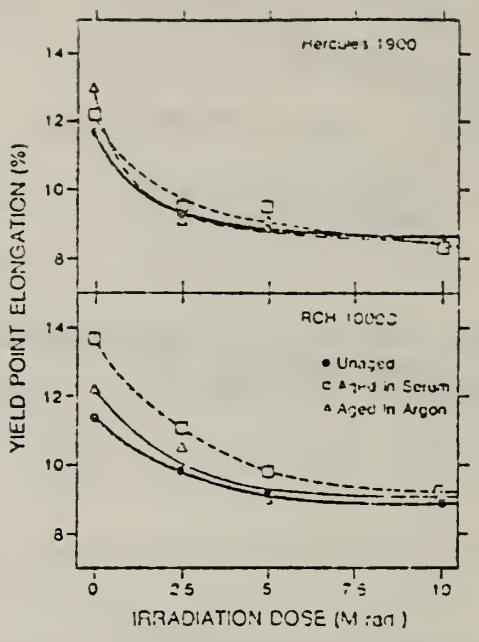
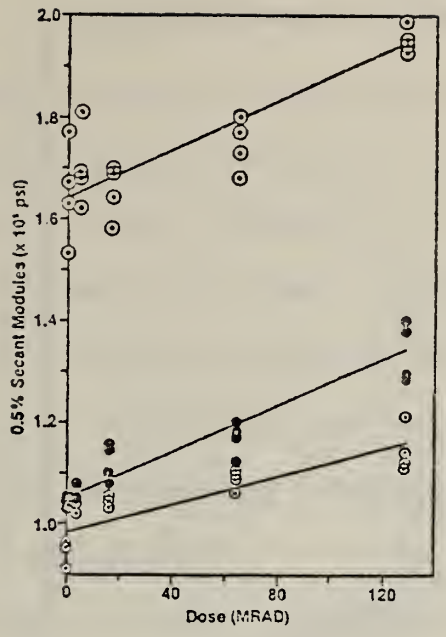
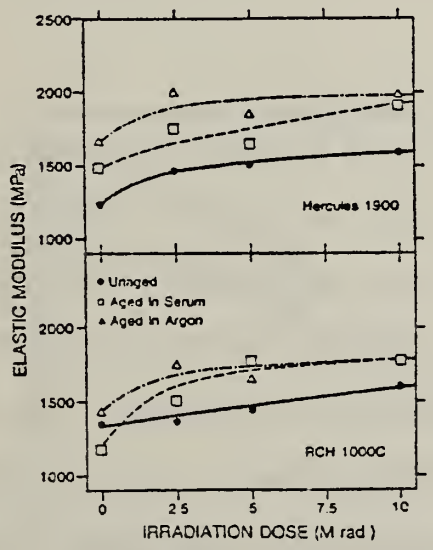


Figure 17. Elongation at the yield point stress as a function of irradiation dose for two different commercial UHMWPE polymers. γ - irradiation (From reference 12).



(a) β - irradiation, 0.5% secant modulus, ⊙ ,● - Two different experimental samples of UHMWPE, ⊖ - normal molecular weight PE. (from reference 9).



(b) γ - irradiation, commercial UHMWPE (from reference 12).

Figure 18. Effect of radiation dose on the tensile modulus of UHMWPE.

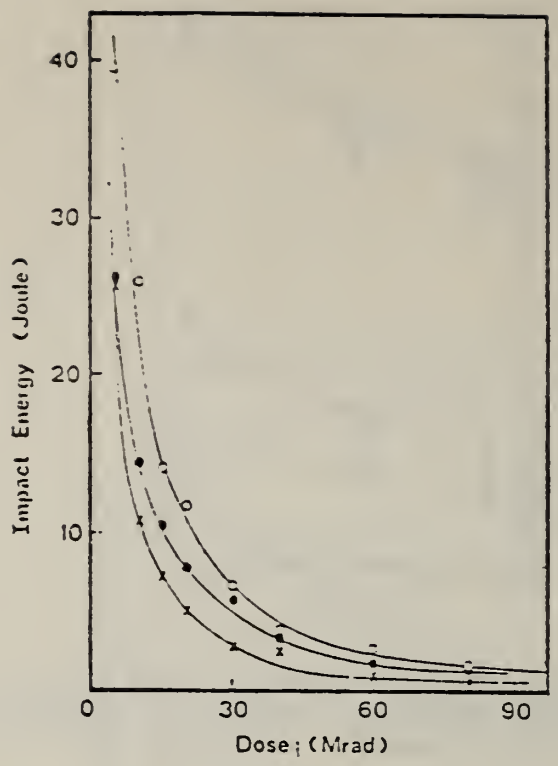


Figure 19. Izod impact energy as a function of dose for UHMWPE radiation crosslinked (γrays) in the presence of crosslinking agents or nitrogen. O-N_2, X-CH≡CH, and ●-CH≡CH + CTFE (chlorotrifluoroethylene). (From reference 14).

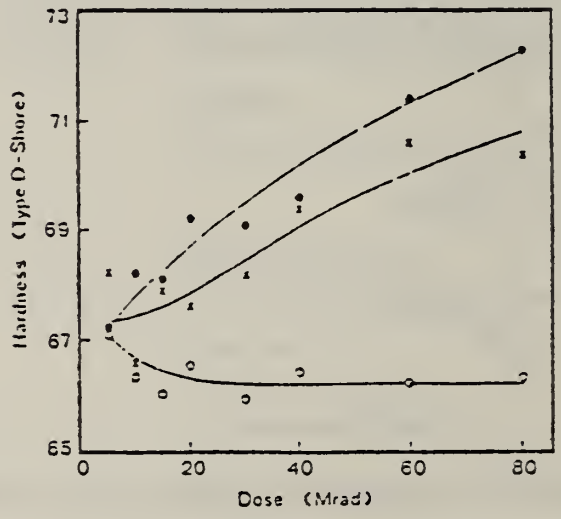


Figure 20. Surface hardness of UHMWPE as a function of radiation dose for UHMWPE radiation crosslinked (α rays) in the presence of crosslinking agents or nitrogen. O-N_2, X-CH≡CH, and ●-CH≡CH + CTFE. (From reference 14).

5.8 Creep

Exposure to high energy radiation improves the resistance of UHMWPE to creep, even at relatively low irradiation doses. An example of the short time creep and recovery behavior at small deformations in uniaxial extension is shown in Figure 21 for specimens of the slowly cooled UH-1 polymer ($M_w \approx 4 \times 10^6$ and $\rho = 0.935$ g/cm^3 prior to irradiation) subjected to relatively low doses of γ-irradiation. The creep strain after 10^3 seconds decreases with increased dose. Figure 22 shows similar data for specimens irradiated with the same dosages as given in Figure 21, but tested at 38 °C.

A comparison of the uniaxial creep behavior over a period of two weeks is shown in Figure 23 for a commercial UHMWPE polymer both unirradiated and irradiated at three different doses. At the longer times the creep strain is significantly less in more highly irradiated samples.

Bhateja and Andrews [15] report a similar behavior for samples of UHMWPE irradiated to doses of β-irradiation as high as 64 Mrad. Their results are shown in Figure 24.

5.9 Fatigue

Only limited data are available on the effect of high energy radiation on the fatigue behavior of UHMWPE. Table 5.9.1 shows some of the fatigue results of Nusbaum and Rose [16]. The samples were cycled for the number of cycles indicated and at the peak stress indicated. After 10^7 cycles at 1.7×10^4 kPa several of the irradiated specimens showed a pronounced neck, whereas unirradiated samples did not. They concluded that the irradiation rendered the UHMWPE slightly weaker than the as-received polymer, and where cyclic loading is concerned, irradiation may aggravate creep under some conditions.

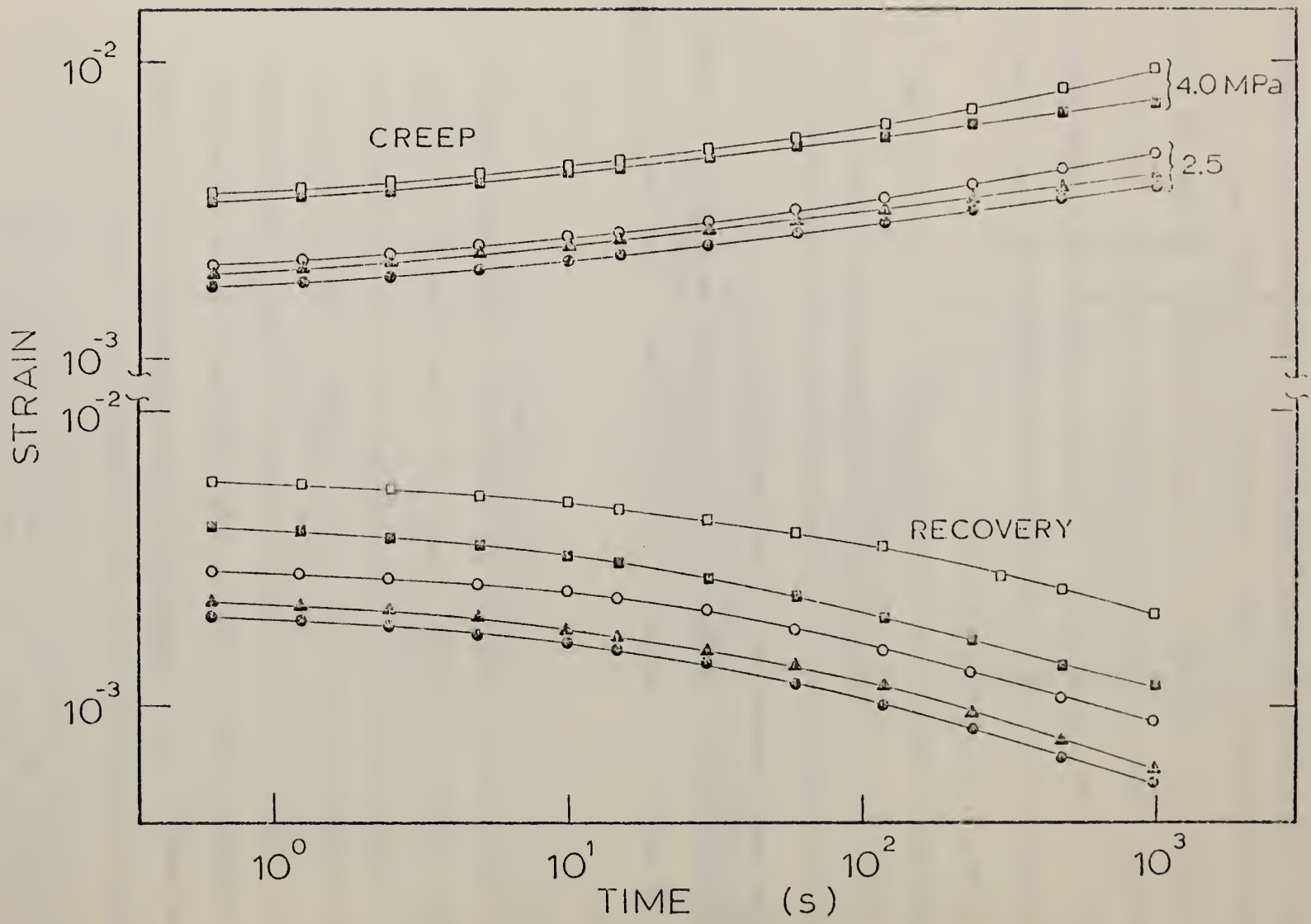


Figure 21. Effect of γ irradiation on the short time (10^3 seconds) creep and recovery behavior in uniaxial extension of the slowly cooled UH-1 polymer at 23 ±5 °C. Engineering stress 2.5 and 4.0 MPa. □,o-0 Mrad, ▲-3.74 Mrad, and ■,●-6.28 Mrad dose

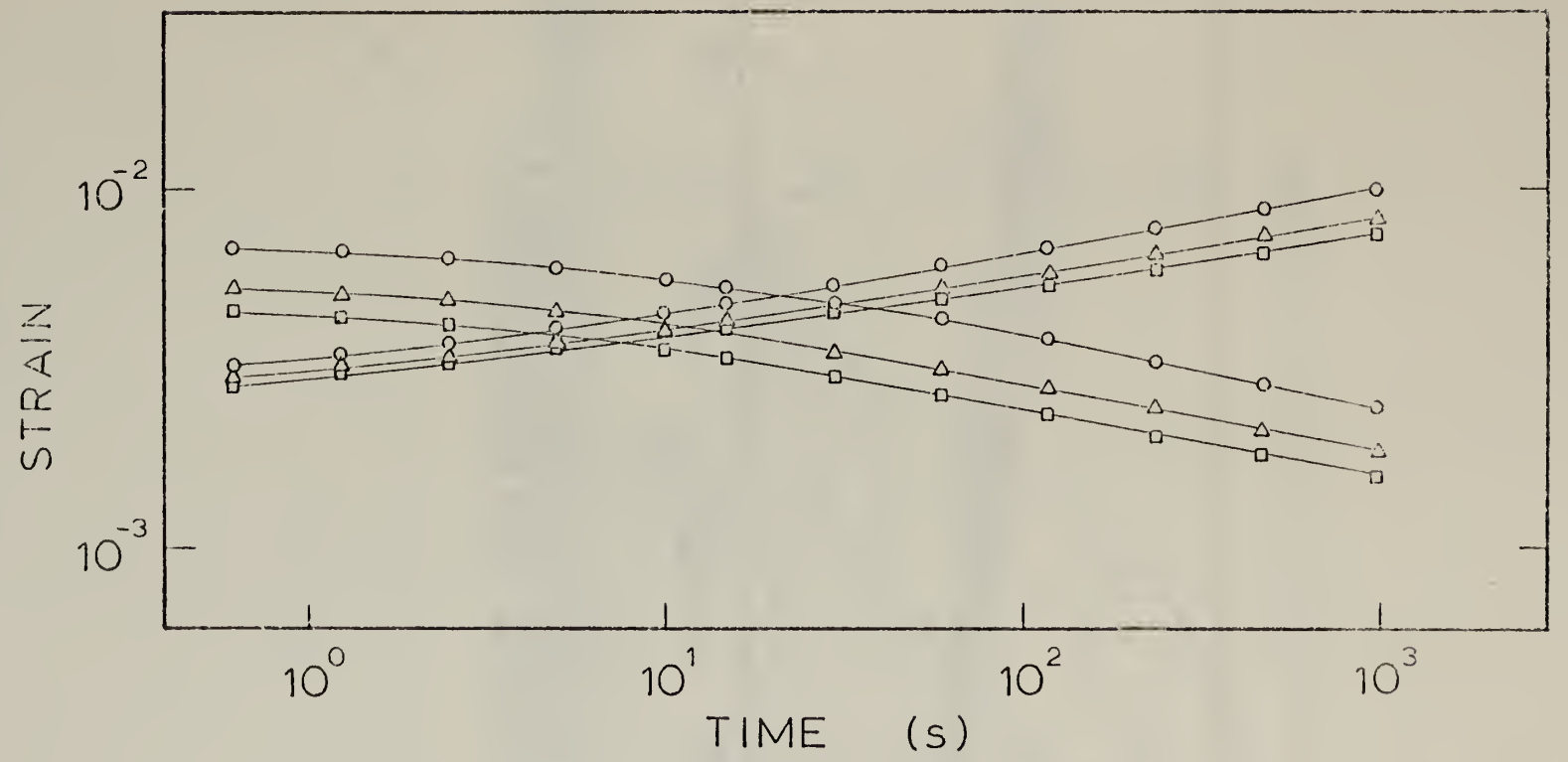


Figure 22. Effect of γ irradiation on the short time (10^3 seconds) creep and recovery behavior in uniaxial extension of the slowly cooled UH-1 at 38 °C. Engineering stress 2.5 MPa. o-0 Mrad, Δ- 3.74 Mrad, and□-6.28 Mrad dose.

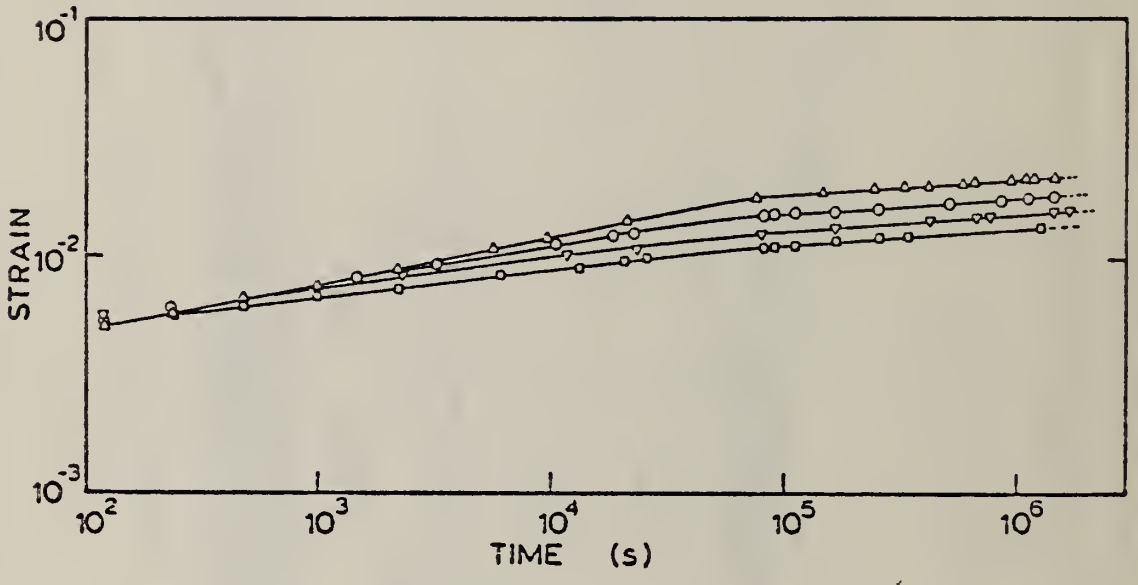


Figure 23. Room temperature uniaxial creep behavior of UHMWPE(the slowly cooled UH-1 polymer) irradiated with various doses of γ-irradiation. Engineering stress 4 MPa. Δ-0 Mrad, O-1.18 Mrad, ∇-3.74 Mrad, and $\square$-6.28 Mrad.

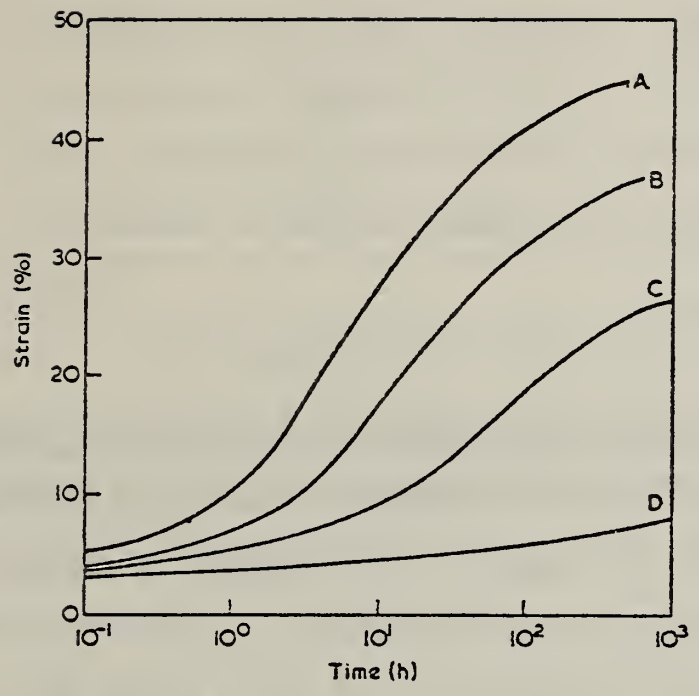


Figure 24. Creep strain (uniaxial extension) versus time for UHMWPE at an engineering stress of 10.3 MPa. A-0Mrad, B-4Mrad, C-16Mrad, and D-64 Mrad. (β radiation) (From reference 15).

Table 5.9.1. Fatigue in Uniaxial Tension of UHMWPE at 23 °C*

	2.5×10^6 cycles in water at a peak stress of 1.03×10^4 kPa		10^7 cycles in serum at a peak stress of 1.72×10^4 kPa	
Specimen	As received	Irradiated**	As received	Irradiated*
Yield Stress ($\times 10^4$ kPa)	2.36	2.47		
Strain	0.15	0.15		
Lower Yield Stress ($\times 10^4$ kPa)	2.22	2.1	2.19	2.05
Strain	0.53	0.67	2.8	3.3

*From reference 16.
**2.5 MPa dose (β-radiation)

5.10 Effect of γ-Irradiation on Environmental Stress-Crack Resistance

The results of tests on the environmental stress-crack resistance (ESCR) of unirradiated UHMWPE at 90 °C and 75 °C were reported in reference [2]. The test method used has been described in references [2] and [17]. During FY 1983 the effect of γ-irradiation on the ESCR of the slowly cooled UH-1 polymer was investigated at 75 °C. The results from these latest tests are presented in Table 5.10.1. The test conditions and specimen preparation (prior to irradiation) were the same as in the previous work where the specimens were tested fully submerged in the stress-cracking agent. The effect of γ-irradiation is in each case one of decreasing the failure time in the presence of the stress-cracking agent. The surprising result is that the specimens irradiated with a dose of 3.74 Mrad failed much sooner than those irradiated with the higher dose of 6.28 Mrad. Two factors may have contributed to the large decrease in failure time observed for the three specimens irradiated with a dose of 3.74 Mrad. Firstly, due to a limited availability of specimens irradiated with the 3.74 Mrad dose, all three specimens had been subjected to prior deformation before the ESCR test,

whereas the specimens irradiated with the higher dose had not. However, the maximum strain to which they were subjected in uniaxial extension was only about 1%. Secondly, the attachment of the extensometer during the creep measurements did cause a slight "nicking" of the surface of the specimen. In order to minimize this effect during the ESCR test the nicked side of the specimen was turned inward to form the inner surface of the bent strip. Examination of the failed specimens under an optical microscope did not reveal any apparent correlation between the position of the failure and the location of the nick. In each case the failure originated on the outer surface and at the center of the strip rather than at an edge. A third possibility is that the ESCR exhibits and minimum at a dose between 0 and 6.28 Mrad.

In reference [2] it was demonstrated that the static fatigue lifetime (lifetime under constant load) represented a lower bound to the cyclic fatigue lifetime. As noted earlier, Nusbaum and Rose [16] concluded that, there cyclic loading is concerned, irradiation may aggravate creep under certain conditions. In view of the ESCR results observed here it would appear to be important to investigate more closely the influence of small doses of γ-irradiation on the fatigue life of UHMWPE.

Table 5.10.1

Stress-Crack Resistance of γ-Irradiated UHMWPE[(a)] at 75°C

Dose (Mrad)	Mean Failure time (Hrs.)	Shortest Failure time (Hrs.)	Longest Failure time (Hrs.)
0	733 (b)	625	911
3.74	117 (c)	110	120
6.28	323 (d)	247	473

(a) Slowly cooled UH-1 polymer
(b) Average for five specimens
(c) Average for three specimens
(d) Average for eight specimens

6. Summary

During FY 1983 work done under Task 80-01 dealt principally with the following aspects of the mechanical behavior of UHMWPE:

1. The temperature dependence of the creep and recovery behavior in uniaxial extension and uniaxial compression at small deformations.
2. The longer term (> 1 day) creep and recovery behavior in uniaxial extension and uniaxial compression at small deformations.
3. The effect of γ-irradiation on the creep and recovery behavior.
4. The effect of γ-irradiation on the environmental stress-crack resistance of UHMWPE.

All of the experiments described in this report which were carried out in our own laboratory were done on specimens of the UHMWPE polymer identified in the previous reports as slowly cooled UH-1 ($M_w \simeq 4 \times 10^6$, density = 0.935 g/cm^3).

The short time creep behavior ($\leq 10^3$ seconds) has been studied in both uniaxial extension and uniaxial compression for a range of applied engineering stresses from 2.5 to 15.6MPa. At stress levels of 8MPa and below no significant difference in behavior is observed between extension and compression. However, at higher levels of stress, where at times approaching 10^3 seconds the true stress becomes significantly different in the two cases, deviations in the creep behavior do occur.

The temperature dependence of the short time creep and recovery has also been studied at temperatures ranging from 23 to 47°C. Most of the experiments were done in uniaxial extension at a stress of 4MPa. With respect to conditions which may pertain to the clinical environment, it is observed that the creep curve for 23°C and 4MPa is roughly equivalent to that at 38°C and 2.5MPa. It is found that the nonrecoverable component of the creep, or

"plasticity," which was described in detail in reference [3], at the higher temperatures can still be represented by the relation:

$$\phi(\hat{g}(\sigma)t_1) = g(\sigma)t_1^{\alpha}.$$

However, the exponent α is found to decrease with increasing temperature, changing from 0.333 at 23°C, to 0.271 at 38°C, to 0.225 at 47°C.

Investigation of the creep behavior at longer times in both uniaxial extension and uniaxial compression reveals that at times longer than about 1 day (at 23°C) a break occurs in the creep curve beyond which the creep proceeds more slowly and on log-log coordinates can be represented by a straight line having a slope of about 0.06. The slope of this portion of the creep curve is found to be independent of either the temperature or applied stress, at least within the temperature and stress range for which the long time experiments were carried out. Further examination of the "break point" indicates that it moves to shorter times as either the applied stress or temperature is increased. Study of the creep and recovery behavior for creep times up to 405 hours show that beyond the break point the plasticity term $\phi(\hat{g}(\sigma)t_1)$ approaches a constant value and no longer obeys the relation $g(\sigma)t_1^{\alpha}$.

The effect of γ irradiation on the performance of UHMWPE has also been investigated. In addition to sterilization, high energy radiation also causes crosslinking and/or degradation which can alter the mechanical behavior and other properties of the polymer. At doses in the range used for sterilization (2-4 Mrad) the density is found to increase and there is some evidence that the melting point may also be increased. Furthermore, both the tensile yield stress and tensile modulus increase with increased dose, whereas the tensile

yield point elongation and impact strength decrease. Exposure to high energy radiation improves the resistance of UHMWPE to creep, even at relatively small doses. Both short term and long term creep experiments indicate that the amount of creep is reduced, even for a dose as small as 1.18 Mrad (σ = 4MPa). At larger stress levels (10.3 MPa) a significant reduction in the creep is observed for doses of 4 Mrad and greater. There are only very limited data on the effect of high energy radiation of the fatigue behavior of UHMWPE. The available data do suggest that where cyclic loading is concerned, radiation may result in a greater amount of creep under certain conditions.

Finally, the effect of γ-irradiation on the environmental stress-crack resistance of UHMWPE has been investigated. Tests carried out on specimens irradiated with doses of 0, 3.74, and 6.28 Mrad indicate that a significant decrease in ESCR occurs as a result of γ-irradiation, however, the results are surprising in that the specimens irradiated with the lesser dose failed much sooner than those irradiated at the greater dose. It is not clear at this point whether the observed behavior resulted from the fact that the three specimens tested which were irradiated at 3.74 Mrad had been subjected to small deformations in uniaxial extension prior to testing, or whether the ESCR goes through a minimum in the dose range between 0 and 6.28 Mrad.

It has been demonstrated that the static fatigue lifetime (lifetime under constant load) represented a lower bound to the cyclic fatigue lifetime. Also, Nusbaum and Rose [16] concluded that, where cyclic loading is concerned, irradiation may aggravate creep under certain conditions. In view of the ESCR results observed here it would appear to be important to investigate in much greater detail the influence of small doses of γ-irradiation on the fatique life of UHMWPE.

References

[1] G. B. McKenna, F. Khoury, and J. M. Crissman, "Relationship Between Morphology and Mechanical Properties of Ultra High Molecular Weight Polyethylene," First Annual Report to the Food and Drug Administration (FDA), Bureau of Medical Devices (BMD), under Task 80-01, NBS-BMD Interagency Agreement, October, 1980 (NBSIR-2209 FDA).

[2] J. M. Crissman, F. Khoury, and G. B. McKenna, "Relationship Between Morphology and Mechanical Properties of Ultra High Molecular Weight Polyethylene," Second Annual Report to the FDA, Bureau of Medical Devices (BMD), under Task 80-01, NBS-BMD Interagency Agreement, December, 1981 (NBSIR 82-2493 FDA).

[3] J. M. Crissman, L. J. Zapas, and F. Khoury, "Relationship Between Morphology and Mechanical Properties of Ultra High Molecular Weight Polyethylene," Third Annual Report to the FDA, Bureau of Medical Devices (BMD), under Task 80-01, NBS-BMD Interagency Agreement, March, 1983 (NBSIR 83-2696 FDA).

[4] S. Turner, Poly. Eng. & Sci., 6, 306 (1966).

[5] D. R. Moore and S. Turner, Plastics & Polymers, 42, 41 (1974).

[6] A. Charlesby, Atomic Radiation and Polymers, Pergamon, New York, 1960.

[7] F. A. Makhlis, Radiation Physics and Chemistry of Macromolecules, Wiley, New York, 1975.

[8] M. Dole, Polym. Plast. Technol. Eng., 13, 41 (1979).

[9] S. K. Bhateja, E. H. Andrews, and R. J. Young, J. Polym. Sci., 21, Polymer Physics Edition, 523 (1983).

[10] E. H. Andrews and I. G. Voigt-Martin, Proc. R. Soc. London Ser. A, 327, 251 (1972).

[11] R. Nagaeawa and K. Kobayashi, J. Appl. Phys., 41, 4276 (1970).

[12] R. J. Roe, E. S. Grood, R. S. Shastri, C. A. Gosselin, and F. R. Noyes, J. Biomed. Mat. Res., 15, 209 (1981).

[13] S. K. Bhateja, Polymer Commun., 23, 645 (1982).

[14] T. A. du Plessis, C. J. Grobbelaar, and F. Marais, Radiat. Phys. Chem., 9, 647 (1977).

[15] S. K. Bhateja and E. H. Andrews, Polymer, 24, 160 (1983).

[16] N. J. Nusbaum and R. M. Rose, J. Biomed. Mater. Res., 13, 557 (1979).

[17] J. M. Crissman, J. Testing and evaluation, JTEVA, 11, No. 4, 273 (1983).

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11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

This report describes work done during FY 1983 under task 80-01, NBS-FDA/BMD (Bureau of Medical Devices) Interagency Agreement. The report covers the fourth year of a four year project concerned with the study of the morphology and mechanical properties of ultra high molecular weight polyethylene (UHMWPE). The work done during FY 1983 dealt principally with the following aspects of the mechanical behavior of UHMWPE, (1) the temperature dependence of the creep and recovery behavior of uniaxial extension and compression at small deformations, (2) longer term (>1 day) creep and recovery behavior of uniaxial extension and compression at small deformations, (3) the effect of γ-irradiation on the creep and recovery behavior, and (4) the effect of γ-irradiation on the environmental stress-crack resistance of UHMWPE.

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Creep; gamma irradiation; polyethylene; recovery; ultra high molecular weight.

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