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Relationship Between Morphology and Mechanical Properties of Ultra High Molecular Weight Polyethylene

Second Annual Report for the Period
October 1, 1980 - September 30, 1981

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

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RELATIONSHIP BETWEEN MORPHOLOGY AND MECHANICAL PROPERTIES OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE

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Abstract

This report describes work done during FY 1981 under task 80-01, NBS-FDA/BMD (Bureau of Medical Devices) Interagency Agreement. The report covers the second year of a four year project concerned with the relationship between morphology and mechanical properties of ultra high molecular weight polyethylene (UHMWPE). Various aspects of the UHMWPE being investigated include (1) the establishment of procedures for compression molding (under vacuum) sheets and cylinders of the polymer, (2) the influence of thermal history and molecular weight on the time dependent mechanical behavior such as creep and stress relaxation in both uniaxial extension and compression, (3) dynamic fatigue under conditions of zero-tension sinusoidal loading, (4) environmental stress-crack resistance, and (5) the optical and electron microscopy of sheets of the UHMWPE which have been deformed to varying degrees in uniaxial extension.

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I. Introduction

This report describes work done during FY 1981 under task 80-01, NBS-BMD (Bureau of Medical Devices) Interagency Agreement. The work plan followed was basically that outlined on pages 34 and 35 of the First Annual Report [1].[†] In addition, we have examined various aspects of components of a number of commercially manufactured orthopedic prostheses obtained for our study by the Bureau of Medical Devices. These devices were acetabular cups and tibial plateaux of various sizes and designs.

The work described in reference [1] was directed primarily toward two areas of study. One was concerned with the establishment of procedures for compression molding sheets of ultra high molecular weight polyethylene (UHMWPE) suitable for mechanical behavior studies. As part of that phase of the work three aspects of the raw polymer were examined, its morphological characteristics, its melting behavior, and its crystallinity. The morphology of the molded sheets was also examined. As a consequence of its very high melt viscosity, an important feature of the UHMWPE is that both molded and machined prosthesis components made from it retain a memory of the particulate nature of the raw polymer.

The second principal area of study involved the characterization of the mechanical behavior of compression molded sheets prepared under varied thermal histories. Experiments in creep and stress relaxation in uniaxial extension were begun, and failure studies under both static and sinusoidal loading conditions were initiated. In addition, aspects of the deformation and recovery of molded sheets subjected to uniaxial stretching were examined.

The work described in reference [1] was carried out on two different lots of UHMWPE obtained from the same manufacturer. The two polymers were

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[†] Numbers in brackets indicate references found at the end of this report.

identified as UH-A and UH-B. Both had the same manufacturer specified intrinsic viscosity of ≈25 dl/g which corresponds to a molecular weight of approximately 4×10^{6}*. Since the two polymers were found to be so similar in behavior no future work is planned for material UH-B. However during FY 1981 we have extended our studies to a third UHMWPE obtained from the same manufacturer. This material, which we shall identify as UH-C, has a manufacturer specified intrinsic viscosity of ≈18 dl/g which corresponds to a molecular weight of approximately 2×10^{6}.

2. Polymer Morphology

2.1 Aspects of the Density (ρ) and Crystallinity (χ)† of Compression Molded UHMWPE.

Among the features which are currently being investigated in connection with the characterization of the dependence of the mechanical behavior of the polymer on the structure and morphology of UHMWPE, is the determination of the range of crystallinities which can be achieved in compression molded samples of UHMWPE made from the two batches of raw polymer whose limiting viscosity numbers are 25 dl/g and 18 dl/g respectively.

As indicated in the First Annual Report [1] the density of sheets made from UH-A when molded at 200°C and cooled slowly to room temperature (~1°C per minute) was in the range 0.934-0.936 g/cm^3 (χ=51%). In order to determine whether appreciably higher crystallinities could be attained in sheets from this batch of raw polymer the effect of annealing in the

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* See reference [1], page 5, for a brief discussion of the intrinsic viscosity - molecular weight relationship in UHMWPE. Reference [2] provides a detailed discussion of this relationship.

† Wt.% crystallinity.

the range 125°C on the density of slowly cooled samples has since been examined. The results, which are summarized in Table 1, show that the maximum density which could be attained even after successive annealings at 130°C (48 hrs.) and 135°C (96 hrs.) was only 0.941_6 g/cm^3 (χ=63.4%).

Table 1

Effect of Annealing* on the Density (ρ) and Crystallinity (χ) of Slowly Cooled Sheets of Compression Molded UH-A UHMWPE.

Annealing Treatment	Density (ρ) g/cm^3†	Crystallinity (χ) %
(i) Unannealed	0.934_5	58.7
(ii) 125°C (48 hrs.)	0.935_3	59.2
(iii) 125°C (48 hrs.)+130°C (48 hrs.)	0.936_8	60.2
(iv) 125°C (48 hrs.)+130°C (48 hrs.) + 132°C (48 hrs.)	0.939_7	62.1
(v) 130°C (48 hrs.) + 135°C (96 hrs.)	0.941_6	63.4

* Annealing was carried out in N_2 atmosphere
† Measured at 23°C in a water/ethanol density gradient column

Experiments have been started on samples made from the UHMWPE raw polymer having a limiting viscosity number of 18 dl/g (UH-C). Sheets molded at 200°C and cooled slowly to room temperature (~1°C per minute) had a density of 0.941_2 g/cm^3 (χ=63.1%). The density of these samples after they were annealed at 130°C (72 hrs.) and then at 135°C (48 hrs.) was 0.952_7 (χ=70.7%) which is appreciably higher than that of sheets of the higher molecular weight polymer (UH-A) annealed under comparably conditions. On the other hand, quenching the UH-C from the melt resulted in a density at 0.925_0 g/cm^3, a value which was only slightly higher than that for the quenched UH-A. The densities of the UH-C samples, prepared under the three different treatments described, are summarized in Table 2.

Table 2

Density (ρ) of Compression Molded Sheets of UH-C UHMWPE Prepared Under Various Thermal Histories.

Treatment	Density (g/cm^3)†	Crystallinity (χ)%
Quenched	0.925_0	52.2
Slowly Cooled	0.941_2	63.1
Annealed at 130°C (72 hours) Followed by 135°C (48 hours)*	0.952_7	70.7

*Annealing was carried out in N_2 Atmosphere

†Measured at 23°C in a water/ethanol density gradient column

In addition to indicating that higher densities can apparently be attained with the lower molecular weight UH-C, which nevertheless still falls under the appellation UHMWPE, the results summarized above provide some initial guidelines for the preparation of sheets of UHMWPE of different molecular weights but which have the same density and crystallinity. Comparison of the mechanical properties of such sheets should provide insights into the influence of molecular weight on the time dependent mechanical behavior of UHMWPE as distinct from the effects of crystallinity.

In order to determine how the densities of the sheets of UH-A and UH-C compare with those of manufactured prostheses, the densities of ten commercially available unused and sterilized UHMWPE prostheses of different origins have been determined. Most were labeled as having been γ-irradiated for sterlization and the dosage was often specified as 2.5 Mrad minimum. In some cases the dosage was not specified and in others the method of sterilization was not given. Table 3 lists the devices and the sterilization information provided.

Table 3

Summary of UHMWPE Commercial Prosthesis Components

Specimen Designation	Device Type	Method of Sterilization
1-A	Acetabular Cup, 57mm O.D.	Unknown
1-B	Acetabular Cup, 45mm O.D.	Unknown
2-C	Acetabular Cup, 42mm O.D.	γ-ray, 2.5 Mrad minimum
2-D	Acetabular Cup, 58mm O.D.	γ-ray, unknown dosage
2-E	Tibial Plateau, Reg.,thick	γ-ray, 2.5 Mrad.minimum
2-F	Tibial Plateau, Small	γ-ray, unknown dosage
3-G	Tibial Plateau, Large	γ-ray, 2.5 Mrad.
3-H	Tibial Plateau, Small	γ-ray, 2.5 Mrad.
4-I	Tibial Plateau, Large	Unknown
4-J	Acetabular Cup, 45mm O.D.	Unknown

In each case density measurements were made on two pieces cut from each prosthesis, one near a portion of the surface and the other from the interior. The results are listed in Table 4. With the exception of the pieces of specimen 2-E, in which case the difference in density between the two pieces was ~.009 g/cm^3, the differences in density between the two pieces of the other prostheses were less than 0.003 g/cm^3. There were however substantial differences in density among the prostheses whose densities ranged from 0.923_5 (Specimen A) to 0.952_8 g/cm^3 (outer piece of Specimen E). These values correspond respectively to that of the quenched sheets of UH-A polymer and that of the slow cooled sheet of UH-C annealed successively at 130°C and 135°C (see above). In short, the densities of our laboratory prepared sheets are certainly comparable to those of implants used in the field. It should be borne in mind however that the implants were subject to sterilization by irradiation, a treatment which may have affected their densities [3,4].

Table 4

Density of Commercial Prostheses

Specimen	Density* (ρ) g/cm^3 Surface, Interior	Crystallinity (χ) % Surface, Interior
1-A Acetabular Cup	0.923_5, 0.923_5	51.2, 51.2
1-B Acetabular Cup	0.934_3, 0.934_3	58.5, 58.5
2-C Acetabular Cup	0.935_2, 0.934_8	59.1, 58.9
2-D Acetabular Cup	0.935_0, 0.937_5	59.0, 60.7
2-E Tibial Plateau	0.952_8, 0.944_0	70.7, 65.0
2-F Tibial Plateau	0.950_5, 0.948_2	69.3, 67.8
3-G Tibial Plateau	0.937_7, 0.936_7	60.8, 60.1
3-H Tibial Plateau	0.936_0, 0.937_1	59.7, 60.4
4-I Tibial Plateau	0.945_8, 0.944_8	66.2, 65.5
4-J Acetabular Cup	0.942_9, 0.942_9	64.3, 64.3

* Measured at 23°C in a water/ethanol density gradient column.

Experiments have also been started on the preparation and characterization of cylindrical specimens produced for use in compression tests. The following procedure was established for vacuum molding of cylinders having a length of 2.54 cm and diameter of 1.27 cm.

1. The UHMWPE powder is initially compacted in the mold at room temperature using an arbor press.
2. The mold is placed in a platten press with light contact pressure, the heat turned on, and vacuum applied.

3. The press is heated to 200°C (requires about 45 minutes) and is held at that temperature for ten minutes.
4. The press is then turned off and the light contact pressure released.
5. After the press has cooled for about 30 minutes to ~170°C a platten pressure of approximately 20 MPa is applied.
6. The specimen is then slowly cooled in the mold under pressure to below 90°C before removing the cylinder from the mold. After removal from the mold the ends of the cylinders are ground flat and parallel on a lathe using a high speed grinding wheel.

In order to obtain some measure of material uniformity in the molded cylinders one specimen of the UH-A polymer was sectioned and the density of pieces taken from the interior and surface regions was determined. The densities were 0.934_3 and 0.934_0 g/cm^3 respectively for the two regions, which indicates a high degree of uniformity throughout the specimen. The values were also very close to those determined for the slowly cooled sheets of the UH-A polymer.

We have also investigated the effect of molding cylinders at a much lower temperature. For example, one cylinder was molded using a maximum platten temperature of 165°C and following the same procedures outlined above except for step 5. In this case the pressure was applied immediately after the press was turned off. In Table 5 we compare the density of the complete sample, the density of an annular ring of material, and that of a piece taken from the center of the cylinder. As can be seen, there is a significantly higher density in the core region than at the outer edge. Visual and optical microscopic examination of cross sections of the cylinder revealed that the interior region had a highly granular texture surrounded by a smooth outer skin layer. This was most likely the result of a temperature gradient in the mold, whereby incomplete melting occurred in the center, and the center portion retained a more pronounced "grain memory" than did the surface layer.

Table 5

Density Variation within a Cylinder of UH-A Polymer Slowly Cooled from 165°C

Sample Description	Density,* g/cm^3
Bulk Specimen (Disc 2mm thick)	0.949
Outer Surface (2 mm thick annular ring)	0.940
Central Core (6.5 mm dia.plug, 2mm thick)	0.957

* Determined by hydrostatic weighing.

2.2 Uniaxial Stretching of UHMWPE

An aspect of the behavior of compression molded samples of UHMWPE which is of interest in the context of implant performance is their recovery from imposed strains below the breaking strain. Some preliminary results carried out on slowly cooled samples of UH-A which had been stretched at 37°C have been previously reported [1]. Data have since been obtained for slowly cooled UH-A samples which were stretched at 23°C and for slowly cooled samples of the lower molecular weight UH-C samples which were stretched at 23°C and 37°C. The imposed strains and corresponding residual strains after the samples were released and stored at room temperature for twenty-four hours are listed in Table 6. The specimens used in these experiments were dumbbell shaped having a length in the gauge section of 1.3 cm, a width of 0.32 cm and a thickness of ~0.1 cm. They were stretched uniaxially at a constant rate of clamp separation (1 cm/min.) corresponding to a specimen strain rate of ~0.02/min. The densities of the UH-A and UH-C samples were 0.935 and 0.941 g/cm^2 respectively.

As was the case for the UH-A samples stretched at 37°C [1] no necking was observed during the stretching of the specimens in the present experiments. This contrasts with lower molecular weight linear polyethylene ($M_w \simeq 190{,}000$) which, under similar stretching conditions, undergo necking at strains >0.2-0.3. As can be seen from Table 6 both the UH-A and UH-C samples exhibited considerable recovery from deformation from the various strain levels imposed upon them. This latter behavior distinguishes UHMWPE from lower molecular weight polyethylenes in which recovery from straining is minimal if necking occurs unless the specimen is heated to a temperature near the melting point. It may be noted in this connection that the UH-A and UH-C samples stretched at 23°C and 37°C to strains of up to 2.00 contract in length, after being released and stored for 24 hours at room temperature, by close to or more than half the initial strain. The data in Table 6 also indicate that the fractional strain recovery (relative to the imposed strain) which the samples undergo is larger the smaller the imposed strain. The measurements reported in Table 6 are the results of single tests at each strain, we shall therefore not attempt any comparisons between the behavior of the UH-A and UH-C samples or between the effects of temperature on both types of samples at this stage, except to point out that the residual strains in samples subjected to initial strains in the range 0.25-0.50 are about twice as large in the UH-C samples as compared to the UH-A samples.

Table 6

Residual Strain in Samples Stretched Uniaxially at 23°C and 37°C after Unloading and Storage at Room Temperature for 24 hrs.

	Residual Strain			
Stretching Temperature	23°C		37°C	
	UH-A	UH-C	UH-A*	UH-C
Imposed Strain				
0.25	0.05	0.10	0.06	0.11
0.50	0.12	0.20	0.12	0.24
1.00	0.31	0.45	0.34	-
1.50	0.46	-	0.55	-
2.00	0.84	0.90	0.92	1.09
2.50	1.32	-	-	-
3.00	1.72	1.92	1.84**	1.86
3.50	-	-	2.45	-
4.00	-	-	2.80	2.98

* See Reference 1.

**We have previously reported a value of 1.15 [1] which, for reasons which remain obscure, was much lower than expected when compared with the residual strains obtained with the samples subjected to lower and higher strains than 3.00. This new measurement is consistent with the data corresponding to these other strains.

The changes in crystalline orientation corresponding to increasing residual strains in UH-A samples stretched at 37°C were described in a previous report [1]. The wide angle X-ray diffraction patterns exhibited by four samples of UH-C which had also been initially stretched at 37°C are shown in Fig.1(a-d). The imposed strains were 0.50, 2.00, 3.00 and 4.00. The corresponding residual strains (Table 6) after storage at room temperature for 24 hrs. were 0.24, 1.09, 1.86 and 2.98 respectively. It should be noted that the residual strains in the samples after six weeks storage, toward the end of which period the diffraction patterns were recorded, had decreased to 0.20, 0.84, 1.75 and 2.92. Accordingly the latter figures will be referred to in identifying these samples in what ensues.

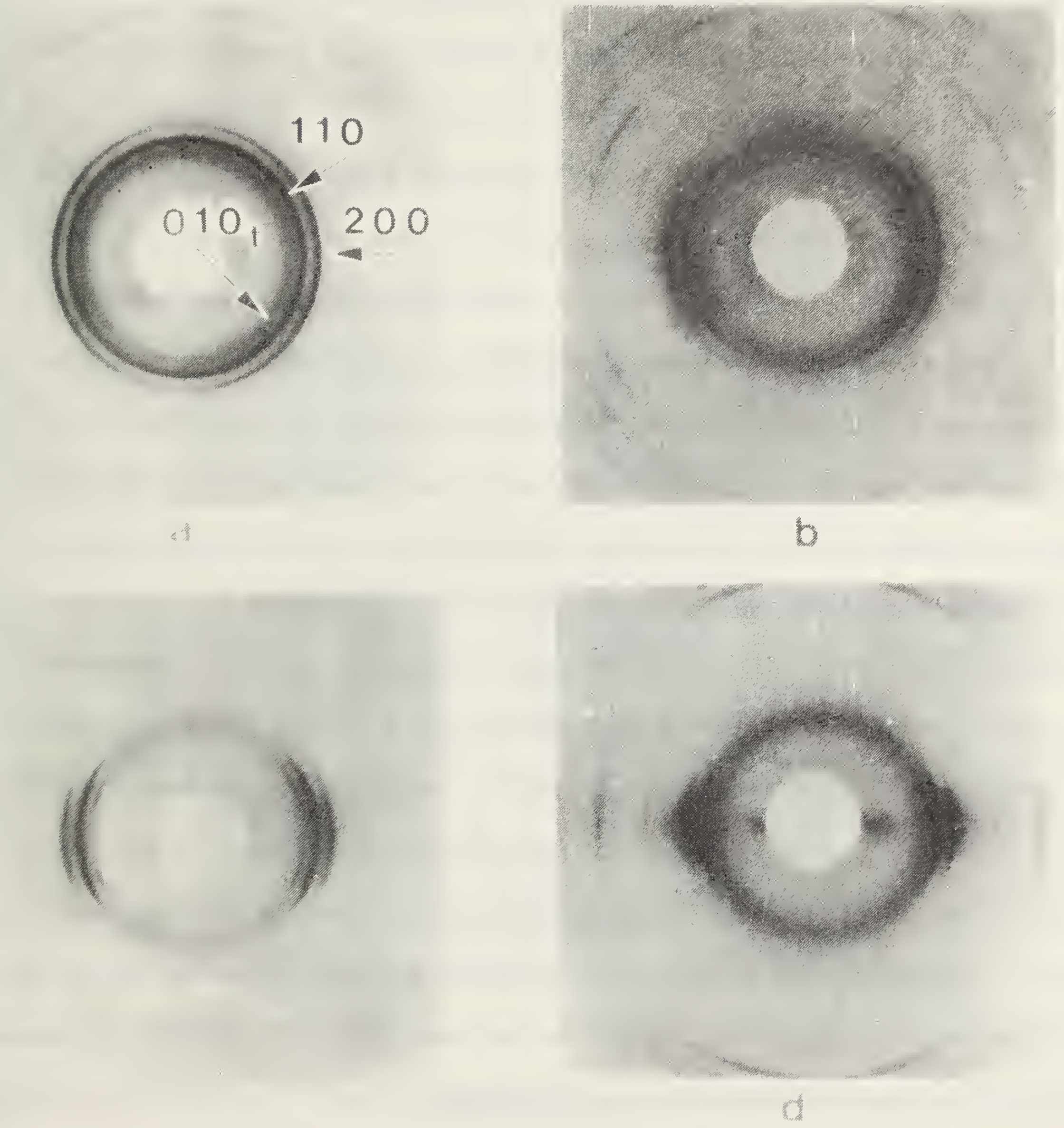


Fig. 1. Wide angle x-ray diffraction patterns showing the changes in orientation of the orthorhombic 110 and 200 reflections and the triclinic 010_t reflection exhibited by specimens of slow cooled UH-C sheets which had been stretched at 310K (37°C) to strains of (a) 0.5, (b) 2.0, (c) 3.0, and (d) 4.0, and then released and stored at room temperature. The residual strains after storage for 24 hours were 0.24, 1.09, 1.86 and 2.98 respectively. The corresponding residual strains after six weeks (at the end of which period these diffraction patterns were recorded) had decreased to 0.20, 0.84, 1.75, and 2.92.

The wide angle X-ray diffraction pattern of the unstrained UH-C was similar to that of the UH-A[1]. The progressive changes in the diffraction patterns with increasing residual strain illustrated in Fig.1 were also similar in character to those found previously in the case of the UH-A samples [1]. As the residual strain increases there is a progressive increase in the intensity of the orthorhombic 200 reflections in the equatorial region and a corresponding diminution of the azimuthal spread of the arcs which are centered about the equator. Simultaneously the orthorhombic 110 reflections become broadly split with the most intense portions of the arcs tending to be closer to the equatorial direction with increasing residual strain. The split 110 reflections eventually merge on the equator in the sample having a residual strain 2.92 (Fig. 1d). In addition to the features described above, and paralleling the case of the UH-A samples [1] the diffraction patterns of the stretched UH-C samples also exhibited reflections associated with the metastable triclinic [5] form of polyethylene. The most intense of these reflections can be seen in each of the patterns shown in Fig. 1 in which they are identified as 010_t (indexing according to Turner-Jones [5]). The changes in the azimuthal dispositions of these arcs with increasing residual strain paralleled very closely those of the orthorhombic 110 arcs. The 010_t arcs are situated at the equator in the sample having a residual strain of 2.92 (Fig. 1d).

We are in the process of recording the small angle X-ray diffraction characteristics of the same samples in order to compare them with those previously obtained from the UH-A samples [1]. It can be reasonably anticipated that the results will be similar to those found in the case of the UH-A samples.

In addition to the experiments described above we have started to examine in more detail the fine structure of sheets of UH-A and UH-C which had different residual strains. Examination of the surfaces of samples subjected to initial strains in the range 1.0-3.0 under the optical microscope and in a scanning electron microscope indicated that stretching did not occur uniformly throughout the samples and, correspondingly, that the residual strain was not uniform throughout the released samples.

The manifestation of non-uniform deformation was evidenced in particular in scanning electron micrographs of the surfaces of the samples by the occurrence of regions (valleys) which exhibit an apparent "fibrillar" appearance with the 'fibrils' oriented parallel to the stretching direction. These regions of higher deformation [see eg. marker X in Fig.2] are interspersed between regions (hills) of lower deformation which exhibit no evident fibrillar character (see e.g. Y in Fig. 2). This apparent non-uniformity in the distribution of the deformation in the sheets is on a scale (~tens of microns) which suggests it might be associated with the memory of the coarse grain-like character of the raw polymer particles which is retained in the compression molded sheets [1]. It is tempting to speculate that deformation of the polymer is initiated preferentially at the boundaries between the fused raw polymer particles. This possibility will be investigated further.

3. Mechanical Behavior Studies

The mechanical behavior studies described in the First Annual Report [1] dealt primarily with the characterization of the UH-A material in uniaxial extension. During FY 1981 this work was continued and now includes preliminary results for simple compression. Also, as we noted earlier our study has been expanded to include the UHMWPE (UH-C) material which has a lower molecular weight.

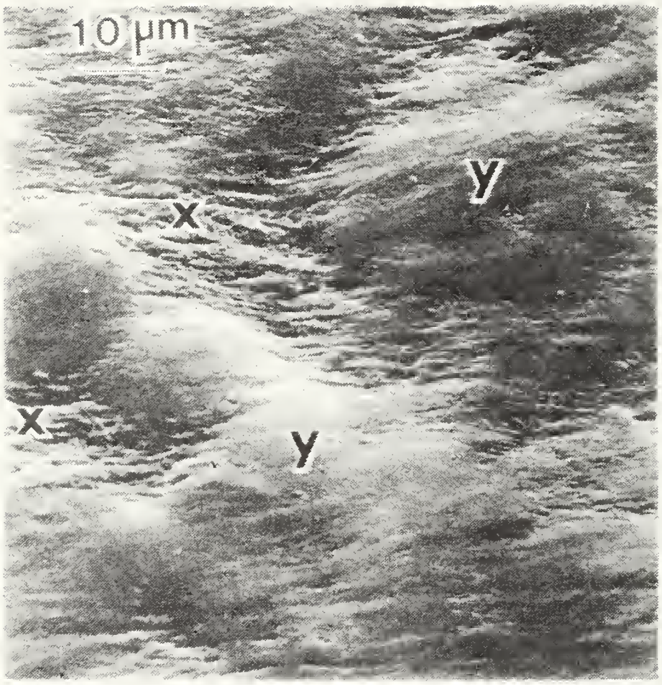


Fig.2. Scanning electron micrograph of a portion of the surface of an UHMWPE sheet which was stretched at $37^{\circ}C$ to a strain of 2 and then released and stored at room temperature. (Residual strain after 24 hrs., 0.92, stretching direction horizontal). Note apparent 'fibrillar' appearance of regions (x), and the absence of this feature in regions (y). See text.

As will be seen in what follows distinct differences were observed between the mechanical behavior of the UH-A and UH-C samples.

3.1 Creep and Stress Relaxation in Uniaxial Extension

Uniaxial creep data are shown in Figure 3 on log-log coordinates for the slowly cooled UH-A, the polymer having the higher molecular weight. The data cover times up to about one year. At the present time only the specimen having an applied stress of 27.5 MPa has failed (by fracture) as is indicated by the arrow in the diagram. Unlike lower molecular weight polyethylenes, these samples of UHMWPE did not exhibit the phenomenon of necking and cold-drawing, but rather extended homogeneously (on a gross scale) to a maximum stretch of approximately $\varepsilon=5$. In the case of the annealed UH-A (data not shown), two specimens tested at loads of 27.5 and 9 MPa showed essentially the same creep behavior as the slowly cooled material under the same loads. The one difference that did occur was that the annealed specimen loaded at 27.5 MPa failed at about one decade in time sooner than did the slowly cooled material.

By way of further comparison, creep curves for the quenched UH-A are presented in Figure 4. This material is more compliant than the slowly cooled UH-A, as is evidenced by the fact that the time taken to reach a strain of unity for the quenched sample is about one tenth that for the slowly cooled sample. However the maximum elongation obtained for the quenched UH-A ($\varepsilon \simeq 5$) is still essentially the same as that for the slowly cooled or annealed materials. A most interesting feature of the creep behavior was exhibited by the quenched polymer under a load of 9MPa. At the early times the creep rate was nearly constant. After about one day the creep rate decreased and the creep curve appeared to be

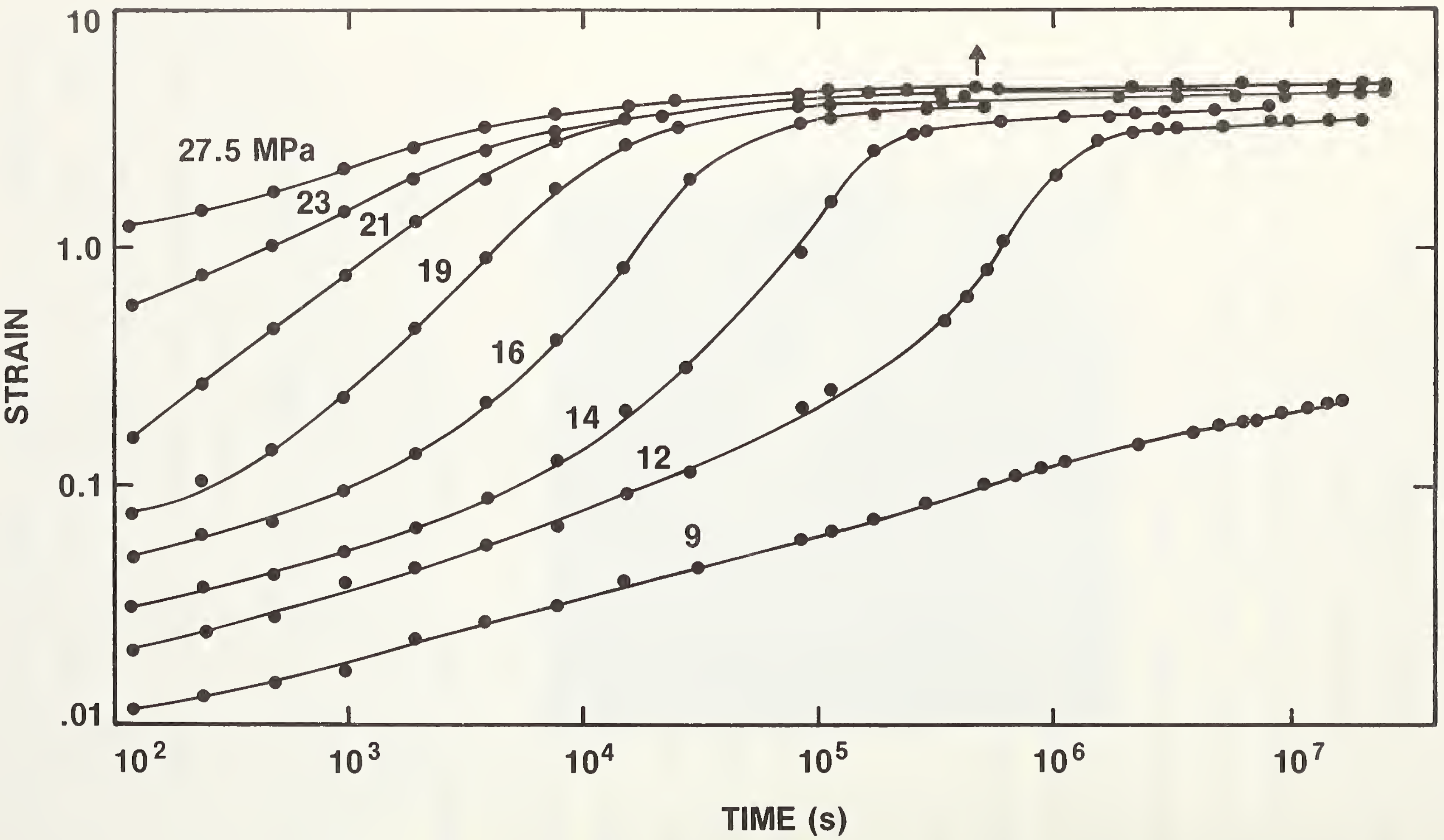


Figure 3. Creep strain versus time for the slowly cooled UH-A. The numbers indicate the magnitude of the applied engineering stress and the arrow the time at fracture for the specimen loaded at 27.5 MPa.

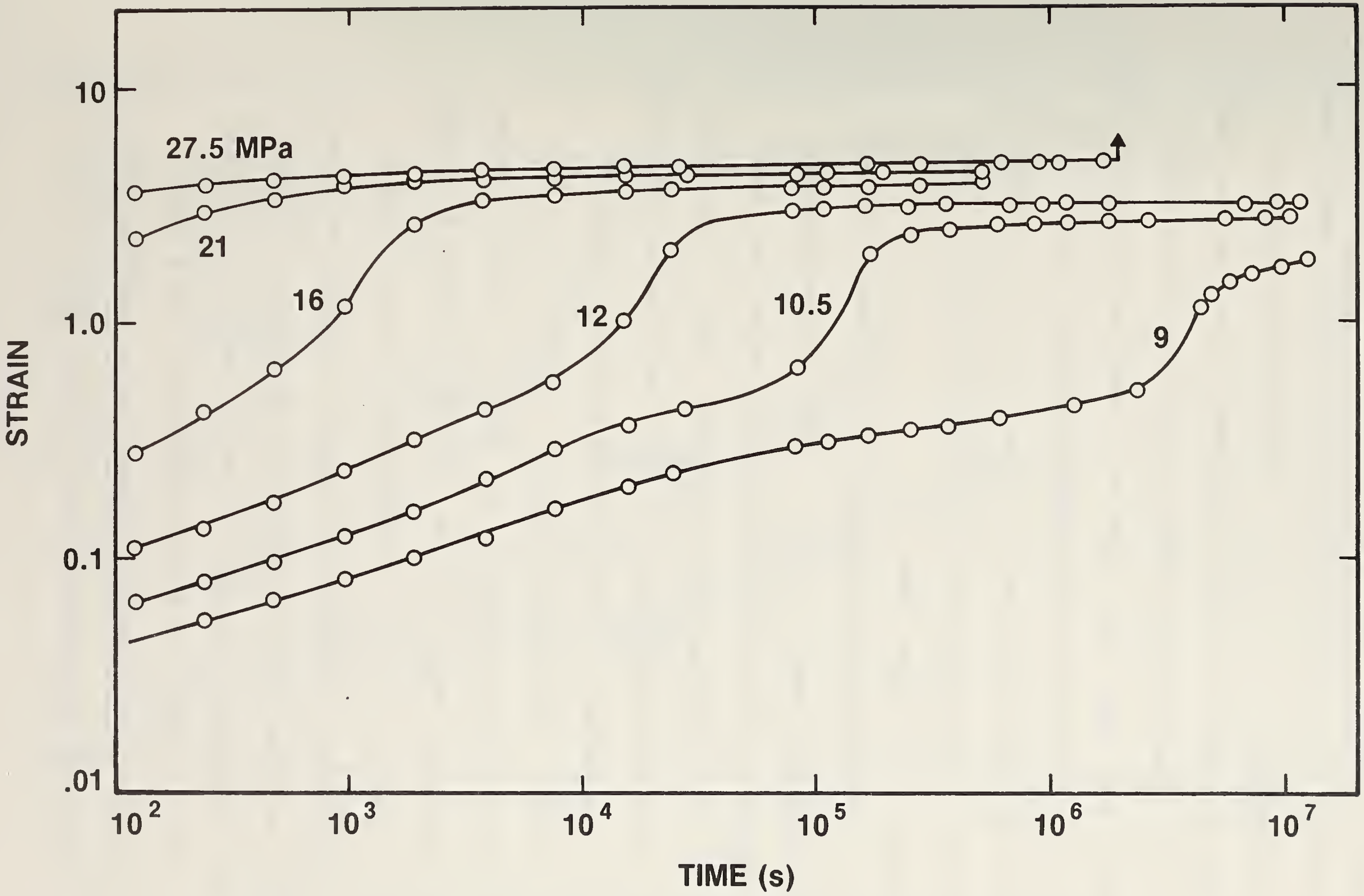


Figure 4. Creep strain versus time for the quenched UH-A. The numbers indicate the magnitude of the applied engineering stress and the arrow the time at fracture for the specimen loaded at 27.5 MPa.

tending toward a plateau. However, after about one month, a sharp increase occurred in the creep rate before again reaching a new plateau. If the same phenomenon were to occur in the case of the slowly cooled sample under the same load (9 MPa), then because of its lower compliance one would expect that the abrupt change in creep rate would manifest itself after a much longer time. Based on a comparison of the creep data for the quenched and slowly cooled specimens subjected to higher loads, we can speculate that in about one to two more years there may occur a sharp increase in the creep rate of this specimen followed by a new plateau region at even longer times.

Creep curves have also been obtained for the slowly cooled UH-C, and these results are shown in Figure 5. While they are similar in overall appearance to the curves for the slowly cooled UH-A (Figure 3), two distinct differences are worthy of mention. First, at the higher loads ($\geq$ 11 MPa) and in the region of rapid creep (strains in the range 0.2 to 3.0) the maximum creep rate attained is larger for the UH-C than for the UH-A. The second difference in behavior is that the creep curves for the UH-C show less of a tendency to reach a plateau value at the highest levels of strain. The UH-C continues to elongate to an ε as large as 7 or more, in contrast with $\varepsilon \simeq 5$ for the UH-A.

In Figures 6 and 7 are shown the results of single step stress-relaxation experiments done on specimens of the slowly cooled UH-A and UH-C. The same data are replotted as isochrones of true stress versus strain in Figure 8 on log-log coordinates. While there is very little difference in behavior between the two materials over most of the strain range examined, both materials exhibit in their

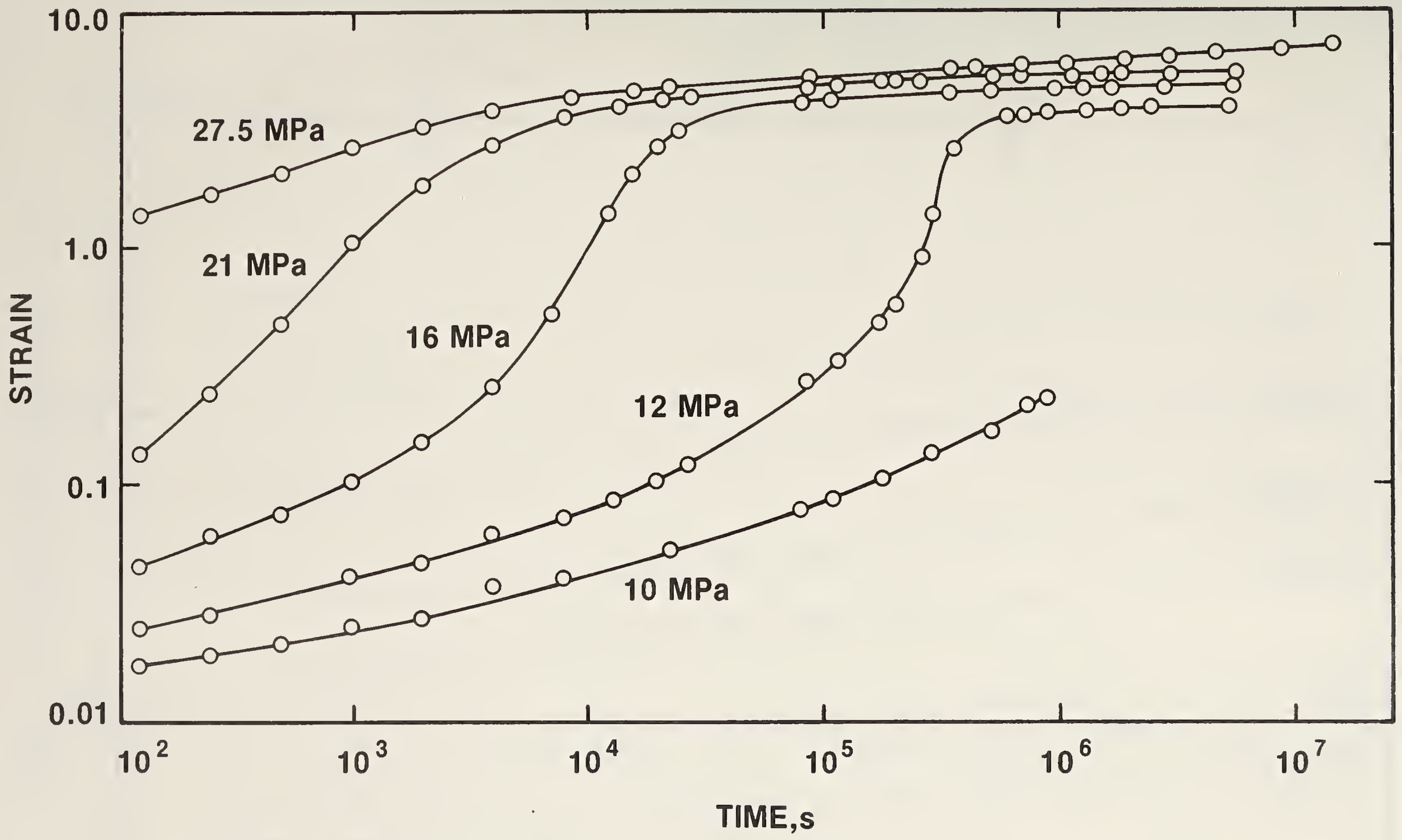


Figure 5. Creep strain versus time for the slowly cooled UH-C. The numbers indicate the magnitude of the applied engineering stress.

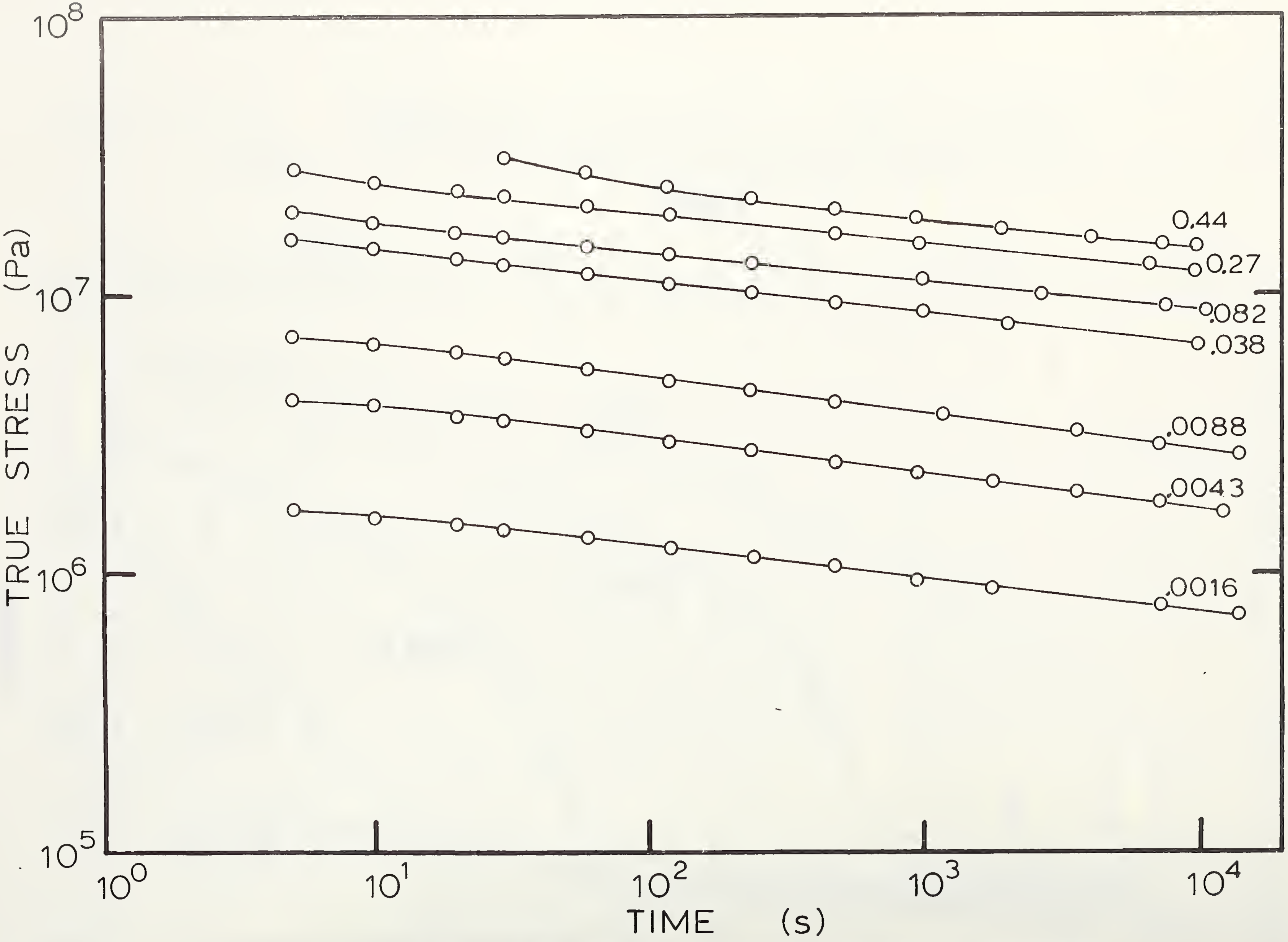


Figure 6. True stress versus time for the slowly cooled UH-A. The data were obtained from single step stress-relaxation experiments in extension and the numbers indicate the magnitude of the applied step in strain.

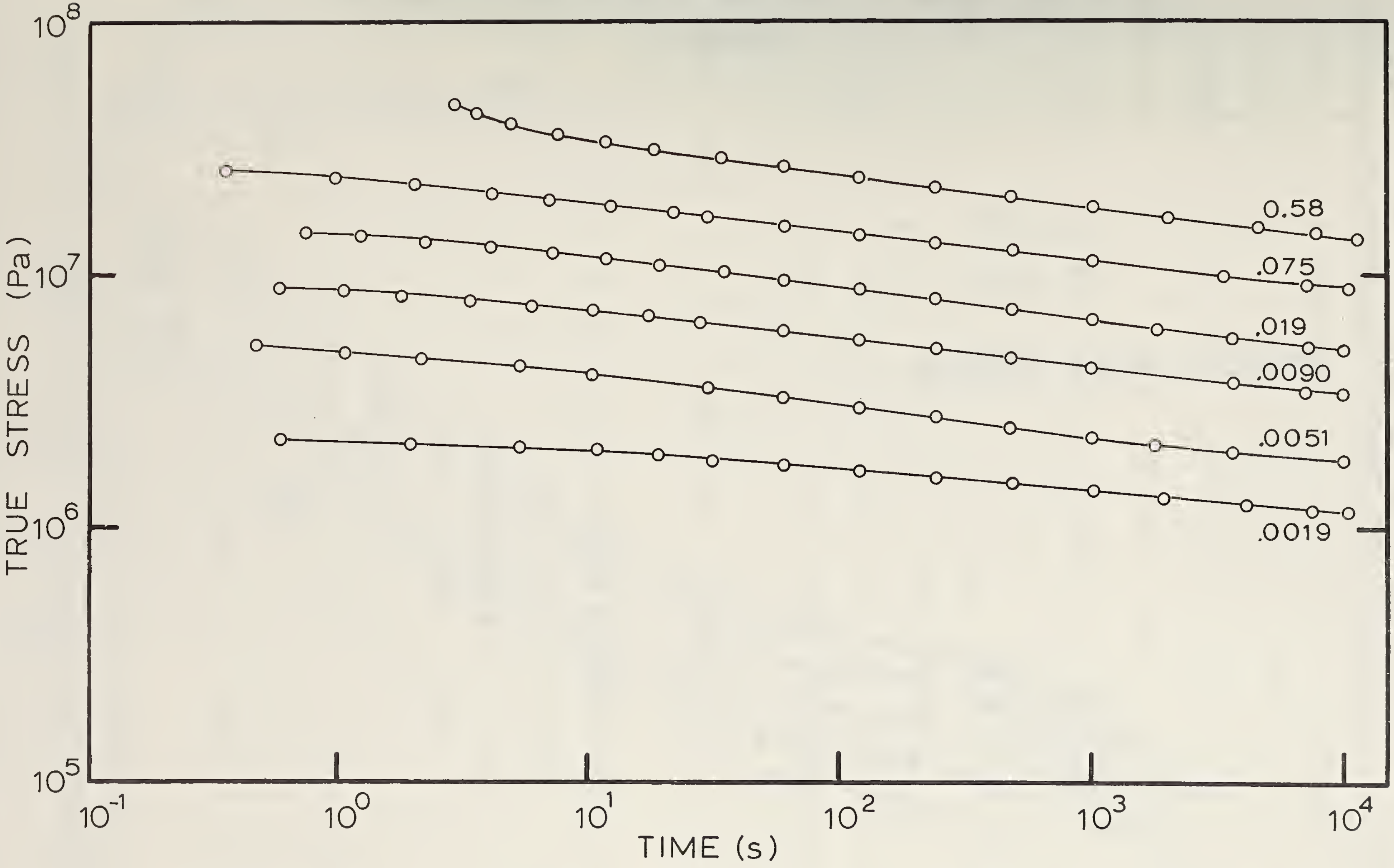


Figure 7. True stress versus time for the slowly cooled UH-C. The data were obtained from single step stress-relaxation experiments in extension and the numbers indicate the magnitude of the applied step in strain.

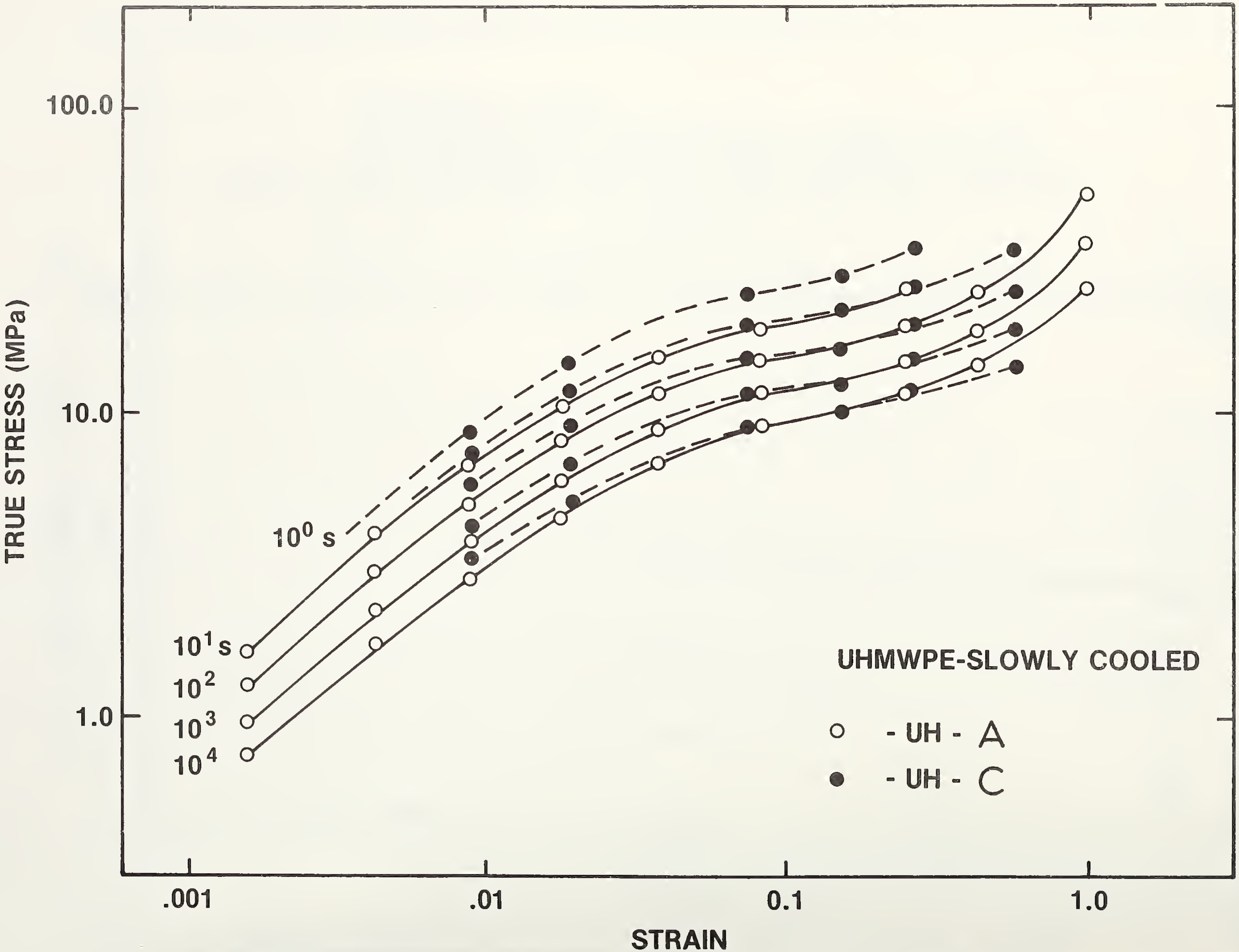


Figure 8. Isochrones of true stress versus strain for samples UH-A and UH-C slowly cooled from the melt (from single step stress-relaxation data). The isochrones are for times of from 10^0 to 10^4 seconds.

behavior at the larger strains (ε>0.08) a departure from that observed for lower molecular weight polyethylenes and many other semicrystalline polymers. In a single step stress-relaxation experiment the specimen is subjected to a sudden step in strain and the stress is monitored as a function of time. For many semicrystalline polymers it is not possible to obtain data in the region of large strain, since at strains larger than about 0.08 to 0.10 the specimen either necks or fractures upon application of the step in strain. Normally on a plot such as that shown in Figure 8 the isochrones tend to flatten as the strain is increased. When the point is reached where the isochrones become flat the material undergoes an instability and necking or fracture results. In the case of the two slowly cooled UHMWPE samples this condition is not reached. Although the isochrones tend to flatten towards a plateau as the strain is increased in the range from 0.01 to 0.10, they do not become flat, but rather continue to rise at higher levels of strain, at least up to a strain of unity.

Quenching of the UH-A polymer produced the stress-strain behavior shown in Figure 9. Qualitatively these curves are similar to those for the two slowly cooled materials. The main differences are that (1) the isochrones for the quenched material show somewhat less of a tendency to flatten in the region of strain from 0.01 to 0.30, and (2), because of lower crystallinity, they are shifted to smaller stresses. For example, at a strain of 0.01 and time of 10 seconds the stress for the quenched UH-A (ρ=0.923 g/cm^3) is smaller by a factor of 1.8 than that for the slowly cooled UH-A (ρ=0.935 g/cm^3).

The effect of annealing on the stress-strain behavior of slow cooled UH-A has been examined and is compared with the unannealed UH-A in Fig. 10. Whereas for the slowly cooled material the isochrones increase at all levels of strain, such is not the case for the annealed

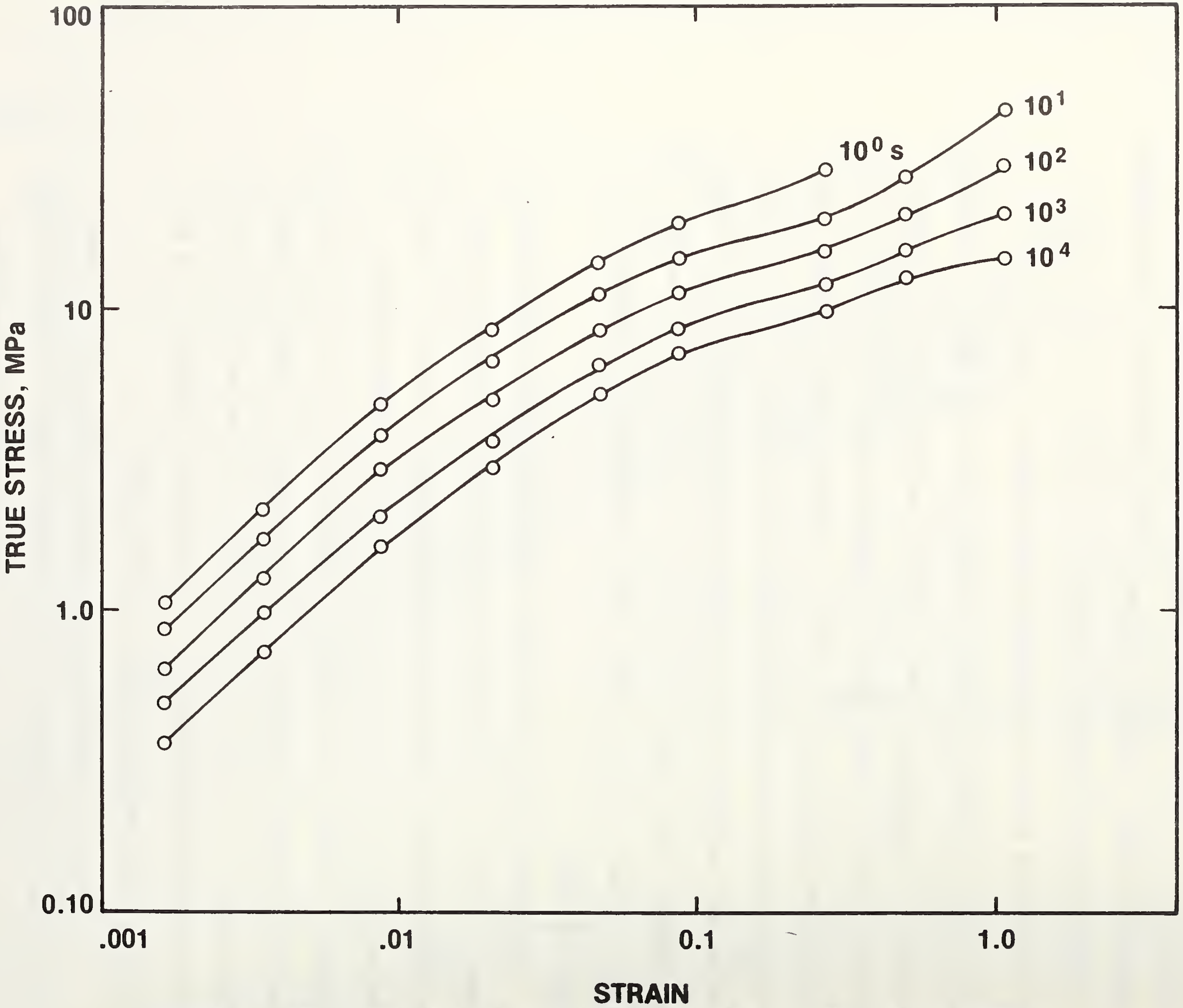


Figure 9. Isochrones of true stress versus strain for the quenched UH-A (from single step stress-relaxation data). The isochrones are for times of from 10^0 to 10^4 seconds.

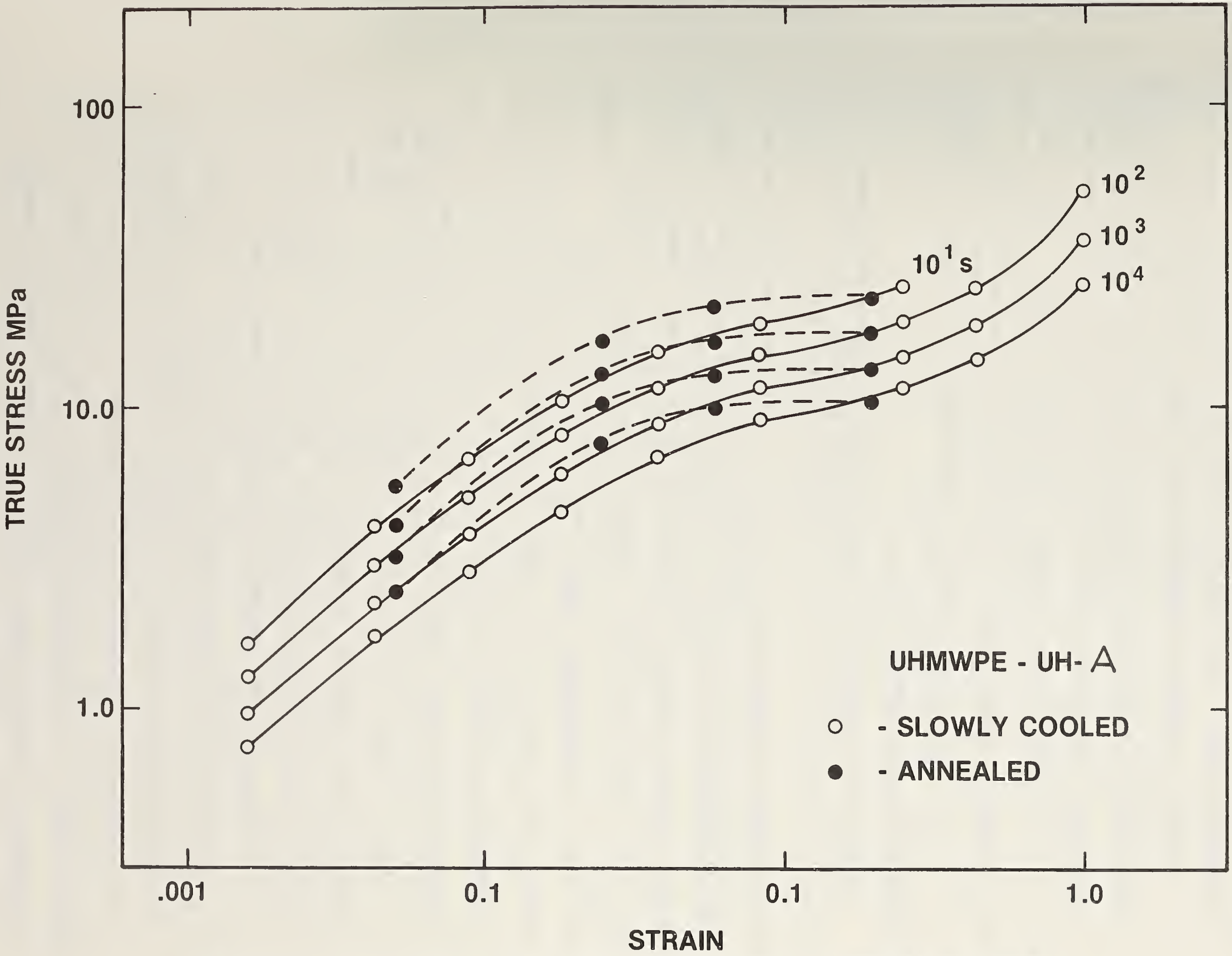


Figure 10. Isochrones of true stress versus strain for samples UH-A slowly cooled from the melt (density=0.934 g/cm^3) and slowly cooled followed by annealing (density=0.942 g/cm^3).

material. During application of the largest step the annealed UH-A necked, and its behavior, shown in Figure 10, is more typical of lower molecular weight polyethylenes. This same result was also found to be true for a specimen of annealed UH-C. Thus, by increasing the crystallinity of the UH-A from that of the slowly cooled state ($\simeq$0.935 g/cm^3) by only about 5% the nature of the stress-strain behavior, as determined from stress-relaxation data, has been significantly altered. Note also that although the slowly cooled UH-C (ρ=0.941 g/cm^3) and annealed UH-A (ρ=0.942 g/cm^3) have approximately the same density, one material exhibits necking whereas the other does not.

We have also carried out creep and stress relaxation experiments on specimens machined from two of the commercial implant devices. The two tibial plateaux labeled 3-G and 4-I were the only ones from which large enough specimens could be machined to fit our stress relaxation apparatus. Material 3-G had a density of $\simeq$0.937 g/cm^3 which is about comparable to that of our slowly cooled UH-A. Sample 4-I had a density of $\simeq$0.945 g/cm^3 which is intermediate between our slowly cooled UH-C and annealed UH-C. The behavior of these two commercial materials can be summarized as follows. Material 3-G showed a creep and stress relaxation behavior very similar to that of the slowly cooled UH-A (see for example Figures 3 and 8). The only exception was that in creep two specimens tested at applied stresses of 25 and 16 MPa failed in times of 6x10^2 and 1.1x10^7 seconds respectively, whereas the two specimens of the slowly cooled UH-A tested at comparable stresses (Figure 3) have not yet failed after more than one year (3.15x10^{7}s). In contrast with the 3G material, material 4-I exhibited a behavior more reminiscent of the annealed UH-A or annealed UH-C (Figure 10). In creep, a specimen under a stress of 16 MPa necked at a strain of about 30% and then fractured in a time less than 1.5x10^{5}s. In stress relaxation necking occurred during the application of a 20% step in strain.

In summary, uniaxial stretching of the UHMWPE, on a microscopic scale, does not occur uniformly throughout the sample. Correspondingly, upon release the residual strain in the sample is not uniform throughout. Examination under the optical microscope and in a scanning electron microscope reveals that there are regions of the surface (valleys) which exhibit a "fibrillar" appearance with the 'fibrils' oriented parallel to the stretching direction. These regions of higher deformation are interspersed between regions (hills) of lower deformation which exhibit no evident fibrillar character. The apparent non-uniformity in the deformation of the sheets is on a scale (~tens of microns) which suggests it may be associated with the memory of the coarse grain-like character of the raw polymer particles.

The processing conditions can significantly influence the mechanical behavior of UHMWPE in uniaxial extension. In creep and stress relaxation tensile specimens of either quenched or slowly cooled UH-A and UH-C are observed to deform uniformly, on a gross scale, up to the point of fracture. This behavior departs from that found for lower molecular weight polyethylenes which exhibit necking in creep at a strain greater than 20-30% and in stress relaxation necking occurs during the application of a step in strain greater than about 8-10%. However, when annealed at a temperature near the melting point, both the UH-A and UH-C do exhibit necking in a manner reminiscent of lower molecular weight polyethylenes. Therefore, under a specific set of deformation histories we see that by increasing the crystallinity only a few percent through annealing (by 5% in the case of the UH-A) the nature of the stress-strain behavior has been completely changed. An interesting result is that the slowly cooled UH-C (ρ=0.941 g/cm^3 and the annealed UH-A (ρ=0.942 g/cm^3) have very nearly the same density, yet one material necks and the other one does not. Therefore, density alone is not a reliable parameter for predicting the mechanical behavior of UHMWPE.

3.2 Creep and Stress Relaxation in Simple Compression

An investigation of the creep and stress relaxation behavior of UHMWPE in simple compression was started this year. Preliminary results are presented below.

For the compression experiments molded cylinders of the slowly cooled UH-A and UH-C were used. In the work to be described the maximum strain was generally less than 15% which represents the limit which could be achieved with our extensometer. A new apparatus is currently under construction which will allow us to examine the creep behavior both at longer times and at strains greater than 15%.

Creep data for slowly cooled UH-A and UH-C are presented in Figures 11 and 12 respectively. Overall, the behavior of both materials is rather similar. For a given stress the creep rate is initially relatively low, then increases somewhat with time reaching a maximum rate at around 100 seconds. Also, the curves are not quite parallel to one another and tend to diverge at the longer times. In creep the principal difference between the two polymers is that the UH-C, which is the more highly crystalline of the two, is slightly less compliant. For example, at a stress of 17.5 MPa and time of 3355 seconds the UH-A has crept to a strain of 0.14 whereas the UH-C has reached a strain of only 0.10. In comparing the results for compression with those for uniaxial extension (Figures 3 and 5) it is found that within much of the region for which the data overlap there is very little, if any, difference in creep behavior. However, differences do appear at the highest levels of applied stress. In this case the material creeps more slowly in compression than it does in extension. At an engineering stress of 16 MPa and time of 3300 seconds we can estimate that the UH-A would creep by about 12% in compression (Figure 11), whereas in extension it has crept about 20% (Figure 3). This

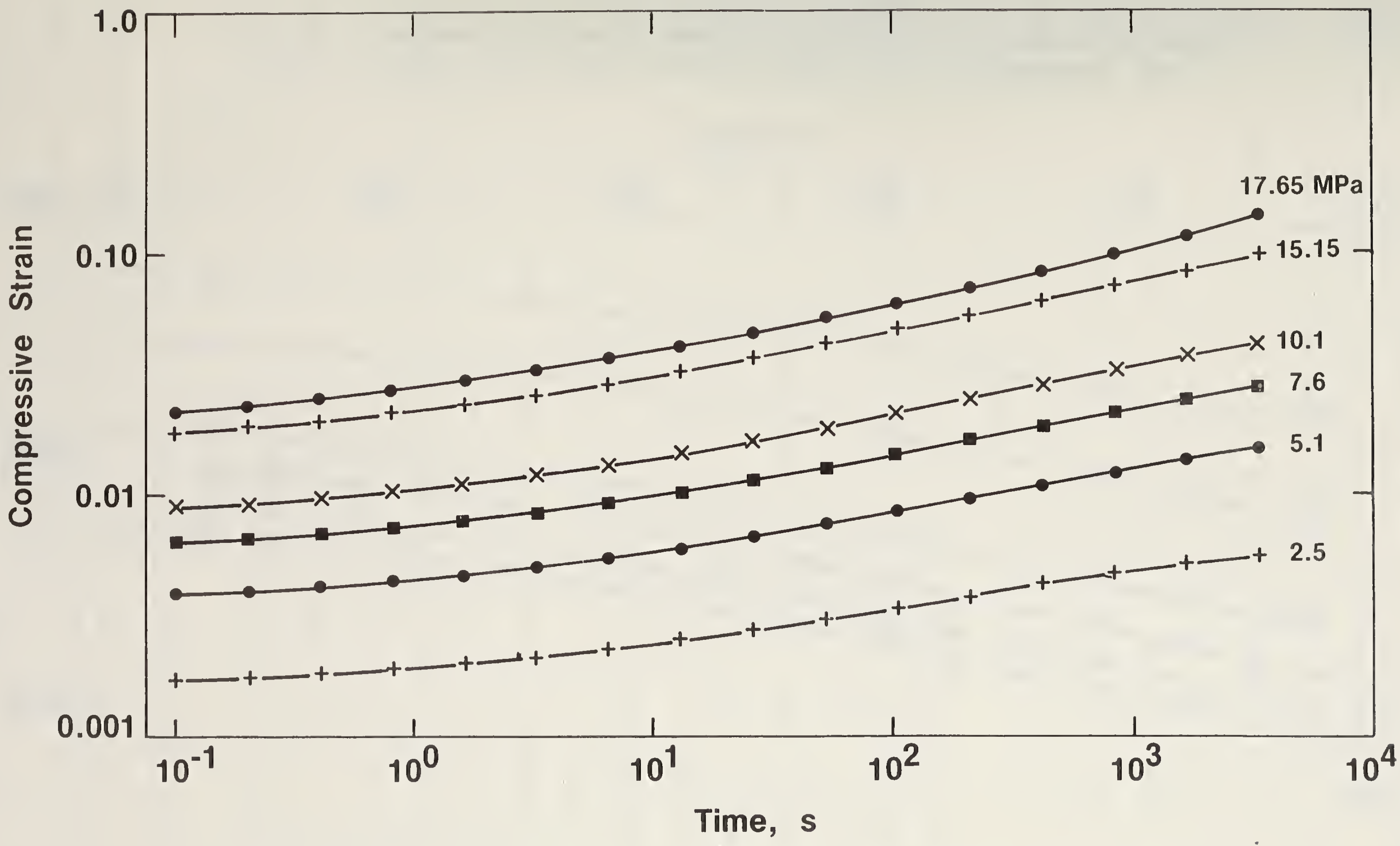


Figure 11. Creep strain versus time for sample UH-A in compression. The numbers indicate the magnitude of the applied engineering stress.

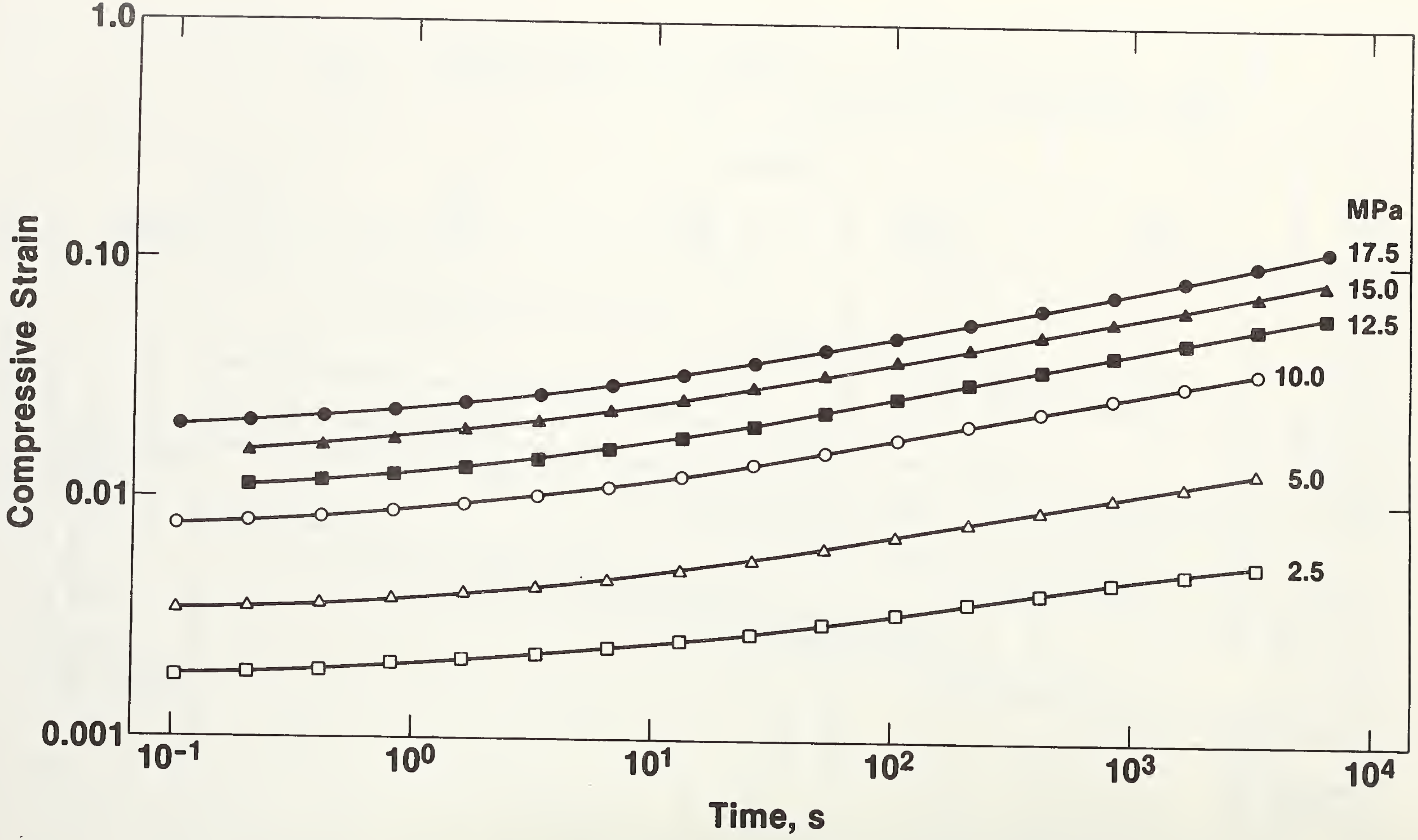


Figure 12. Creep strain versus time for sample UH-C in compression. The numbers indicate the magnitude of the applied engineering stress.

difference may be a consequence of the fact that in compression the true stress decreases with time, while in extension the opposite is true.

Stress-relaxation experiments have also been done on the UH-A and UH-C in compression. The results are shown in Figures 13 and 14 in which the values shown along the ordinate represent engineering stresses. Although we do not show the plots here, when the data in Figures 13 and 14 are replotted as isochrones of true stress versus strain, the resulting stress-strain curves are essentially the same as those shown in Figure 8 for uniaxial extension.

It is evident from the creep and stress-relaxation data in compression just described, and those in extension, that UHMWPE does not exhibit a linear viscoelastic behavior even at the smallest strains. If the behavior were linear, then the isochrones plotted in Figure 8 would form a set of parallel straight lines having a 45 degree slope. Another feature of linear behavior is that it is possible from creep data to predict the amount of recovery the material will experience upon being unloaded and allowed to recover back toward its initial state. As an example of the extent to which the UHMWPE polymer deviates from linear behavior we have carried out a series of creep and recovery experiments on the UH-A material using the same applied loads for which data are shown in Figure 11. The results are presented in Figure 15 where the actual recovery data are compared to the values predicted from linear viscoelasticity. As can be seen, the actual recovery is significantly less than is the predicted recovery.

3.3 Fatigue under Creep and Cyclic Loading

The fatigue behavior under conditions of constant load (static fatigue) and sinusoidal loading has been investigated for slowly cooled sheets of both the UH-A and UH-C at 296°C in air. In fatigue testing it is common practice to subject specimens to a sinusoidal loading history in tension of the form

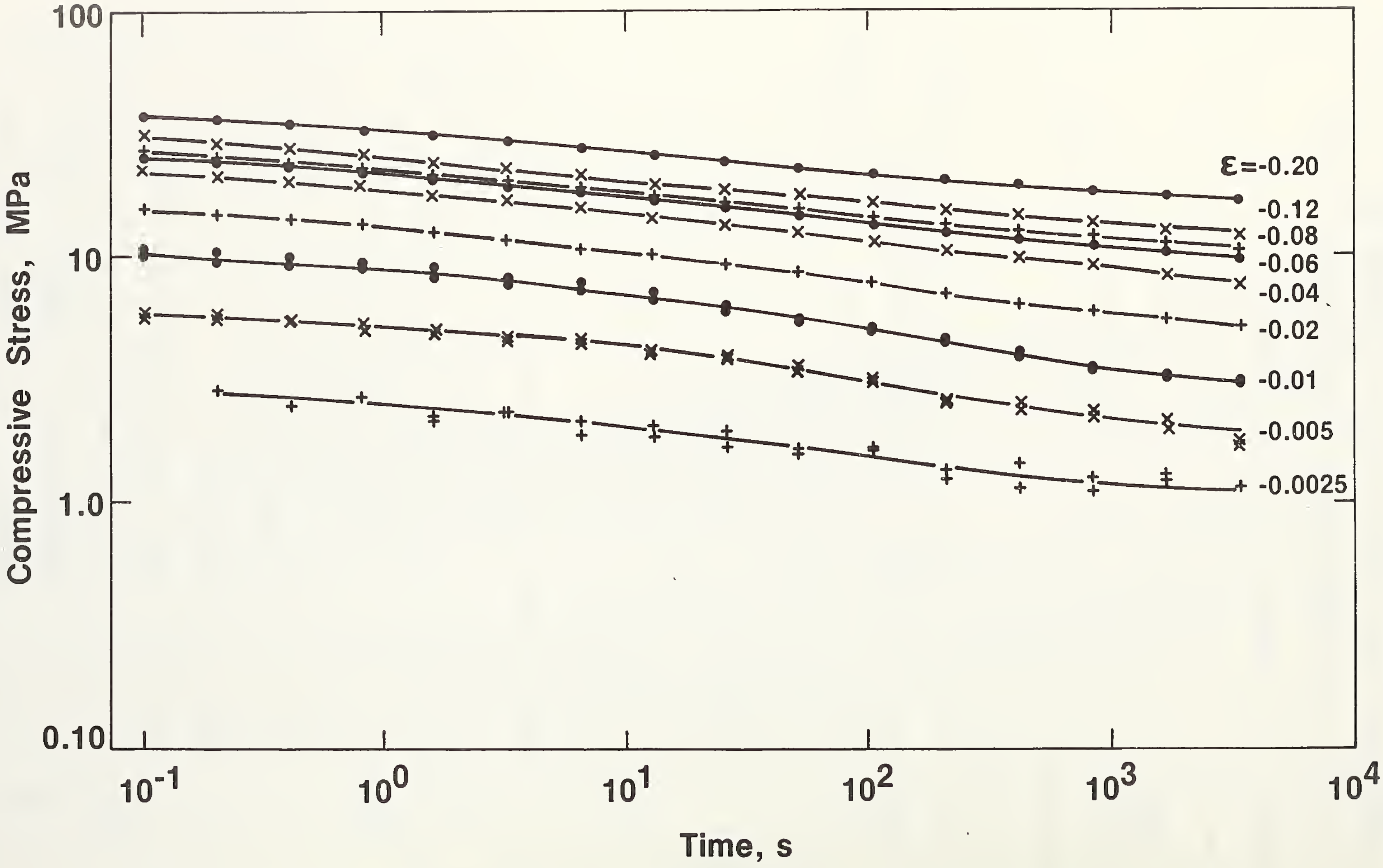


Figure 13. Engineering stress versus time for the slowly cooled UH-A in compression. The numbers indicate the magnitude of the applied step in strain.

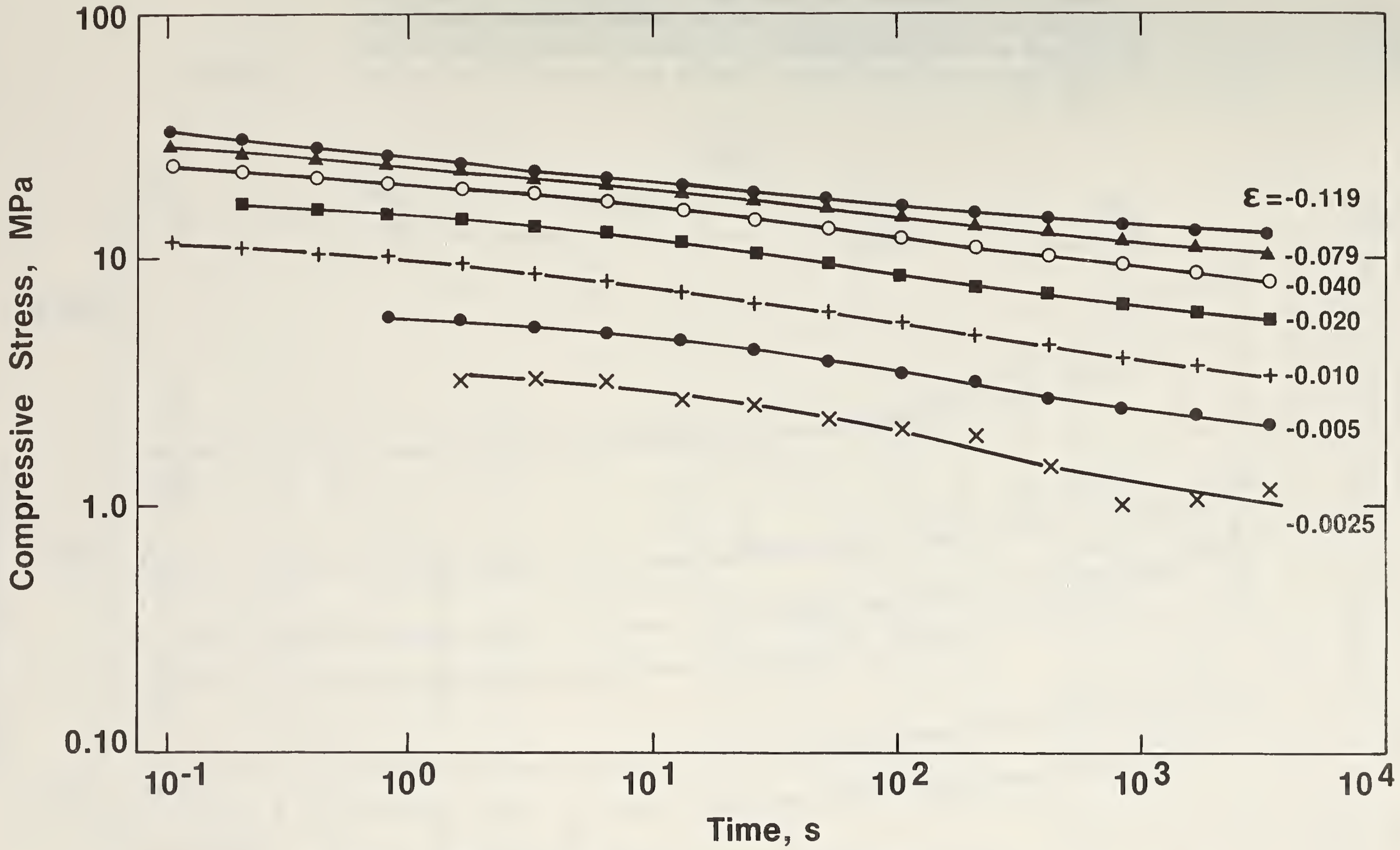


Figure 14. Engineering stress versus time for the slowly cooled UH-C in compression. The numbers indicate the magnitude of the applied step in strain.

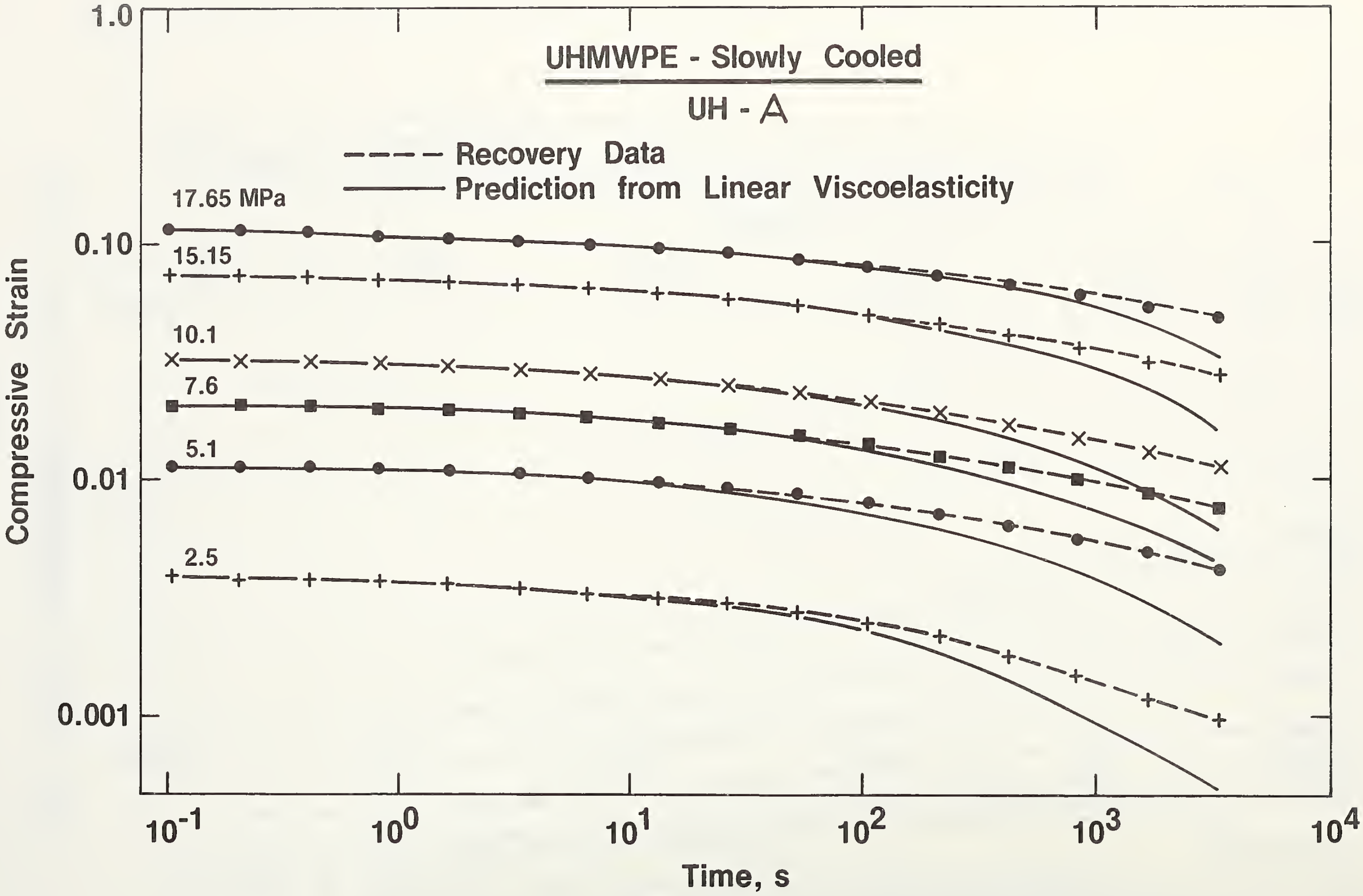


Figure 15. The extent to which the slowly cooled UH-A deviates from linear viscoelastic behavior as determined from a series of creep and recovery experiments in compression. The numbers indicate the magnitude of the applied engineering stress.

$$\sigma(t) = P+Q \sin \omega t \ , \qquad (1)$$

where P is the mean level and Q sin ωt is the oscillatory component of the applied engineering stress, ω being 2π times the test frequency. In our experiments we have chosen one type of loading history often used in fatigue tests, namely zero-tension sinusoidal loading, meaning that in equation (1) P and Q are equal. For this loading history the maximum strain in the specimen does not remain fixed, rather the specimen elongates during the course of the experiment and may reach several times its original length before fracture occurs.

As an aid in analizing fatigue data, various damage rules, or failure criteria, have been proposed. We shall consider two here. The first one, proposed initially by Bailey [6], is based on the assumption that failure is the result of damage accumulation due to stress alone. In integral form the time to fail, t_B, is related to the stress history, $\sigma(\xi)$, by the expression

$$\int_0^{t_B} \frac{d\ \xi}{\tau_B[\sigma(\xi)]} = 1 \ , \qquad (2)$$

where $\tau_B(\sigma)$ is the time to fail function determined from experiments done at constant stress, σ, and ξ is a dummy variable in time. In principle, if the function $\tau_B(\sigma)$ is known, then the lifetime in any other stress history can be predicted. In our own work and the work of others [7-10] it is found that for experiments involving a constant load history of the time to fail data can be described by an exponential function of stress of the form

$$\tau_{B}(\sigma) = Ae^{-B\sigma} , \qquad (3)$$

where A and B are constants determined experimentally. We can predict the time to fail for the loading history described by equation (1) by substituting equation (1) into equation (3) and then carrying out the integration of equation (2). Such a procedure yields the following relation

$$\hat{t}_B = \frac{t_B\ (P)}{I_o(BQ)} \quad , \qquad (4)$$

where $\hat{t}_B$ is the fatigue lifetime, $t_B(P)$ is the lifetime in a constant load experiment carried out at a mean stress P, and I_o (BQ) is the zeroeth order modified Bessel function. B, P and Q have the same meaning as in equations (1) and (3). As can be seen, in this formulation the fatigue lifetime is predicted to be independent of the test frequency.

In Figure 16 the logarithm of the time to fail is plotted as a function of the peak stress (P+Q) for specimens of the slowly cooled UH-A tested at three different frequencies. Each data point represents the average value of the logarithms of the failure times for a minimum of six specimens. Also shown (solid line) are the results for specimens tested to failure under constant load P. Two features may be noted. First, it appears that the lifetime under constant load defines a lower bound to the lifetime under cyclic loading, at least within the range of frequencies covered in our experiments. Second, the behavior shown in Figure 16 is clearly not that predicted by equation (4) since there is a decided frequency dependence associated with the time to failure under zero-tension sinusoidal loading. In short, the Bailey criterion does not apply.

The second damage rule which we shall consider is one based on the assumption that the failure process is "cycle dependent". By cycle dependent is meant that the failure occurs after a constant number of cycles independent of the frequency. This infers that the lifetime of a given

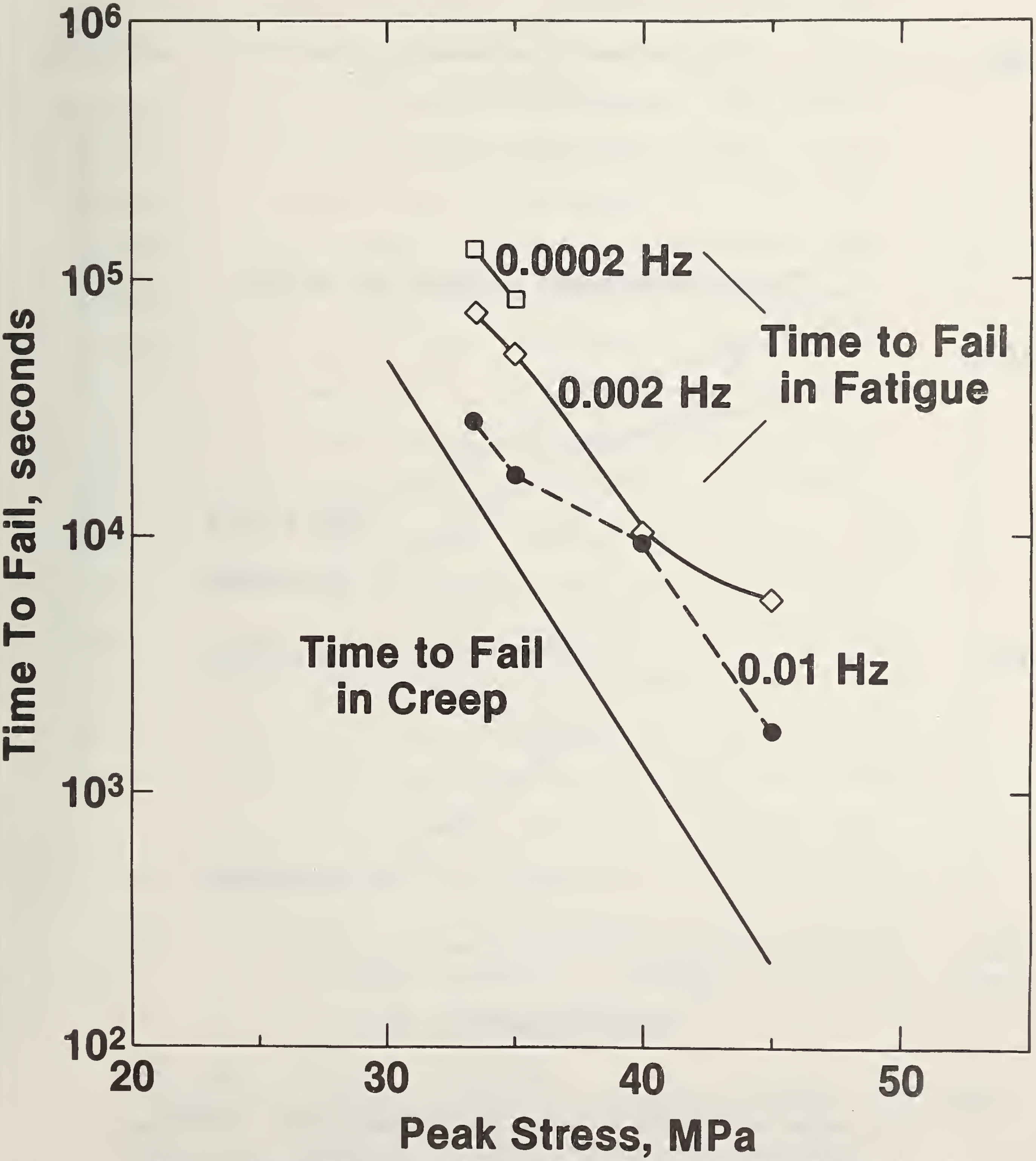


Figure 16. Logarithm of the time to fail versus peak engineering stress for specimens of the slowly cooled UH-A fatigued under zero-tension sinusoidal loading. The solid line corresponds to the behavior observed for specimens tested to failure at a constant load equal to one half the peak stress under sinusoidal loading.

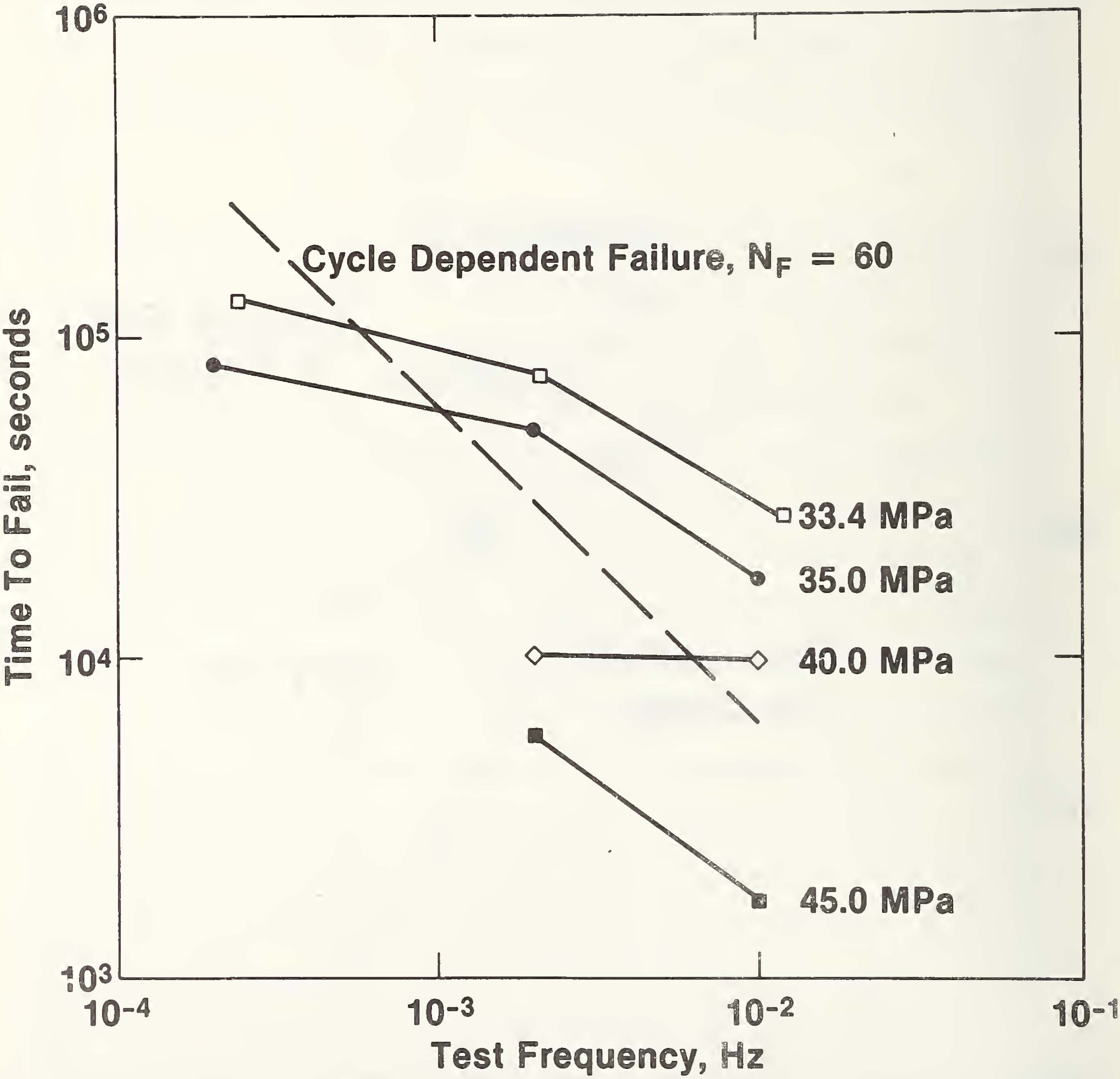


Figure 17. Frequency dependence of the fatigue lifetime of the slowly cooled UH-A tested at four levels of peak stress. The dashed line is the behavior which would be observed if the lifetime were cycle dependent where it has been assumed that failure occurred after 60 cycles.

sample is inversely proportional to test frequency (i.e., a Miner's Rule [7] type of damage accumulation). In instances where the behavior can be described by such a rule routine fatigue testing can be accelerated simply by increasing the test frequency. The frequency dependence of the fatigue lifetime of the slowly cooled UH-A is shown in Figure 17 for specimens tested at four levels of peak stress (P+Q). Also, the behavior which would be observed if the lifetime were cycle dependent is indicated by the dashed line where it has been assumed that failure occurs after 60 cycles. This line is not unique, but will shift up or down depending upon the assumed number of cycles to failure. However, the slope of the line will be independent of the number of cycles to failure. It can be seen from Figure 17 that the observed behavior is also not "cycle dependent" since there is a clear difference between the slopes of the experimental curves (full lines) and that based on the "cycle dependent" rule (dashed line), the slopes of the former being smaller than the latter. In the case of the slowly cooled UH-A we conclude that the fatigue behavior under zero-tension sinusoidal loading lies between those predicted by the two damage rules considered. It should also be pointed out that the behavior of the UHMWPE is not necessarily characteristic of other polyethylenes. In similar tests carried out in our laboratory on a lower molecular weight polyethylene [7] the lifetime was found to increase with increasing test frequency, a behavior which is opposite to that of the UHMWPE.

4. Environmental Stress-Crack Resistance

In addition to the mechanical studies reported above, we have been investigating the environmental stress-crack resistance (e.s.c.r.) of UHMWPE. A schematic of the apparatus being used is shown in Figure 18. The method is a bent strip test, but it differs from the ASTM bent strip test [11] in three ways: (1) All the specimens are constrained in such a way as

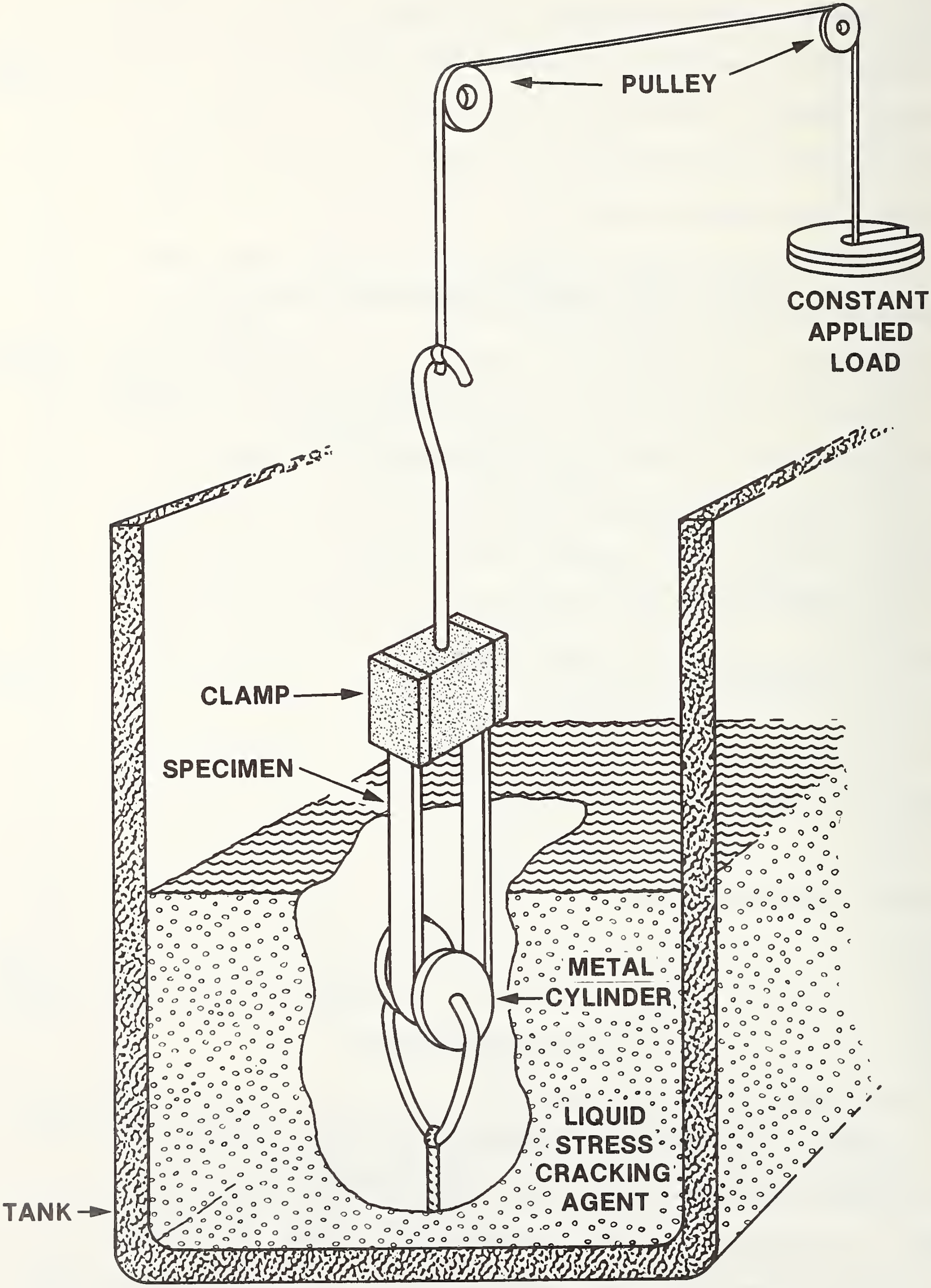


Figure 18. Diagram of the apparatus for determining environmental stress-crack resistance.

to maintain a constant geometry, (2) the specimens are subjected to a constant applied load, and (3) the specimens are unnotched. The stress cracking liquid being used is a ten percent solution of nonylphenoxypoly(ethyleneoxy ethanol) in distilled water. Results for the UH-A and UH-C polymers prepared under varied processing conditions are presented in Table 8. The tests were carried out at a temperature of 90°C and an applied load of 5 MPa. This rather high temperature was chosen in order that data could be obtained in a reasonable period of time.

Notwithstanding the scatter in the data shown in Table 7, it is apparent that the e.s.c.r. of specimens made from UH-A and UH-C depend upon the processing conditions, although there is no clear-cut correlation of failure time with density. Based upon the available data, annealing has reduced the e.s.c.r. of both materials substantially. Yet in the case of the UH-A the e.s.c.r. of the quenched specimens falls between that of the slowly cooled and that of the quenched materials. Although there is a considerable spread in the failure times shown in Table 8, even the shortest failure time for the UHMWPE (annealed UH-A) is substantially greater than for lower molecular weight polyethylenes slowly cooled from the melt. For example, a linear polyethylene ($M_w \simeq 10^5$) and an ethylene-hexene copolymer ($M_w \simeq 2.2\mathrm{x}10^5$), under the same test conditions, had average failure times (average of ten specimens) of 1.0 and 4.4 hours respectively.

Table 7

Environmental Stress-Crack Resistance* of UHMWPE at 90°C Prepared Under Various Thermal Histories

Material	Average Failure Time (Hrs.)	Shortest Failure Time (Hrs.)	Longest Failure Time (Hrs.)	Density (g/cm^3)
UH-A (slowly cooled) tested in vapor only	133 (a)	109	160	0.935
UH-A (slowly cooled) tested fully submerged	207 (a)	156	256	0.935
UH-A (Quenched)†	151 (b)	82	308	0.923
UH-A (slowly cooled and Annealed) †	69 (c)	69	69	0.942
UH-C (Slowly Cooled) †	408 (d)	133	983	0.941
UH-C (Slowly cooled and Annealed) †	100 (c)	80	120	0.952

* In a ten percent solution of nonylphenoxypoly(ethyleneoxy ethanol) in distilled water.

† Tested Fully Submerged.

(a) Average for five specimens

(b) Average for four specimens

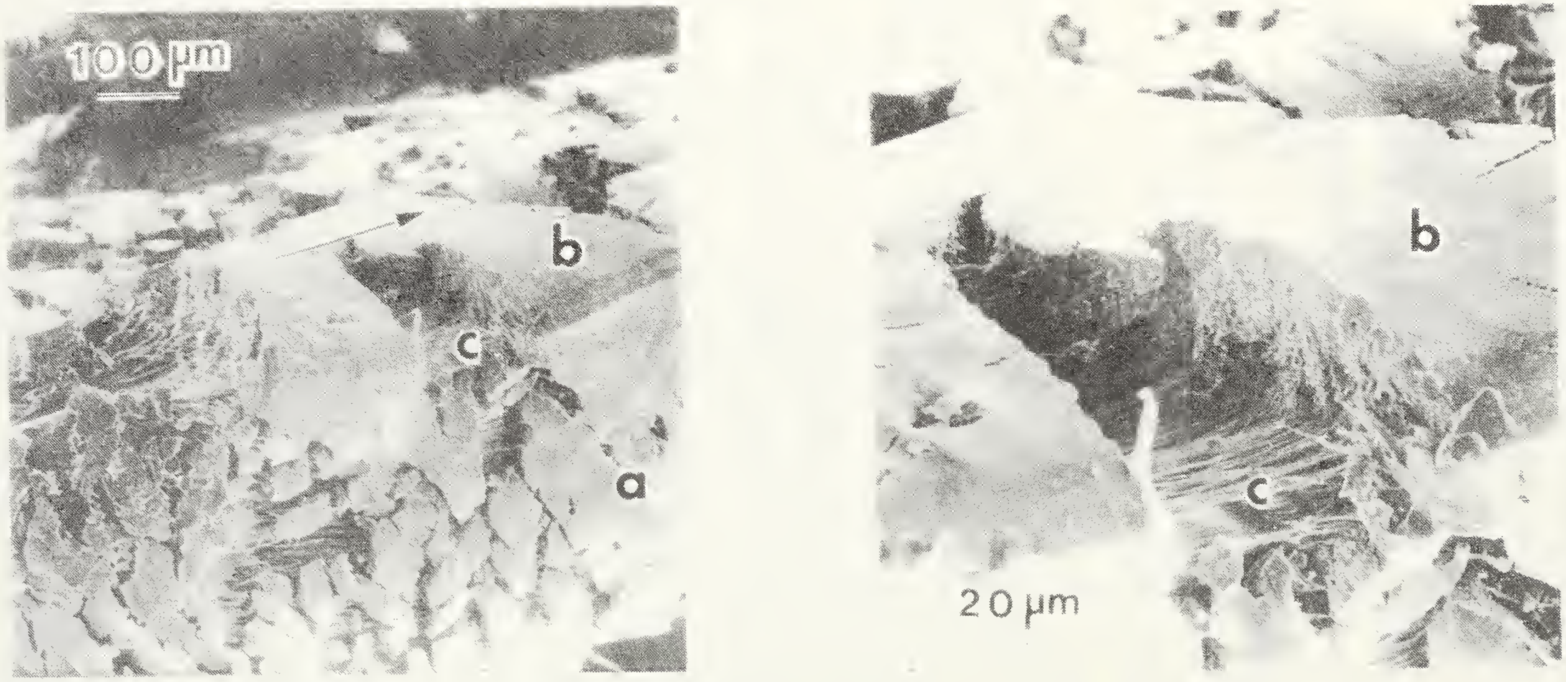
(c) Average for two specimens

(d) Average for ten specimens

One consequence of operating at a temperature as high as 90°C is that the stress-cracking agent is also present in the form of vapor if the specimen is not fully submerged. It has long been suspected that in the vapor phase the stress-cracking agent is even more effective in damaging the polymer than it is in the liquid phase. In the case of the UHMWPE, confirmation of this effect has been obtained (see Table 8). Of the ten specimens of the slowly cooled UH-A tested five were tested in the vapor alone and five were kept totally submerged. The average failure time for the five in vapor was 133 hours, whereas for those kept submerged it was 207 hours. This effect may become less important if the test is conducted at a lower temperature where there may be less surfactant in the vapor.

The use of an applied stress of 5 MPa and a temperature of 90°C produced an interesting effect concerning the failure mode. An underlying feature of a bent strip test is that the stress is concentrated in the bent region of the specimen and that failure will consequently occur in that region. Typically, a crack forms in the center of the strip at some point within the bent portion and it then grows outward toward the edges. Just prior to failure some cold-drawing may occur near the edges of the strip. For the two lower molecular weight materials referred to above the point of failure always occurred in the region of the bend irrespective of the temperature at which the test was done. This was not the case, however, for the slowly cooled UH-A and UH-C. For these two materials, which are softer than the more highly crystalline lower molecular weight polymers, the applied stress of 5 MPa was sufficient to cause significant elongation of the material during the tests at 90°C. Under these conditions stress-cracking , elongation, and failure occurred preferentially along the straight unbent sections of the specimen.

The scanning electron micrographs in Fig. 19 serve to illustrate the nature and extent of the damage which occurs in the unbent parts of samples of UH-A during the course of the e.s.c.r. experiments. A view of portions of the side surface (a) and the large surface (b) of a rectangular strip which had failed in the stress cracking agent at 90°C is shown in Fig.19 (i). A mosaic of irregularly shaped blocks of different sizes which are interspersed by deep 'canyons' can be seen at both surfaces. This appearance is typical of all the surfaces of the strips. Another typical feature is that examination of the base of the canyons [e.g. (c) in Fig. 19 (i) and Fig. 19 (ii)]



(i)

(ii)

Fig.19. (i) Scanning electron micrograph showing a portion of the side surface 'a' and the large surface 'b' of a rectangular strip which had failed in the stress cracking agent at 363 K. Arrow indicates deformation direction. Note the mosaic of irregularly shaped blocks of different sizes in both surfaces. The blocks are interspersed by deep canyons such as 'c'. (ii) A view at higher mangnification of a portion of (i). See text.

reveals an apparent ribbon-like fine texture oriented parallel to the stressing direction. This latter feature suggests that the material underlying the blocks is appreciably stretched, in contrast with the material in the blocks themselves.

The nature of the successive stages (e.g. crazing, stretching, fracture) in the evolution of the morphological features summarized above remains to be characterized.

We have also carried out a number of tests on the slowly cooled UH-A and UH-C at 75°C and an applied stress of 5 MPA. These results are summarized in Table 8. In this case all eight specimens tested were kept totally submerged in the stress-cracking agent and, unlike the situation at 90°C the specimens showed very little tendency to elongate during the experiment and the failure occurred in the region of the bend.

Finally, two specimens from the commercial implant 4-I were tested at 363K. Of the ten devices examined this was the only one from which large enough specimens could be machined to fit our test equipment. The density of material 4-I (0.945 g/cm^3) lies between that of the annealed UH-A (0.942 g.cm^3) and that of the annealed UH-C (0.952 g/cm^3). The observed failure times for the two specimens of 4-I were 69.5 and 99.4 hours. The average failure time of 84.4 hours is also between those for the annealed UH-A (69 hours) and annealed UH-C (100 hours). For these three material the e.s.c.r. is found to be inversely proportional to the specimen density.

Table 8

Stress-Crack Resistance of UHMWPE at 75°C

Material	Average Failure Time (Hrs.)
UH-A (slowly cooled)	761 (a)
UH-C (slowly cooled)	906 (a)

* - in a ten percent solution of nonylphenoxy poly(ethyleneoxy ethanol) in distilled water.

(a) average of 4 specimens.

5. Summary

This report describes work done during FY 1981 under task 80-01, NBS-FDA/BMD Interagency Agreement. The study is concerned with the relationship between morphology and the mechanical behavior of ultra high molecular weight polyethylene (UHMWPE), which is the material commonly used as one component of orthopedic implant devices. An important aspect of this study is to determine the range of material behavior variability which can be introduced by changes in the processing conditions and choice of starting material. The project was begun in FY 1980 and the initial years' activities are described in the First Annual Report [1]. In the summary which follows we shall include a restatement of several of the more important results which were reported in the First Annual Report [1].

The materials being investigated are two commercial grade UHMW polyethylenes which were obtained from the same manufacturer. Based upon the manufacturer's method of estimating molecular weight from dilute solution viscosity measurements they have molecular weights of approximately $4x10^6$ and $2x10^6$. They have been designated UH-A and UH-C respectively.

Three aspects of the raw polymer have been examined, its morphological characteristics, its melting behavior, and its crystallinity. The polymer, as received, is in its as-polymerized state and consists of fine particles. Because of its very high melt viscosity both molded and machined prosthesis components made from it retain a memory of the particulate nature of the raw polymer. This was also true for specimens molded in our laboratory at temperatures as high as 90°C above the melting point. This observation emphasizes the importance of characterizing the structure of UHMWPE products, not only to determine their crystallinity, spherulite morphology, and lamellar fine structure, but also to monitor those aspects of their morphology which are directly related to, and a consequence of, the particulate nature of the raw polymer. Since the nature of the shapes, sizes, and fine textures of nascent polyethylene particles vary depending upon the polymerization conditions, knowledge of the morphology of the raw polymer is a necessary aspect of the present study.

The raw polymer particles were examined in a scanning electron microscope. The particles, which are irregularly shaped, and which differ in size in the range 80μm - 300μm, exhibit at low magnifications an external appearance resembling that of compact clumps of grapes. Examination at high magnifications revealed regions which were highly porous. The voids in these regions were bridged by microfibrils, 50nm - 100nm in diameter, which probably result from the deformation of the polymer during polymerization as a consequence of the progressive expansion of the particles caused by the continued generation of fresh polymer at the surface of underlying encapsuled catalyst.

Differential scanning calorimetry (DSC) was used to examine the melting behavior and crystallinity of the raw polymer. The melting point was found to be between 140 and 141°C. The precent crystallinity, as determined from the area under the melting curve, was 78%, which represents a value significantly higher than can be expected for the same material compression molded at temperatures above the melting point.

Procedures were established and molding equipment constructed for compression molding (under vacuum) the powder into sheets ≈1 mm thick. Sheets were prepared by various thermal treatments which ranged from quenching of the polymer from 200°C into ice water to slow cooling it from 200°C follow by annealing at a temperature as high as 135°C. The densities and percent crystallinities of the various samples were as follows.

Treatment	Density(g/cm^3)	Wt.% Crystallinity (χ)
UH-A (Quenched)	0.923	51.0
UH-A (Slowly Cooled)	0.935	59.0
UH-A (Annealed at 130°C for 72 hrs. followed by 135°C for 48 hours)	0.942	63.4
UH-C (Quenched)	0.925	52.2
UH-C (Slowly Cooled)	0.941	63.1
UH-C (Annealed at 130°C for 72 hrs. followed by 135°C for 48 hours)	0.953	70.7

> We have examined pieces cut from ten commercially available unused and sterilized UHMWPE prosthesis components of different origins. Their densities varied from a low value of 0.924 g/cm^3 to a high value of 0.953 g/cm^3. This large variation in density among the commercial products is comparable to that found among our sample preparations which range from the quenched UH-A to the annealed UH-C. However, no direct comparisons can be made since all ten of the commercial products had been sterilized by γ-irradiation which is known to affect the density [10].

Examination of cross-section of our molded sheets under a light microscope using phase contrast optics revealed the retention of a memory of the original particulate nature of the raw polymer in the sheets. Examination of cross-sections of the slowly cooled sheets under a polarizing light microscope showed that there was a wide variation in the sizes of the birefringent structures in them. The larger among these structures appeared to be axialitic or spherulitic in character. Retention of a memory of the raw polymer particles and the wide variation in the sizes of the birefringent structures were also observed in sheets compression molded at 230°C.

An aspect of the behavior of UHMWPE which is of interest in the context of implant performance is its recovery from imposed strains below the breaking strain. Unlike lower molecular weight polyethylenes, which exhibit necking when stretched in uniaxial extension, the slowly cooled UH-A and UH-C elongate uniformly on a gross scale up until the point of fracture. A series of experiments was carried out in which specimens of the slowly cooled UH-A and UH-C were stretched to strains of from 0.25 to 4.0. After stretching, the specimens were released and allowed to relax at 23°C for a period of 24 hours. The specimens which were stretched initially to strains of up to 2.0 all recovered after 24 hours by close to or more than half the initial strain. Examination of the surfaces of samples subjected to initial strains in the range 1.0-3.0 under the optical microscope and in a scanning electron microscope indicated that stretching did not occur uniformly throughout the samples and, correspondingly, that the residual strain was not uniform throughout the released samples.

The manifestation of non-uniform deformation was evidenced in particular in scanning electron micrographs of the surfaces of the samples by the occurrence of regions which exhibit an apparent "fibrillar" appearance with the 'fibrils' oriented parallel to the stretching direction. These regions of higher deformation are interspersed between regions of lower deformation which exhibit no evident fibrillar character. This apparent non-uniformity in the distribution of the deformation in the sheets is on a scale (~tens of microns) which suggests it might be associated with the memory of the coarse grain-like character of the raw polymer particles which is retained in the compression molded sheets. It is tempting to speculate that deformation of the polymer is concentrated preferentially at the boundaries between the fused raw polymer particles.

The influence of the different thermal treatments on the mechanical behavior of UHMWPE has been investigated with experiments in uniaxial creep and single step stress relaxation in extension. As noted earlier, in uniaxial extension both the slowly cooled UH-A and UH-C do not exhibit necking, rather, they extend uniformly on a macroscopic scale up to the point of fracture. The overall creep behavior of the two slowly cooled materials was found to be similar, except that the UH-C creeps somewhat faster at large strains and creeps to a maximum elongation at fracture of about $\varepsilon=7$ as compared to $\varepsilon=5$ for the UH-A. The stress strain behavior (true stress), as determined from stress-relaxation data, was also found to be similar for strains of up to $\varepsilon=1$. However, after annealing both materials did exhibit necking in stress relaxation experiments. In the case of the UH-A increasing the crystallinity by only 5% through annealing had the effect of significantly altering the nature of the stress-strain behavior. It was also observed that, although the slowly cooled UH-C ($\rho=0.941$ g/cm^3) and annealed UH-A ($\rho=0.942$ g/cm^3) have very nearly the same density, one material exhibited necking while the other did not. Therefore, density alone is not a reliable parameter for predicting the mechanical behavior of UHMWPE in the uniaxial extension.

Experiments were also started on the preparation of cylindrical specimens for use in compression tests. Procedures were established for compression molding (under vacuum) cylinders having a length of 2.54 cm and diameter of 1.27 cm. In order to obtain some measure of material uniformity in the molded cylinders one specimen of the UH-A polymer was sectioned and the density of pieces taken from the interior and surface regions was determined. The densities were 0.934_3 and 0.934_0 g/cm^3 respectively for the two regions, which indicates a high degree of uniformity throughout the specimen. The values are also very close to those determined for the slowly cooled sheets of the UH-A polymer. At this time only preliminary creep and stress relaxation data have been obtained for cylinders of slowly cooled UH-A and UH-C. An apparatus is currently under construction which will allow us to examine the creep behavior at long times and large strains.

The fatigue lifetime behavior of the UHMWPE has been studied under conditions of constant load (static fatigue) and zero-tension sinusoidal loading. For this loading history the maximum strain in the specimen does not remain fixed, rather the specimen elongates during the course of the experiment and may reach several times its original length before fracture occurs. As an aid in analyzing the fatigue data we have considered two damage rules. One is based on the assumption that failure is a result of damage accumulation due to stress alone. In this formulation the fatigue lifetime is predicted to be independent of the test frequency. The second damage rule is based on the assumption that the failure process is "cycle dependent". Cycle dependent failure implies that the failure occurs after a constant number of cycles independent of the test frequency. Fatigue data have been obtained at different levels of peak stress and test frequency for samples of the slowly cooled UH-A. The observed fatigue lifetime is found not to obey either damage rule. The fatigue lifetime exhibits a clear frequency dependence and the slopes of the curves representing the fatigue lifetime versus test frequency are smaller than those which are based on the cycle dependent rule. Also, the fatigue behavior of the UHMWPE is not necessarily characteristic of other polyethylenes. In similar tests carried out in our laboratory on lower molecular weight polyethylene [7] the lifetime was found to increase with increasing test frequency, whereas for the UHMWPE the opposite is found to be true.

In addition to the studies of morphology and mechanical behavior we have investigated the environmental stress crack resistance (e.s.c.r.) of UHMWPE. The results for specimens of the UH-A and UH-C cut from sheets prepared under the varied processing conditions described earlier can be summarized as follows. The e.s.c.r. of both polymers depends upon the processing conditons, although there is no clear-cut correlation of the failure time with density. Based upon the available data, annealing reduces the e.s.c.r. of both materials substantially. Yet in the case of the UH-A the e.s.c.r. of the quenched specimens falls between that of the slowly cooled and that of the annealed materials. Although there is a considerable spread in the failure times depending upon the processing conditions even the shortest failure times for the UHMWPE are substantially greater than for lower molecular weight polyethylenes slow cooled from the melt. Scanning electron micrographs of portions of the specimen after failure indicate a mosaic of irregularly shaped blocks of different sizes which are interspersed by deep canyons. Examination of the base of the canyons reveals an apparent ribbon-like fine texture oriented parallel to the stressing direction. This latter feature suggests that the material underlying the blocks is appreciably stretched, in contrast with the material in the blocks themselves.

6. Work Plan for FY 1982

1. Experimental work begun in the area of uniaxial creep in extension and compression at 23°C will be continued. Attention will be given to the construction of an apparatus for the purpose of investigating the long term creep behavior in compression. Of particular interest here will be the influence of thermal history on the long time behavior in compression. The creep experiments in uniaxial extension will be extended to a higher temperature (37°C) and to an environment of saline solution in addition to air.

2. In the area of morphology studies we shall continue to investigate changes in morphology associated with deformation. This work will include the examination with wide and low angle x-rays of the polymer at various

stages of deformation under load. It is of interest to ascertain whether differences in morphology can be identified for samples prepared under varied thermal histories, but subjected to the same deformation history. Another important aspect of this study is to determine the extent to which the memory of the particulate nature of the raw polymer may influence the deformation process.

3. Work already begun on the environmental stress-crack resistance of UHMWPE will be continued. At the present time both the UH-A and UH-C polymers have been examined at 75°C and 90°C. The present plan is to continue these tests at a lower temperature and the tests may be expanded to include liquids other than the standard stress-cracking liquid presently being used.

4. Experiments concerned with the effect of γ-irradiation on the morphology and mechanical behavior will be initiated. For this phase of the work specimens having different densities will be γ-irradiated at varied doses bracketing the range commonly used for sterilization purposes. The mechanical behavior of the irradiated polymer will then be compared to that of the unirradiated material. If deviations occur, examination of the morphology of the irradiated material will be carried out for specimens in the deformed state.

References

[1] G. E. McKenna, F. Khoury, and J. M. Crissman, "Relationship Between Morphology and Mechanical Properties of Ultra High Molecular Weight Polyethylene", First Annual Report to the Bureau of Medical Devices, Task 80-01, NBS-BMD Interagency Agreement, October, 1980.

[2] H. L. Wagner and J. G. Dillon, "A Specification Method for Ultra High Molecular Weight Polyethylene for Implant Use", J. Biomed. Matls. Res., 13, 821 (1979).

[3] R. J. Roe, E. S. Grood, R. Shastri, C. A. Gosselin, and F. R. Noyes, "Effect of radiation sterilization and aging on ultra high molecular weight polyethylene", J. Biomed. Mat.Res., 15, 209 (1981).

[4] H. J. Nusbaum and R. M. Rose, "The Effects of Radiation Sterlization on the Properties of Ultrahigh Molecular Weight Polyethylene", J. Biomed. Mat. Res., 13, 557 (1979).

[5] A. Turner Jones, "The Triclinic Crystal Form of Polymethylenes and Polyethylene", J. Polymer Sci., 62, 533 (1962).

[6] J. Bailey, "An Attempt to Correlate Some Tensile Strength Measurements on Glass: III", Glass Industry, 20, 94 (1939).

[7] G. B. McKenna and R. W. Penn, "Time Dependent Fatigue in Poly(methylmethacrylate) and Polyethylene", Polymer, 21, 213 (1980).

[8] J. M. Crissman and L. J. Zapas, "Creep Failure and Fracture of Polyethylene in Uniaxial Extension", Polym. Eng. and Sci., 19, 99 (1979).

[9] G. B. McKenna and R. W. Penn, "Time Dependent Failure of a Polyolefin Rubber Candidate Material for Blood Pump Applications", J. Biomed. Matls. Res., 14, 689 (1980).

[10] B. D. Coleman, "Application of the Theory of Absolute Reaction Rates to the Creep Failure of Polymeric Filaments", J. Polymer Sci., 20, 447 (1956).

[11] ASTM D 1693-70, "Standard Method of Test for Environmental Stress-Cracking of Ethylene Plastics", 1976 Annual Book of ASTM Standards.

Figure List

Fig. 1. Wide Angle X-ray Diffraction patterns of slow cooled sheets of UH-C polymer which were stretched uniaxially at 37°C to various strains, and then stored at room temperature. The specimens were stretched to strains of (a) 0.50; (b) 2.00; (c) 3.00, (d) 4.00. The residual strains after storage at room temperature for twnety-four hours were 0.24, 1.09, 1.86 and 2.98 respectively. The residual strains after six weeks storage, toward the end of which period the diffraction patterns were recorded had decreased to 0.20, 0.84, 1.75, 2.92 respectively. [Stretching direction vertical; the patterns were recorded with a flat plate camera using CuKoc radiation].

Fig. 2. (a) Low magnification scanning electron micrograph of a portion of the surface of a slow cooled UHMWPE sheet (Polymer UH-A) which was stretched to a strain of 2 and then released and stored at room temperature. The residual strains after 24 hrs. and after eleven weeks were 0.92 and 0.72 respectively. Stretching direction horizontal. (b) A view at higher magnification of a portion of the area shown in (a). Note the apparent 'fibrillar' appearance of the regions (valleys) denoted X and the smoother appearance of the regions (hills) denoted Y. The significance of the faint striations which are orthogonal to the 'fibrils' in the X-regions and can be seen in (b) remains obscure at this stage. (Stretching direction horizontal).

Fig. 3. Creep in uniaxial extension at 296K of sample UH-A slowly cooled from the melt (density = 0.934 g.cm^3). Numbers indicate the magnitude of the applied engineering stress expressed in MPa. The arrow indicates the time at which fracture occurred for the specimen loaded at 27.5 MPa.

Fig. 4. Creep in uniaxial extension at 296K of sample UH-A quenched from the melt (density = 0.923 g/cm^3). Numbers indicate the magnitude of the applied engineering stress expressed in MPa. The arrow indicates the time at which fracture occurred for the specimen loaded at 27.5 MPa.

Fig. 5. Creep in uniaxial extension at 296K of sample UH-C slowly cooled from the melt (density = 0.941 g/cm^3). Numbers indicate the magnitude of the applied engineering stress expressed in MPa.

Fig. 6. True stress versus time for sample UH-A slowly cooled from the melt. The data were obtained from single step stress relaxation experiments and the numbers indicate the magnitude of the strain.

Fig. 7. True stress versus time for sample UH-C slowly cooled from the melt. The data were obtained from single step stress relaxation experiments and the numbers indicate the magnitude of the strain.

Fig. 8. Isochones of true stress versus strain for samples UH-A and UH-C slowly cooled from the melt. The data were taken from Figures 6 and 7. Numbers indicate the time in seconds.

Fig. 9. Isochrones of true stress versus strain for sample UH-A quenched from the melt. Numbers indicate the time in seconds for a particular isochrone.

Fig. 10. Isochrones of true stress versus strain for sample UH-A slowly cooled from the melt - 0, and annealed - 0. Numbers indicate the time in seconds for a particular isochrone.

Fig. 11. Creep in simple compression of sample UH-C slowly cooled from the melt. Numbers indicate the applied engineering stress.

Fig. 12. Creep in simple compression of sample UH-C slowly cooled from the melt. Numbers indicate the applied engineering stress.

Fig. 13. Stress-relaxation behavior in compression of slowly cooled UH-A. The values of stress shown along the ordinate indicate engineering stress and the numbers at the right various levels of strain.

Fig. 14. Stress-relaxation behavior in compression of slowly cooled UH-C. The values of stress shown along the ordinate indicate engineering stress and the numbers at the right various levels of stress.

Fig. 15. Recovery data for simple UH-A compared to the recovery predicted from linear viscoelasticity. The numbers indicate the magnitude of the applied engineering stress.

Fig. 16. Logarithm of the time to failure versus peak engineering stress for sample UH-A under sinusoidal cyclic loading.

Fig. 17. Comparison of the frequency dependence of the fatigue lifetime of sample UH-A to that predicted for cycle dependent behavior.

Fig. 18. Schematic representation of apparatus used to determine environmental stress-crack resistance.

Fig. 19. (i) Scanning electron micrograph showing the side (a) and the large surface (b) of a rectangular strip of compression molded UHMWPE (Polymer UH-A, slowly cooled from the melt) which had failed under tension (5 MPa) while immersed in a 10% aqueous solution of stress cracking agent [nonylphenoxy poly(ethyleneoxy ethanol)] at 90°C. The base (c) of a deep valley between blocks is shown at a higher magnification in (ii). Note the irregularly shaped blocks of different sizes situated through the surface of the strip in (i). Note also the apparent ribbon-like appearance of the material at the base of the "valley" (e) in (ii). The arrows in (i) and (ii) point in the direction parallel to the stressing direction.

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This report describes work done during FY 1981 under task 80-01, NBS-FDA/BMD (Bureau of Medical Devices) Interagency Agreement. The report covers the second year of a four year project concerned with the relatship between morphology and mechanical properties of ultra high molecular weight polyethylene (UHMWPE). Various aspects of the UHMWPE being investigated include (1) the establishment of procedures for compression molding (under vacuum) sheets and cylinders of the polymer, (2) the influence of thermal history and molecular weight on the time dependent mechanical behavior such as creep and stress relaxation in both uniaxial extension and compression, (3) dynamic fatigue under conditions of zero-tension sinusoidal loading, (4) environmental stress-crack resistance, and (5) the optical and electron microscopy of sheets of the UHMWPE which have been deformed to varying degrees in uniaxial extension.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Creep, Fatigue, Morphology, Polyethylene, Stress-Crack Resistance, Stress-Relaxation, Ultra High Molecular Weight.

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