

# EFFECTS OF CHEMICAL AND GAMMA IRRADIATION ENVIRONMENTS ON THE MECHANICAL PROPERTIES OF HIGH-DENSITY POLYETHYLENE (HDPE)

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## ABSTRACT

High-Density polyethylene (HDPE) is currently being used as a high-integrity container material for low-level waste. Because of the need for such containers to maintain their structural integrity for at least 300 years, potential failure, degradation modes must be determined for realistic environmental conditions. These include consideration of mechanical stress, gaseous/liquid environments within an external to the container, and the gamma radiation field. A combination of simple inexpensive tests (stressed U-bend samples) and more sophisticated longer-term creep tests was used to define the ranges of conditions for which mechanical failure/degradation is important. It was found that some simulated contaminants in low-level wastes are detrimental to creep behavior. Gamma irradiation, under some conditions, can also lead to embrittlements of HDPE and cause early failure.

## INTRODUCTION

High-density polyethylene (HDPE) is currently being used as a high-integrity container material for at least 300 years, potential failure/for low-level wastes. Because of the need for such containers to maintain their structural integrity for at least 300 years (NRC Technical Position on Waste Form) potential failure/degradation modes must be determined for realistic environmental conditions. These include consideration of mechanical stress, gaseous/liquid environments within and external to the container, and the gamma radiation field.

In some instances it is necessary to test under conditions more aggressive than those anticipated under shallow-land burial conditions so that failure or degradation modes can be more quickly identified and their relative importance assessed.

A combination of simple inexpensive tests (stressed U-bend samples) and more sophisticated longer-term uniaxial creep tests are being used to define the ranges of conditions for which mechanical failure/degradation is important. The test environments include Igepal CO-630, turbine oil and liquid scintillation fluid as well as air and deionized water, the control environments. Igepal CO-630 is a surfactant specified in standard ASTM tests for environmental stress cracking. Turbine oil is a possible constituent of low-level waste generated at reactor power plants, and is used in the current tests because of its known detrimental behavior to many types of plastic. Liquid scintillation fluids are not likely to be disposed of in burial sites at this time because of more stringent controls on their disposal. However, they are being evaluated here because they are representative of the class of organic solvents containing toluene and xylene. As such they will give valuable insights regarding a type of potential failure or degradation mode for HDPE.

In addition to the above-mentioned test environments, the effect of gamma irradiation on crack initiation and

propagation is being studied. A description of the work is given below.

## Material

The material used in this study was made from Marlex CL-100 (a highly cross-linked HDPE, trademark of the Philips Chemical Co.). The powder was used to rotationally mold a 5000-L drum by Poly-Processing, Inc., Monroe, LA. Test specimens were cut or stamped from the 3.18 mm (0.125 in.) thick walls of the drum. Owing to the molding procedure, the internal surfaces of the drum were oxidized by air during the high temperature molding process, whereas the outer surfaces, being in contact with the mold, were not. Since the oxidized surface is more brittle, it tends to crack more easily during deformation and, as will be shown below, this could lead to shorter failure times when compared to non-oxidized HDPE.

## Crack Initiation and Propagation in a Gamma-Radiation Environment

Crack initiation and propagation could be important in stressed HDPE containers because of the anticipated embrittlement by gamma irradiation. A simple inexpensive test was developed at BNL involving the use of static "U-bend" samples exposed to air and gamma radiation. The first trial tests were made on flat HDPE strips measuring 25 cm x 2.5 cm x 0.32 cm (10" x 1" x 0.125"). The strips were bent into a U-bend shape with the oxidized surface of the plastic on the outer surface of the bend. The bending process caused cracks to form in the oxidized surface. The free ends of the specimens were held together with stainless steel nuts and bolts. The propagation of these cracks under the conjoint action of irradiation and tensile stresses was monitored for three different gamma dose rates (1). It was found that cracking was most severe at the intermediate dose rate ( $9.3 \times 10^4$  rad/h) and at tensile stresses lower than the maximum value that was present at the apex of the bend.

Cracking in Type I HDPE U-Bend Specimens Exposed to Gamma Irradiation in Air at 10°C.

Irrad. Dose (Rad)	No. of Large Cracks	No. of Small Cracks	No. of Full Penetration Cracks	Additional Cracks Close to Full Penet.
0	90	13	0	0
$7.5 \times 10^6$ (at $1.4 \times 10^3$ R/h)	97	3	2	1
$6.0 \times 10^7$ (at $8.4 \times 10^3$ R/h)	95	4	2	4
$1.3 \times 10^9$ (at $4.4 \times 10^5$ R/h)	82	4	0	1

Because of the success of this type of inexpensive test, a more comprehensive set of U-bend tests were designed in order to obtain an improved statistical basis for crack initiation and propagation under stress and irradiation conditions. To efficiently use available space in the gamma irradiation facility, the new U-bend samples were smaller, and prepared from strips of HDPE measuring 10.2 cm x 1.27 cm x 0.32 cm (4" x 0.5" x 0.125"). Holes for the nuts and bolts were drilled at a distance of 1.27 cm (0.5") from the ends of the flat strips. The U-bends were prepared with the outer surfaces in three different conditions:

Type I - the as-received oxidized condition, which will have "natural" cracks present, as a result of bending,

Type II - as above, but with 10 mils of the oxidized surface removed with sandpaper prior to bending. This may still allow a few very fine cracks to be present, since the sanding may not remove all of the oxygen-embrittled material, and

Type III - the as-received "non-oxidized" surface which does not crack during the bending process.

Figure 1 shows the three types of specimens attached to individual aluminum racks. Each rack holds 8 Type I, 8 Type II, and 8 Type III specimens. The three racks shown were irradiated at different dose rates, as described in the figure caption.

Periodic findings that intermediate dose rates and intermediate stress levels were most likely to enhance crack initiation and propagation rates. Table I shows cracking information for Type I HDPE specimens, which showed the greatest tendency for cracking. Large cracks are defined as those with a length greater than one-half of the specimen width (i.e., >0.64 cm). A small crack is one with a length less or equal to one-half of the specimen width. The numbers of cracks given in Table I are the totals for each batch of 8 replicate specimens. For the large cracks, each batch of specimens has approximately 90 - most were formed during the bending process. However, it was found from periodic visual examination that a small number of additional large cracks formed during irradiation at the low and intermediate dose rate levels. Very few small cracks are formed during the U-bending process. However, an interesting observation in Table I is that small cracks are initiated more easily in the unirradiated specimens. A total of 13 small cracks was counted for the 8 specimens, whereas for specimens being irradiated, the numbers were only 3-4.

With respect to crack depth, the deepest cracks also occurred at the low and intermediate dose rates. A total of 4 "full-penetration" cracks was counted which resulted in complete fracture of the U-bend specimens. Most of these very deep cracks were not located at the apex of the U-bend where the initial tensile stress would be highest.

In addition to crack initiation in the Type I U-bend specimens, crack initiation was recently detected in Type II and Type III specimens irradiated at the intermediate dose rate of  $8.4 \times 10^3$  rad/h (Fig. 2). At the time of detection, the accumulated dose had reached  $6.0 \times 10^7$  rads. The cracks observed are very fine, and located away from the highly-stressed apex of the U-bend. Moreover, cracking was less pronounced in the Type II specimens, possibly because of the complete removal of oxidized surface material by the initial surface abrasion process. No crack initiation has yet been found in unirradiated Type II and Type III specimens, or specimens irradiated at the low and high dose rates.

#### Uniaxial Creep Behavior

Creep tests were carried out at 20°C (68°F) using a simple dead-load system. Strains were measured continuously using LVDTs (linearly variable differential transducers). Rates of creep, ductility-at-failure, and weight increase in the specimens caused by the absorption of the test liquids during creep were all measured. Figures 3 and 4 show failure (rupture) times and ductilities as functions of applied stress and test environment. At the highest stresses (> 10.34 MPa, 1500 psi) the failure times tend to converge. This is anticipated since environmental interactions with HDPE, being time dependent, will be minimized if the stress is high enough to cause early failure. Thus, at the higher stress levels, failure is controlled by the stress and not the test environment. As the stress levels are decreased, the data in Fig. 3 shows that the highest creep strengths are for air and deionized water. There is no discernable difference

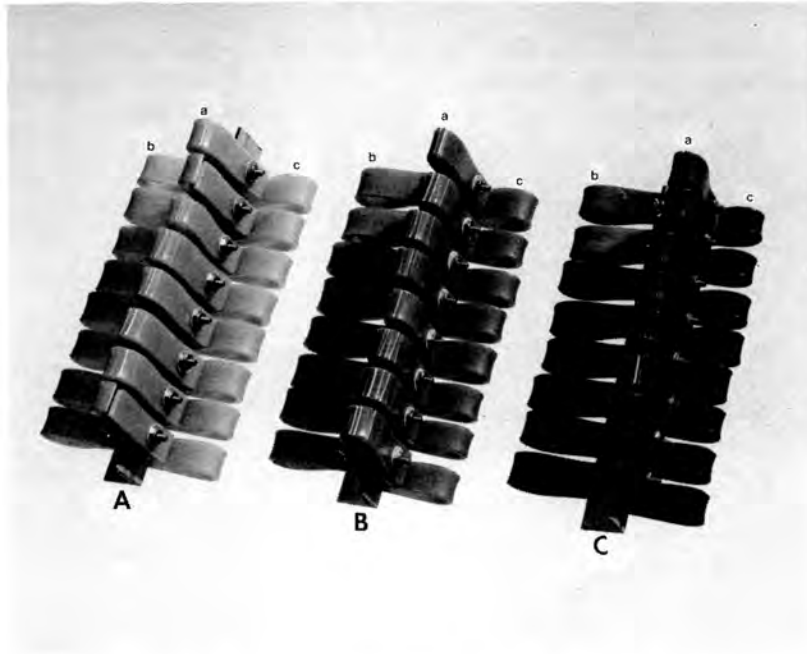


Fig. 1. Appearance of Type I (a), Type II (b) and Type III (c) Marlex CL-100 HDPE U-Bend Specimens Gamma Irradiated to  $7.5 \times 10^6$  rad (A),  $6.0 \times 10^7$  rad (B), and  $1.3 \times 10^9$  rad (C).

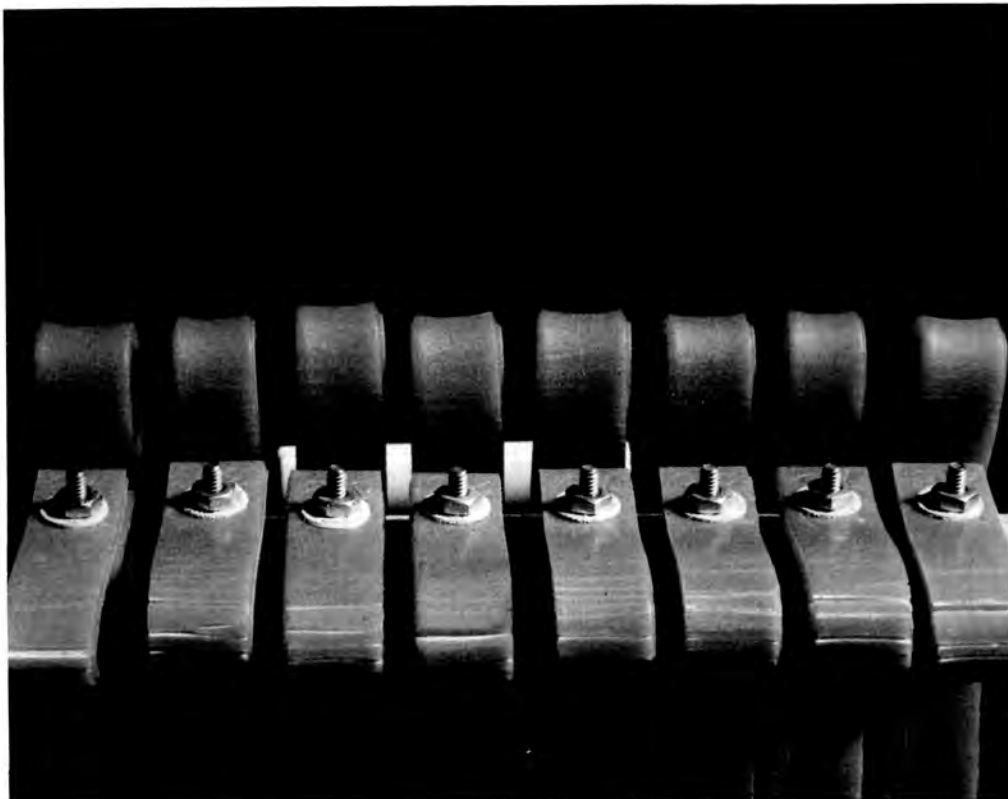


Fig. 2. Severe Cracking in Type I Marlex CL-100 HDPE U-Bend Specimens (Foreground) and Fine Cracking in Type III Specimens After Gamma Irradiation to a Dose of  $6.0 \times 10^7$  rad.

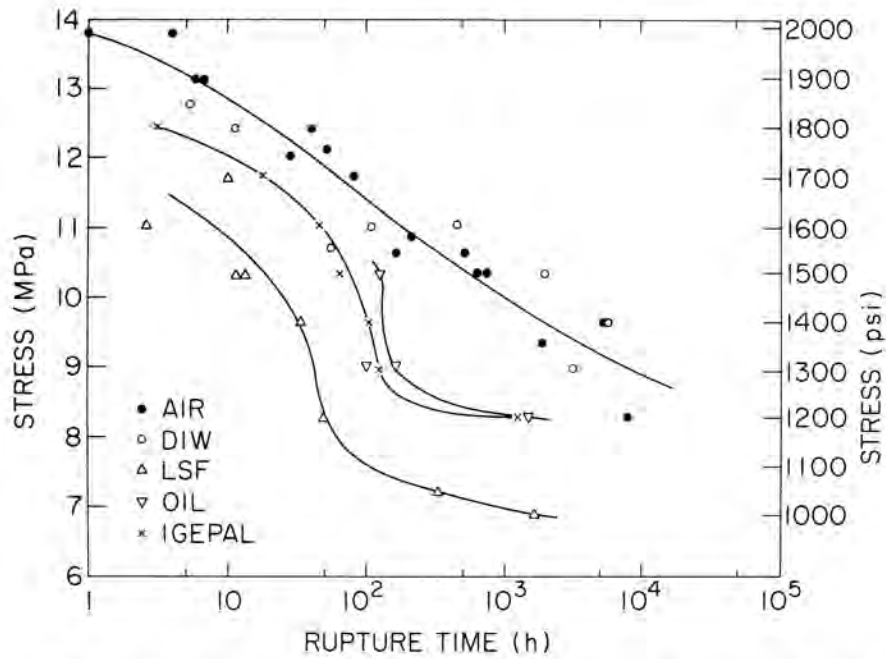


Fig. 3. Stress-rupture Results for Marlex CL-100 HDPE Tested in Various Environments at Room Temperature.

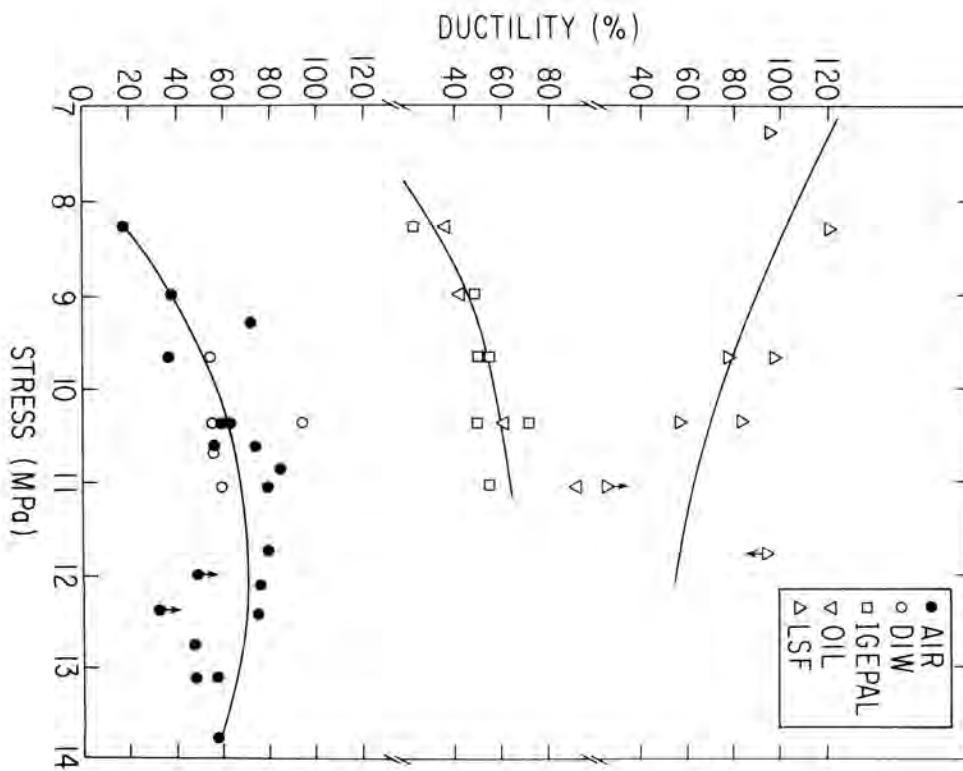


Fig. 4. Ductility of Marlex CL-100 HDPE During Creep Testing in Various Environments.



in stress-rupture behavior for these two environments. Turbine oil and Igepal cause a very large loss in creep life compared to air, and scintillation fluid gives an even larger reduction. It seems, however, that a threshold stress exists, below which creep failure may not occur. For scintillation fluid this appears to be in the range 6-7 MPa (900-1000 psi).

From Fig. 4 it may be seen that at the higher stresses the ductilities also tend towards a value independent of the test environment. The value appears to lie in the 55-60 percent elongation range. This again shows that, at high stresses, failure occurs too rapidly to be affected by time-dependent environmental interactions. Therefore, creep strengths and elongations-at-failure must be similar for all environments.

At the lower stress levels (below 10.34 MPa, 1500 psi) there is a major difference in creep ductility depending on environment. The ductilities for air, water, turbine oil and Igepal are all similar at any given stress level and decrease as the stress is decreased. On the other hand, the ductilities of HDPE in scintillation fluid are larger in the low stress range. At 8 MPa (1160 psi) the elongation is about 110 percent, compared to only about 10 percent for the other four environments. An examination of the failed specimens gives the reason for this behavior. In scintillation fluid, cracks that form early in the oxidized layer, do not grow rapidly compared to those for air, water, turbine oil, and Igepal. This is probably connected with the fact that scintillation fluids contain xylene and toluene, which are known to dissolve HDPE and also are absorbed into the plastic itself. It seems that the scintillation fluid is causing blunting of cracks formed in the oxidized layer, thereby preventing concentrated deformation in these locations.

Because of this, plastic deformation is more evenly distributed throughout the gage length leading to high ductility, as observed. In the cases of air, water, turbine oil, and Igepal, the cracks initially formed in the oxidized surface are large and, often, are long enough to span the width of the specimen. These cracks are regions of concentrated plastic deformation in which fast crack growth is encouraged, leading to failure at low overall ductility.

Based on an analysis of failed specimens, the following general comments may be made (2):

- a. For a given stress level, surface cracking during creep is more prevalent in liquid environments compared to air.
- b. Cracking in air and water increases as the stress is decreased. At the lower stress levels the fracture surface is essentially perpendicular to the stress axis showing that a single crack has propagated in a "brittle" fashion causing final failure. At higher stresses, the fracture is more ductile and local necking occurs leaving behind small "tails" of material at the point of separation.

- c. Cracking in oil and Igepal is not very dependent on stress, and many cracks are present at all stress levels. Final fracture is "brittle."
- d. Scintillation fluid discourages major cracking at high stresses. Failure in this situation is preceded by severe necking; cracks around the failure point are short and blunt, indicating that propagation is difficult. At the lower stresses there is a tendency towards brittle type behavior at the time failure becomes imminent. However, prior to final separation, there is significant plastic deformation and shallow necking in the sample is present, which results in high ductility.

#### Effect of Surface Oxidation on Creep

As mentioned previously, high-temperature rotary molding of HDPE causes oxidation to occur on the internal surface of a container. The oxidized layer in the BNL material is approximately 50 microns (0.002 inch) in thickness and exhibits lower ductility compared to non-oxidized HDPE (3). It has been shown that removal of the oxidized layer, prior to creep testing, prevents early cracking in the specimen. When such cracking is present, it leads to intense local deformation in the cracked regions, resulting in lower overall ductility and early failure (3,4).

During this study the effect of the oxidized layer on the mechanism of creep deformation was investigated. Figures 5 and 6 show creep curves for stress levels between 7.24 to 13.79 MPa (1050 to 2000 psi) inclusive. Some HDPE specimens were in the as-received (oxidized) condition and some had 250 microns (0.01 inch) of material removed from the oxidized side of the specimens prior to testing. The latter treatment is more than sufficient to remove all oxidized material. At the lowest stress levels, 7.24 to 9.65 MPa (1050 to 1400 psi), creep is initially rapid (Stage I) but eventually slows until a linear rate of deformation is established (Stage II). This is true for as-received material as well as for specimens which had the oxidized surfaces removed (Fig. 5). Although comparisons between the two types of specimens can only be made for the 8.27 MPa (1200 psi) stress level, the creep rates are essentially identical except that the as-received material failed first after 7740 hours. The non-oxidized specimen is still creeping. The creep curves in Fig. 5 also show that just prior to failure, as-received specimens show an acceleration in the creep rate (Stage III) which is associated with "necking" in the specimen and imminent failure.

At stresses of 10.34 MPa (1500 psi), and higher, major differences in behavior become evident between as-received and non-oxidized HDPE. From Figs. 5 and 6 it may be seen that the initial creep rates for non-oxidized HDPE are larger than those for as-received material at any given stress. The difference becomes larger as the applied stress is increased. Stage II creep for non-oxidized specimens tends to be shorter and a very large increase in creep rate

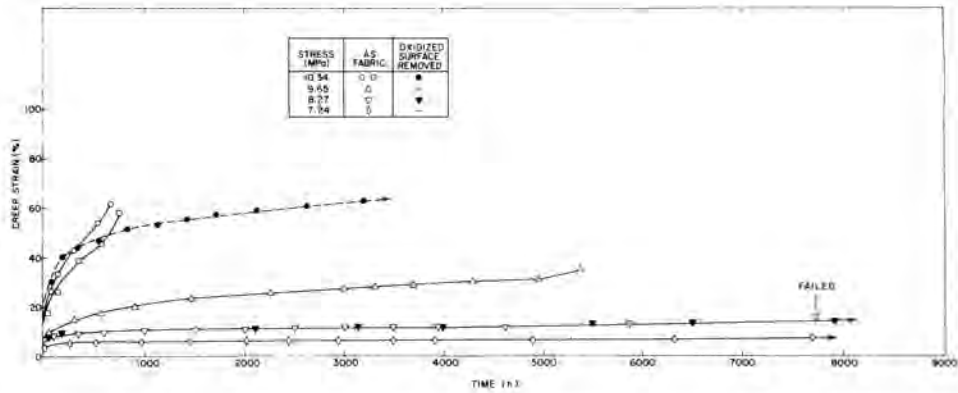


Fig. 5. Effect of Surface Oxidation on the Creep of Marlex CL-100 HDPE in Air at Stresses Between 7.24 and 10.34 MPa (1050 and 1500 psi), inclusive.

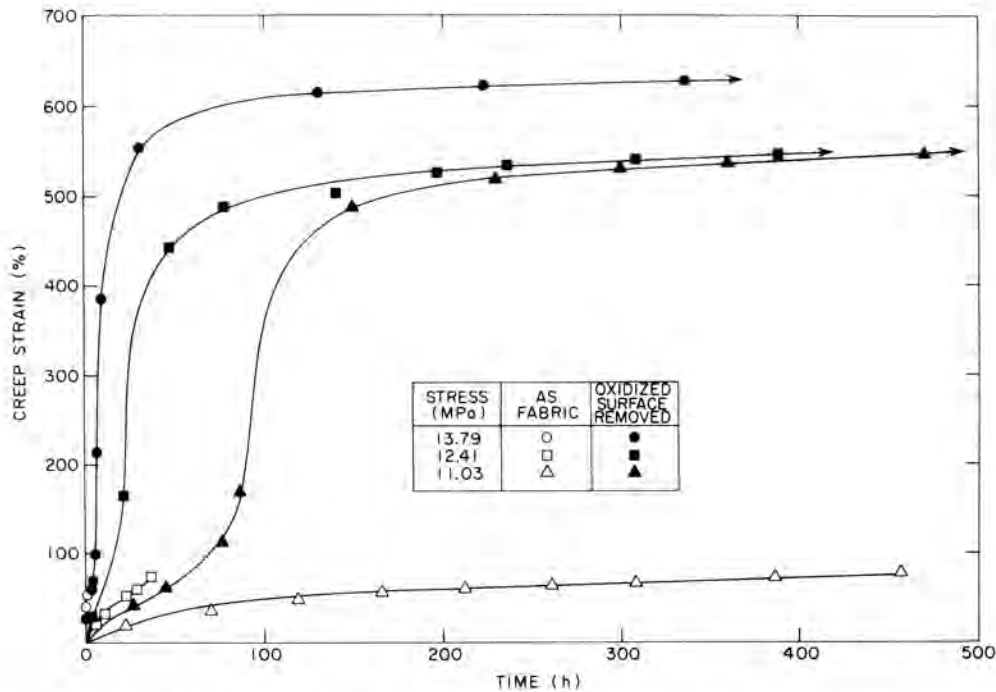


Fig. 6. Effect of Surface Oxidation on the Creep of Marlex CL-100 HDPE in Air at Stresses Between 11.03 and 13.79 MPa (1100 and 2000 psi), Inclusive.

(Stage III) occurs. Observation of non-oxidized specimens during testing showed that this large Stage III strain increment did, indeed, involve local necking in the gage length but it did not lead to immediate failure, as is the case for as-received material, but to a remarkable extension of the necked region as it propagated throughout the gage length. As soon as this was completed, the rate of creep again decreased giving rise to a long "Stage IV" which is not found in as-received HDPE. The important points to note are that, at very high tensile stresses, non-oxidized material will creep faster than as-received HDPE but it will have far superior

ductility and rupture life. At stresses of about 8.27 MPa (1200 psi), and probably lower, the creep rates for the two materials are likely to be very similar during Stage I and Stage II creep because of limited cracking in as-received HDPE at low strains. However, after very extended creep, when cracking starts to become important, non-oxidized material should give greatly improved creep performance.

In summary, based on data, obtained from a single batch of HDPE, removal of the oxidized layer from HDPE will likely yield the following changes in creep behavior in air when compared to as-received material:

- a. It will greatly increase the time-to-failure by about one order of magnitude for a given stress level.
- b. It will increase the creep rate during Stage I and Stage II deformation, but not in an unacceptable way.
- c. It will increase the elongation at failure by a factor of about six at the higher stresses and about four at the lower stresses.

### DISCUSSION

HDPE failure under a mechanical stress is closely associated with the presence of surface cracks. For example, the U-bend specimen data, given in Table I, show that large cracks may grow under the conjoint action of tensile stresses and gamma radiation. For creep deformation, cracks also grow, with the severity of cracking and the ductility being dependent on the test environment and stress level.

From the information in the sections above, the following general mechanisms for creep failure in HDPE emerges. At low stress levels, where environmental interactions are important, two types of behavior may be expected:

- a. Environmental stress cracking behavior, where liquids such as turbine oil and Igepal cause cracks to grow quickly in a brittle manner giving rise to low ductilities. Mechanisms for environmental stress cracking involve factors such as crack front wetting effects which prevent mechanical damage at a crack front from healing. This, in turn, slows the rate of crack growth (5,6).
- b. For liquids such as scintillation fluid, containing xylene and toluene which can dissolve HDPE, any cracks forming at low stresses are blunted so that their propagation is severely retarded. Deformation is, therefore, more uniformly distributed along the specimen gage length giving high ductilities. Failure eventually occurs mainly through necking.

Air does not have surface wetting characteristics, such as water has, and cracking is less likely, as was found in this study. Nevertheless, one crack will eventually propagate and cause "brittle" behavior at the lower applied stresses.

When oxidized surface material is removed from specimens prior to creep, the ability to nucleate cracks is almost entirely prevented and elongations of up to about 600%, and higher, are possible in air at high-stress levels (Fig. 6). It should be noted, however, that even if oxidized material is removed prior to creep testing, the test environment may still control the time-to-failure and the ductility. This is clear from the few tests summarized in Table II.

The effects of radiation on plastic behavior are generally known. Usually, irradiation causes increases in strength and losses in ductility. This behavior has been confirmed for HDPE for both tensile and creep behavior (3,7).

Strengthening is associated with irradiation-induced cross-linking of the polymer chains, which makes the material much more rigid and strong. Observations on embrittlement and cracking in the U-bend samples may be generally explained by ductility loss mechanisms. It would be expected that cracking of stressed U-bend specimens would increase with irradiation dose. The data in Table I, indeed, confirm this. As the irradiation dose (and dose rate) are increased, the number of large cracks increased compared to unirradiated U-bends, which showed no major cracks. A discrepancy in this model appears to exist, however, at the highest dose rate where only one large crack was found. It is possible that this could be caused by irradiation-induced chain scission which, at high dose rates, could lead to rapid stress relaxation in addition to changes in polymer chemistry. In fact, at high doses ( $\sim 10^9$  rad) the HDPE samples tend to become sticky, indicating chemical instability. If stress relaxation occurs rapidly enough, crack initiation and propagation should be impeded, as was found in this work (Table I).

The large number of small cracks in non-irradiated samples (Table I) is consistent with the presence of high tensile stresses which are not decreased by irradiation-induced chain scission. Because of this, relatively large numbers of

TABLE II

Effect of Test Environment on the Creep of Non-Oxidized HDPE.

Specimen	Test Environment	Stress MPa (psi)	Failure Time (h)	Elongation (%)
323	Air	10.34(1500)	7704	248.9
327	DIW	10.34(1500)	452	85.2
340	Igepal	10.34(1500)	312	97.3
329	Igepal	9.65(1400)	476	59.4
330	LSF	9.65(1400)	29	76.0

cracks are initiated, but the absence of embrittlement by irradiation prevents them from growing rapidly.

The presence of oxygen during irradiation should also be fully addressed if a detailed knowledge is to be gained on irradiation effects. It has been shown that gamma irradiation in the absence of oxygen does not cause major losses in ductility because irradiation-induced oxidation of HDPE is avoided (8).

In summary, the main failure modes for HDPE nuclear waste containers are found to be connected with specific chemical environments and gamma irradiation. These factors promote crack initiation and propagation, leading to early failure. Container life may be extended by eliminating, if possible, the damaging environments, reducing the stresses on the container, and removing the oxidized surfaces which are usually formed during container molding.

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