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PERFORMANCE OF PLASTIC PACKAGING FOR HAZARDOUS MATERIALS TRANSPORTATION

PART III. STRESS CRACKING

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FINAL REPORT

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NOTICE

PREFACE

This report is Part III of a series prepared for the Office of Hazardous Materials Operations under Research Contract No. DOT AS-50074. Part I was concerned with mechanical properties aspects of the performance of plastic packaging for the transport of hazardous materials. Part II dealt with permeation aspects of performance in the transport of hazardous materials. Part III addresses the problem of stress-cracking of large plastic containers and discusses the mechanical properties aspects of this problem.

The authors wish to acknowledge the assistance and cooperation of the Office of Hazardous Materials Operations Staff, in particular, Mr. Mario Gigliotti, for his continued guidance and support throughout this project, and for the assistance and cooperation of individual members of both the Plastic Drum Institute of the Society of the Plastics Industry and the Manufacturing Chemists Association; as well as Mr. Paul Campbell of the Phillips Petroleum Company. In addition, we are grateful to the editors of the Journal of the Society of Plastics Engineers and the Materials Research and Standards Journal of the ASTM for permission to reproduce several figures from journal articles.

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1. Introduction

In fiscal year 1976 under U. S. Department of Transportation (DOT) Contract AS-50074, the National Bureau of Standards (NBS) Polymers Division initiated studies of mechanical properties affecting plastic container reuse and of permeation properties of ladings through plastics. This effort included a survey of the technical literature, an analysis of tests given in 49 CFR (Code of Federal Regulations), a survey of other test methods, and laboratory studies on damage in polyethylene. The findings of all these investigations are presented in detail in references [1][1] and [2]. The recommendations and conclusions made in reference [1] are directed primarily toward the mechanical properties aspects of polyethylene containers used in the transportation of hazardous materials, while those in reference [2] are concerned with permeation.

The present Final Report, also prepared for the U. S. Department of Transportation Office of Hazardous Materials Operations under Contract AS-50074, describes additional studies carried out in the NBS Polymers Division during fiscal year 1977. The emphasis of this work has been directed toward providing background information and laboratory studies on the subject of stress-cracking, the results of which will be pertinent to the establishment of performance criteria.

For convenience, the report is divided into four sections:

° Section 1 will review stress-cracking tests currently in common use.

° Section 2 is intended to provide background material taken from the technical literature and germane to the subject of stress-cracking in polyethylene.

° Section 3 summarizes laboratory studies carried out in the NBS Polymers Division in the areas of mechanical properties and stress-cracking.

° Section 4 contains recommendations for strengthening current DOT regulations in the areas of mechanical properties and stress-crack resistance, in particular paragraph 178.19 of 49 CFR (Specification 34).

1.1 Review of Current Stress-Cracking Tests

In reference [1], it was noted that one important area not addressed in the present DOT regulations is stress cracking. Container performance under conditions in which the lading may cause stress cracking requires particular scrutiny in cases where paragraph 178.19 of 49 CFR [3] is applicable (Specification 34; reusable molded polyethylene container for use with overpack). In order to maximize the expected service life of a "reusable" container, it is necessary to determine what ladings are stress-cracking agents and what level of stress-cracking agent is acceptable to be shipped and for how long or often. Thus, there is a clear need to incorporate into DOT regulations a test, or tests, to determine stress cracking severity.

Among the various stress-cracking tests presently in common usage are principly those included in the American Society for Testing and Materials (ASTM) 1976 Annual Book of ASTM Standards [4]. It will be useful to briefly review several of these tests, insofar as they apply to plastics such as polyethylene.

(1) ASTM D1693-70: (Standard Method of Test for Environmental Stress-Cracking of Ethylene Plastics).

This test is commonly referred to as the "bent strip test." Specimens in the form of a strip are notched according to a specified procedure and then bent into a U shape in a holder. The specimen is then exposed to a surface-active agent either at 323 K (50 °C) or 373 K (100 °C), and the proportion of the total number of specimens that crack in a given time is observed. From these data, the 50 percent failure point (F_{50}) is determined.

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[1] Numbers in square brackets refer to references at the end of Part III.

However, criticism of this test has been made on at least two counts. In the first place, it is known that the behavior of polymeric materials can be notch sensitive. That is, the time to fail can be significantly different for notched specimens as opposed to unnotched specimens. Even though the notching procedure may be nominally the same for each specimen, it is difficult to assure that differences will not occur from sample to sample as a result of different operators.

The second point is that the strain on the specimen cannot be precisely specified. Because of the sharp bend in the specimen, the outer surface may be highly strained in tension, whereas the inner surface is in compression. If the material being tested is highly crystalline or has a high flexural modulus, the specimen often fails while being bent into the initial u-shape.

(2) ASTM D2561-70: (Standard Method of Test for Environmental Stress-Crack Resistance of Blow-Molded Polyethylene Containers).

Three alternative procedures are included in this test. Procedure A consists of exposing any filled, sealed, blow-molded container to a potential stress-cracking agent within the container at 333 K (60 °C).

Procedure B exposes a partially filled and sealed blow-molded standard container to the action of a specific known stress-cracking agent within the container at 333 K (60 °C), as well as to the action of this agent as an external environment.

Procedure C is similar to Procedure B except that a constant elevated internal pressure is maintained [34.5 kPa (5 psi)] in addition to elevated temperature.

In all three procedures the time to fail is observed and a minimum of 15 containers tested. This test is most useful in isolating the weak point of the container and such factors as the influence of the blow-molding conditions on the stress-crack resistance of the container.

Perhaps the most serious criticism which has been directed at this test is that it is carried out at only one elevated pressure and temperature (Procedure C) and therefore important information may be lost. For example, it has been reported that the failure mechanism may be different depending upon the stress level and temperature [17]. In fact, it has been reported [17] that one constant pressure bottle stress-cracking round robin test was considered to be a total failure because a change in failure mechanism occurred above the 34.5 kPa (5 psi) pressure employed in the test and none of the bottles failed in an acceptably short time.

(3) ASTM D2648-70: (Standard Recommended Practice for Measuring Time-to-Failure by Rupture of Plastics Under Tension in Various Environments).

In this test, a range of fixed loads is applied in tension to specimens exposed to specific environments at constant temperature. The time to failure is then observed. Data obtained from tests of this type are useful in comparing the ability of materials to support a constant applied load for long periods of time. In the presence of stress-cracking agents, the lifetime may be significantly decreased under conditions of an applied stress.

One possible deficiency of this test, with regard to container design, is that the stresses encountered in actual use nearly always contain an element of biaxiality, or multiaxiality, and, therefore, the data gathered under uniaxial conditions may not be appropriate. However, it has been suggested that a scaling may be possible between results obtained from tensile tests in uniaxial extension and comparable data obtained from actual container tests [17]. One major appeal of this latter test lies in its relative simplicity compared to the other more elaborate or expensive tests mentioned previously.

(4) ASTM D2951-71: (Standard Method of Test for Thermal Stress-Crack Resistance of Types III and IV Polyethylene Plastics).

This test is similar to ASTM D1693-70 to the extent that both tests are intended to be used on materials designed for use as jacketing or insulation on wire and cable. Some polyethylenes, in particular those of high density or low molecular weight, are sensitive to embrittlement or cracking at elevated temperatures. As in D1693-70, the specimens are severely bent prior to testing, in this latter case wrapped spirally around a small diameter metal rod, so that again the strain at the outer surface of the specimen may be large.

It is apparent that there remains a need to further develop a stress-cracking test more suited to the testing of containers. Of the three environmental stress-cracking tests just mentioned, D2561-70 is perhaps the most suitable test presently used since, in principle, Procedure A can be applied to any size or type of container. However, this test could be made to yield more quantitative information by requiring tests to be carried out over a range of elevated pressures and temperatures. Some of the experimental work to be described in Section 3 has been carried out with this point in mind.

2. Stress Cracking in Polyethylene

Section 2 of this report is intended to provide the DOT Office of Hazardous Materials Operations with background information on stress cracking of plastics. The technical literature concerned with this subject is extensive, and serves to underscore the importance of the problem to commerce and industry. In the present report, we shall be concerned solely with the environmental stress-cracking of polyethylene, since polyethylene has been established as the most important commercial polymer used for the manufacture of plastic containers. Included at the end of this report are a number of references [5-26] which in our view are representative of the technical literature as a whole. A cursory glance at this work reveals that the major portion of research activity occurred during the 1950's and early to mid 1960's. A fairly comprehensive review paper on the subject up to that time appeared in 1959 [8] and a somewhat more recent article covering stress-cracking can be found in reference [15]. It can also be observed that, more recently, the ever-increasing pressure to use plastic materials in new and more demanding applications has led to renewed interest in the subject.

The term, "environmental stress cracking," as it is commonly used, encompasses any one of several forms of what shall be termed here premature failure of a material in times shorter than experienced in an inert environment due to the presence of an adverse environment, all other factors being equal. Polyethylene gained rapid acceptance commercially in many applications because initially it was believed to be relatively inert to a very broad range of chemical compounds. One of its early uses, which remains so even yet, was in the safe transport of hydrofluoric acid. However, it soon became apparent that, under certain conditions, containers or parts failed after only very short service periods due to cracking. One such observation was that polyethylene insulating material used in the manufacture of wire and cable in many instances cracked very rapidly when treated with certain wetting agents, detergents, or oil lubricants. Since that time the development of new more highly stress-crack resistant polymer resins as well as improved processing technology has greatly reduced the problem in many applications. Another response resulting from much of this effort has been the adoption by ASTM of the several environmental stress-cracking tests discussed in Section 1. However, where the reuse of large free-standing plastic containers for hazardous materials transport is concerned, there remains a need to provide further safeguards insofar as environmental stress-cracking problems may arise.

On a microscopic scale, the mechanism, or mechanisms, of stress-cracking are not well understood. To cite one ~~very~~ recent article [20], "Environmental stress-cracking in polyethylene has been and continues to be a major unknown in materials science." However, on an empirical basis, a good deal of information is available, although there is as yet no general agreement as to what constitutes proper design criteria. There is agreement that, in addition to the presence of an external agent, a large number of material parameters exist which to a greater or lesser extent influence stress-crack behavior. Among these are molecular weight and molecular weight distribution, density, degree of crystallinity, thermal history, branching, spherulitic structure (size), presence of crosslinks, and ambient temperature. Common to most models which have been proposed for stress-cracking are the following features: (1) the appearance of microvoids in the specimen; (2) a rate process by which voids grow and eventually coalesce, and (3) the occurrence of plasticity and "strain hardening" of material surrounding the voids.

As the term implies, "stress cracking" occurs in the presence of stress. Such a stress can come about either as a consequence of an applied deformation, in which case stress relaxation occurs, or due to an applied load in which case the material creeps, or a combination of both. In either case, the ultimate result is what we choose to call premature failure, failure due not because of the imposition of the stress alone, but due in large measure to the presence of an adverse environment which greatly accelerates the process. It was mentioned previously that stress cracking in the broad sense encompasses many forms of premature failure, however, a distinction is often made as to the particular form. In the context of this report, two rather general classifications will be made: (1) stress-cracking due to the presence of surface active agents, and (2) stress cracking in the presence of a solvent or swelling agent. It should be noted that in both cases, chemical alteration of the polymer is not required in order to cause premature failure. In the first instance, failure generally appears in the form of cracks, which eventually enlarge to the point where rupture or fracture occurs. Therefore, fracture can occur well below the yield point of the polymer. Substances which give rise to this form of failure largely include polar compounds such as alcohols, and detergents or wetting agents. Such materials do not necessarily solvate the polymer or attack it chemically, but initiate or enhance the growth of surface or internal defects in the presence of an applied stress. It should be noted, however, that an externally applied stress is not necessary to cause stress cracking. The phenomenon can also occur solely as a consequence of "built-in" or residual stress in the material which arises during processing.

Solvent-cracking, on the other hand involves actual solvation of the polymer. Many liquids, such as organic solvents, are absorbed to a limited extent into the polymer, causing swelling. For example, for one type of polyethylene it is reported [6] that at 298 K (25 °C) about ten weight-percent of n-dodecane ($C_{12}H_{26}$) is absorbed, whereas at 333 K (60 °C) the amount absorbed is about thirty weight-percent. In solvent-cracking, the cracking agent is absorbed into the polymer giving rise to internal triaxial stresses which presumably weaken the material by interfering with the normal intermolecular bonding forces. In Section 3 of this report, examples of both types of stress cracking will be demonstrated for two different polyethylenes, one a linear polymer, and the other an ethylene-hexene copolymer which is branched. It might also be noted that, as a rule, those substances falling into the category of solvent-cracking agents also have high permeation rates through polyethylene. In Table 2.1 are listed a number of typical environmental stress-cracking agents. No attempt has been made in the list to distinguish whether a particular chemical compound is a "surface active" stress-cracking agent or a "solvent-cracking" agent, since in some cases the distinction may not be clear cut. It can be observed that several of the substances listed fall into the category of hazardous materia

TABLE 2.1

Typical environmental stress-cracking agents*

Aliphatic and aromatic liquid hydrocarbons
Alkali hydroxides
Alkanolamines
Alcohols
Animal, vegetable, and mineral oils
Organic acids
Concentrated sulfuric acid
Ester-type plasticizers
Detergents, wetting agents, and soaps
Lubricants and mold release agents
Aldehydes and ketones
Plating bath additives
Sulfated and sulfonated alcohols
Depolymerized rubbers
Polybutenes and polyglycol esters
Silicone oils
Sulfonated fluids

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*List compiled from references [6] and [7].

The remainder of this section will be concerned with a brief description of how some of the material parameters influence stress-cracking and of the direction taken by a number of researchers in attempting to predict time to fail due to stress cracking under an arbitrary condition of stress, environment, and temperature. In preparing this section, we have drawn heavily from the literature cited previously [5-25] and in some instances from our own laboratory studies. Properties which influence stress-crack resistance generaly fall into one of three categories; those involving the polymer chemistry, those describing the physical state of the material, and external variables such as temperature. All three can have a profound effect on lifetime behavior under stress in the presence of an adverse environment.

2.1 Molecular Weight and Molecular Weight Distribution

Two characteristics of the polymer itself which are known to affect stress-crack resistance are molecular weight and molecular weight distribution. As a general rule, it is found that stress cracking is more severe the lower the molecular weight of the polyethylene. In terms of melt index, the higher the melt index, the poorer is the stress-crack resistance. This result is demonstrated schematically in figure 2.1 which shows a possible stress versus time to fail behavior for three different high density polyethylenes in nonylphenoxypoly(ethyleneoxy)ethanol. Note that in the example of figure 2.1 the functional form, or shape, of the failure curve is not drastically changed from one sample to the other, but rather the major difference is an overall shift of the curves. However, when comparing failure curves for different polymer types, this may not be the case.

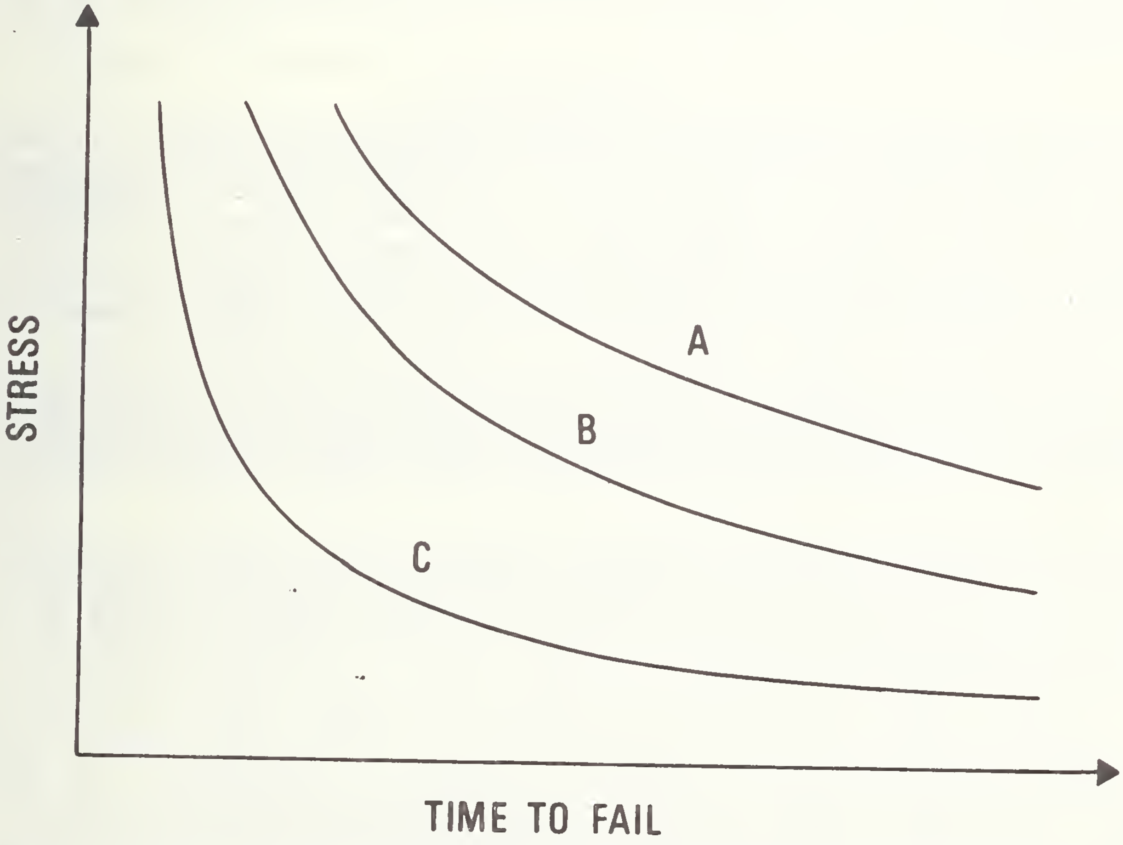

Figure 2.1 - Schematic representation of how molecular weight influences stress-crack resistance for three different molecular weights of high density polyethylene in nonylphenoxypoly(ethyleneoxy)ethanol [MW(A) > MW(B) > MW(C)].

A second parameter also related to molecular weight is molecular weight distribution, or polydispersity. There is ample evidence that the presence of low molecular weight material impairs stress-crack resistance. For example, it has been reported [9] that the removal of most low molecular weight polymer from one sample, resulted in the average time to crack increasing from 490 minutes to 648 minutes. In another instance, it was found [15] that the removal of less than 10 percent of the lowest molecular-weight component increased the cracking time from 6 hours to more than 2 months. Such behavior is one reason why melt index may not always be an effective measure of stress-crack resistance, since it is most nearly a function of weight-average molecular weight and may not be sufficiently sensitive to a relatively large number of low molecular weight species present.

From the point of view of qualification tests, parameters such as molecular weight and molecular weight distribution underscore the importance of running tests on pieces taken from the finished product, as was pointed out in the previous report [1]. In order to achieve a better finish on the final product or improved melt flow properties, it is common practice to alter the molecular weight distribution of the base polymer by the addition of selected low molecular weight polymer. Even the addition of only a few percent of such material can dramatically affect physical properties, including stress-crack resistance. Moreover, the addition of color or stabilizing compounds is generally accomplished by first blending the substance (pigment, carbon-black, etc.) with a lower molecular weight polymer which is then added to the base resin at the time of processing. Also, recycling of material left over during processing can lead to overall deterioration of the polymer, since the recycled polymer may have suffered some degradation prior to its addition to a later batch.

2.2 Branching

The third parameter associated with the polymer chemistry is branching. It is well known, for example, that the introduction of branches along the polymer main chain can vastly improve stress-crack resistance. Many of the commercial polymer resins currently in use, particularly those used for containers, are branched in one way or another. The question as to just what distribution of branch points, the type of branching, or branch length will optimize stress-crack performance has been difficult to assess in view of the experimental problems encountered in characterizing the polymer. Recently, new techniques such as C^{13} NMR (Nuclear Magnetic Resonance) offer hope in this direction.

There is agreement that it is primarily the shorter branches that control the cracking behavior of olefinic polymer (in particular polyethylene) by virtue of their much greater abundance. On the assumption that any given branch point is about equally disruptive, irrespective of the length of the branch, the more abundent shorter branches are expected to dominate in influencing the amount and structure of the crystalline phase.

Density has generally been regarded as one of the most useful measures for determining branching. However, as we shall see presently, the density can be highly misleading. It is pointed out in reference [15], "other facets of crystalline texture ascribable to the effects of branching, but not reflected in density also exercise potent influence on cracking behavior. The size of the crystallites and spherulites present appear to be among the more important of these."

A comparison of behavior which might be expected for typical commercial branched and unbranched polyethylene is shown schematically in figure 2.2. In Section 3 of this report such behavior will be demonstrated by data obtained for two different polyethylenes. Note that in the high stress region the linear polymer is superior in terms of time to fail, whereas with decreasing stress the two curves cross so that at small stresses (the region of stresses under normal operating conditions in transport), the branched material eventually becomes far superior. In the previous Final Report [1], such behavior was shown for branched and unbranched polyethylene, but in the absence of stress-cracking agent.

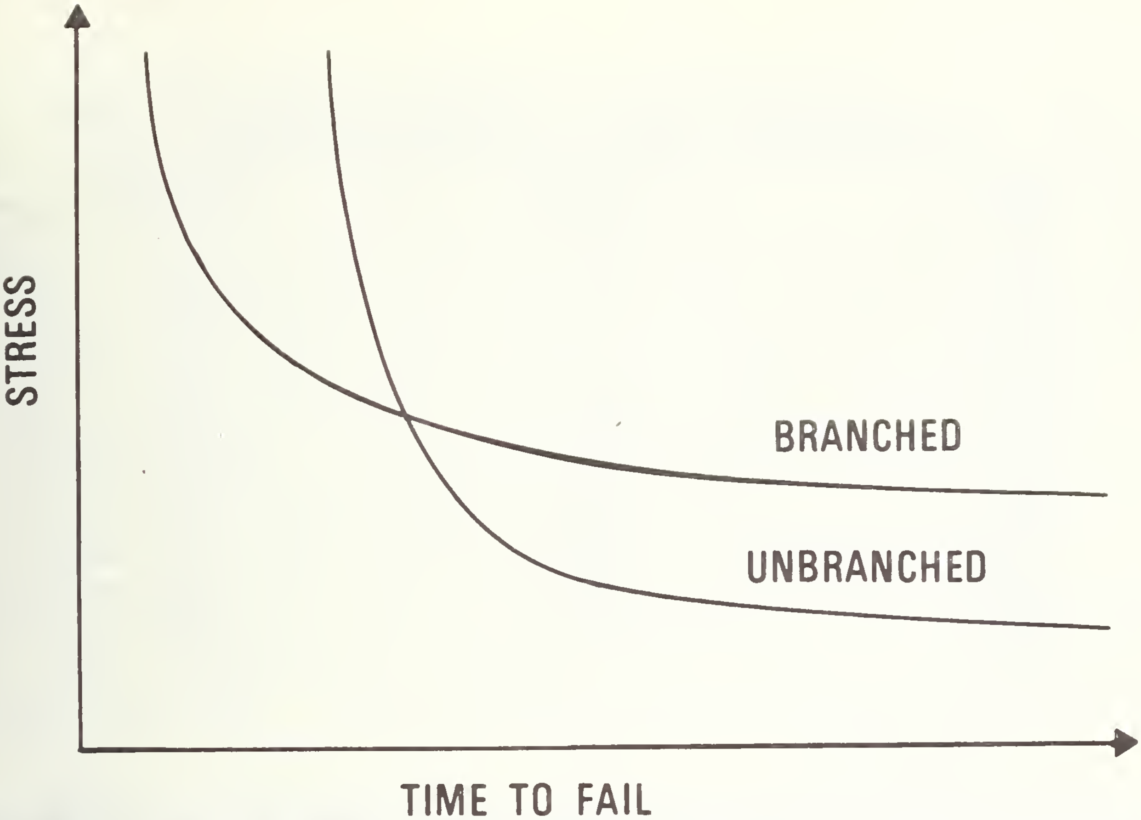

Figure 2.2 - Schematic representation of the behavior expected from branched and unbranched polyethylene in the presence of a stress-cracking agent such as nonylphenoxypoly(ethyleneoxyl)ethanol.

2.3 Density, Crystallinity, and Thermal History

A number of parameters which describe physical state of the material are also influencial in determining stress-crack behavior. Two of the most important of these are density and degree of crystallinity; but, because of their strong interdependency on one another through thermal history, it is appropriate to consider them together. Noted already was the extent to which branching influences both density and crystallinity and, in turn, stress-crack resistance. However, even in the absence of branching, both the density and crystallinity can be altered significantly through differences in thermal history during processing.

Also, it was alluded to earlier that density alone may be highly misleading in predicting stress-crack resistance. That this statement is true has been shown by Lander [26]. Shown in Table 2.2 are data for several specimens either similar or increasing in density. In the absence of additional information, such as the melt index, there is no apparent correlation to lifetime per se. Another complication is the fact that a number of these specimens were branched. However, if the lifetimes in the presence of a stress-cracking agent are compared under conditions of a constant melt index, then there is better correlation, the trend being that with increased density the lifetime increases.

Clearly, a problem exists when attempting to compare stress-crack behavior of different polyethylenes on a basis of density or crystallinity alone. There are many ways in which to arrive at the same density, while allowing other key parameters to vary. For example, a branched polyethylene can be slow cooled in such a manner as to arrive at a density of, say, 0.950 g/cm^3. At the same time, a linear polyethylene (unbranched) can be rapidly cooled to the same density, yet their mechanical or stress-crack behavior may be significantly different. Moreover, a given polytheylene resin can be processed under different thermal conditions such that they have the same density but quite different spherulitic structure (texture) and, consequently, stress-crack behavior [9].

Table 2.2 Lifetime versus density in the presence of a stress-cracking agent for polyethylene at 41 kgf/cm^2 (600 psi) and 353K (60 °C). [+]

Density (g/cm^3	Melt Index (g/10 min)	Lifetime (Hours)
0.914	1.8	0.2
0.919	0.3	350.0
0.918	0.8	60.0
0.918	1.6	0.7
0.917	3.0	0.2
0.917	20.0	0.1
0.919	3.0	9.0
0.927	1.4	120.0
0.928	3.0	20.0
0.930	16.0	0.7
0.948	0.4	170.0
0.950	8.0	20.0
0.950	20.0	5.0
0.960	1.0	250.0
0.960	4.2	250.0

[+] Data from Reference 26.

In addition to the parameters already cited, there are other important considerations in the design of a new test, or tests, for stress-crack resistance. Howard [15] has pointed out that data obtained via the bent-strip test (ASTM 1693) indicate that as the density increases, the likelihood of premature failure also increases, all other factors being equal. Yet the results of Lander [26], which were obtained from constant load experiments done in extension, suggest the opposite behavior. Apparently, it is to be expected that the results obtained depend in large measure on the type of test employed, i.e., the type of deformation applied.

2.4 Temperature

Perhaps one of the most critical factors of all, insofar as stress cracking is concerne is the ambient temperature. Such a statement will be particularly applicable to the transportation of hazardous materials where temperatures as high as 60 °C (140 °F) are not unreasonable. In reference [15], it is shown that for one type of polyethylene an increase in temperature of about 24 °C (from about 38 °C to 62 °C) decreased the 50 percent failure time (F_{50}, ASTM D1693 test) by nearly a factor of 1000 in time. Numerous similar observations can be found throughout the technical literature [9,12,17,26].

However, some care must be exercised when attributing a decrease in lifetime at an elevated temperature to the presence of stress-cracking agent. A seeming deficiency of some results reported in the literature is that the only data presented are those for which the experiment was done in the presence of a stress-cracking agent, and few, if any, data are provided indicating behavior in an inert environment. In some instances, the acceleration of failure due to increased temperature has been attributed primarily to presence of the stress-cracking agent. In the previous Final Report [1], it was shown that for one linear high density polyethylene (Sample A) in air, an increase in temperature of 34 °C (from 23 °C to 57 °C) resulted in a decrease in time to fail by a factor of 600 at a stress of 150 kgf/cm^2. For the same polymer at 97 °C and 75 kgf/cm^2, a drop in failure time of nearly 5.5 decades from the room temperature value was recorded. Therefore, although the presence of stress-cracking agent may actually accelerate failure at higher temperatures, the primary effect may simply be one of an overall degradation of the mechanical properties, in particular, a decrease in modulus. Experimental data showing just this behavior will be presented in Section 3 of this report.

2.5 Prediction of Stress Crack Performance

Although the mechanism, or mechanisms, of stress-cracking may not be well understood at the molecular level, some success can be achieved in predicting stress-crack behavior of a given polymer when the conditions of stress, temperature and stress-cracking agent are specified. Ideally, one wishes to obtain experimental data on the very long time behavior under a wide variety of conditions (failure times of the order of years) in order to predict lifetime use. However, from a practical point of view, such tests are not feasible, especially where quality control in production is concerned; and in the absence of such data one must then rely on accelerated test methods. Underlying the success of accelerated testing are two assumptions. The first of these is that within the range of temperature extremes expected in use, the mechanism, or mechanisms, of failure do not change. By this, we mean that the functional form, or shape, of the time to failure versus stress curve does not change significantly with temperature, but simply is shifted either vertically or horizontally, or both. The second assumption is that, in addition to temperature, the accelerating effect (to failure) due to the presence of the adverse environment also does not measureably alter the shape of the failure curve. This means that data collected on a variety of different stress-cracking agents can, for a given polymer under arbitrary conditions of stress and temperature, be superposed onto one master curve. In principle, the relative severity of a given stress-cracking agent can be judged by specifying a set of shift factors which have as their reference point the master curve. Then, the extent to which accelerated testing will be useful as a predictive tool will depend in large measure on the amount of scatter in the data comprising the master curve, i.e., the extent to which the predicted long time values can be bounded in an acceptably narrow band. Realistically, the best one can probably hope to do is to establish a lower bound to the failure curve.

The one major unknown confronting this approach lies in predicting long time behavior under conditions of a non-simple thermal or stress history. Such a situation will be of particular importance in transportation where not only the temperature-stress history may be complex, but also with regard to specification 34 where reuse is intended, it may be difficult to assure that a container has not been exposed to more than one possible type of stress-cracking agent. In such a case, as is the case with mechanical properties in general, the concept of additivity of damage enters. Such an additivity of damage rule was mentioned briefly in the previous report [1] and will be considered further in Section 3 of this report. Suppose that a container is exposed to a lading, a potential stress-cracking agent, under conditions of temperature and stress severe enough that some damage occurs. Such damage may not necessarily be detectable by ordinary means. Upon its return, even a very careful and thorough cleaning cannot insure that all of the previous lading has been removed. In fact, the body of evidence to date suggests that if the conditions of exposure have been sufficiently severe to cause damage to the material, then it will probably not be possible to remove by ordinary cleaning a small amount of lading trapped in or near microvoids, or other defects, which on a subsequent trip may again cause further damage if the stress-temperature conditions are severe enough. That this is true will be demonstrated for several simple histories in Section 3, the implication being that a simple additivity of damage concept may not be applicable.

In Section 7 of reference [1], the influence of temperature on the time to failure versus stress behavior was shown for several different polyethylenes. Those results were obtained for specimens under constant load in uniaxial extension and in the absence of an adverse environment (see figure 7.1). In Section 3 of this report more extensive work will be presented for two polyethylenes in both air and a variety of stress-cracking liquids. However, before presentation of the experimental work, we shall cite two studies chosen from the literature which will serve to point out the utility of accelerated test methods insofar as stress-crack behavior is concerned.

In figure 2.3 are shown data obtained by Fulmer [17] for commercial bottles of polyethylene tested to failure at different temperatures in nonylphenoxypoly(ethyleneoxy)-ethanol. The bottles were tested according to a procedure similar to the ASTM D2561 test, except that all the bottles were tested to actual failure at different levels of internal pressure.

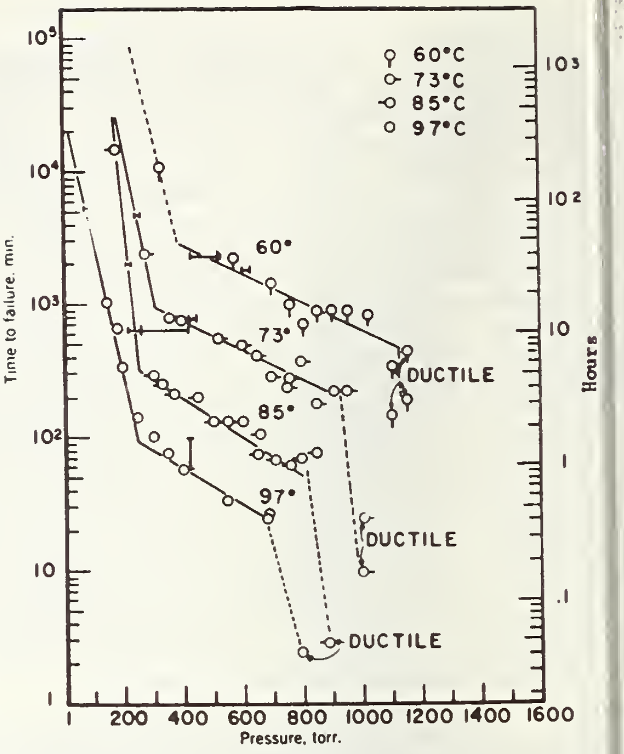

Figure 2.3 - Time to fail for commerical bottles of polyethylene as a function of pressure and temperature. Data of Fulmer [17] courtesy of the SPE Journal.

Now, if the data of figure 2.3 are treated such that the pressure is divided by the absolute temperature (reduced variable) and the resulting values at different temperatures superposed, they appear as in figure 2.4. From figure 2.4, it can be seen that a reasonably good superposition is obtained with an acceleration of a factor of nearly 100 in testing time resulting from increasing the temperature from 60 to 97 °C.

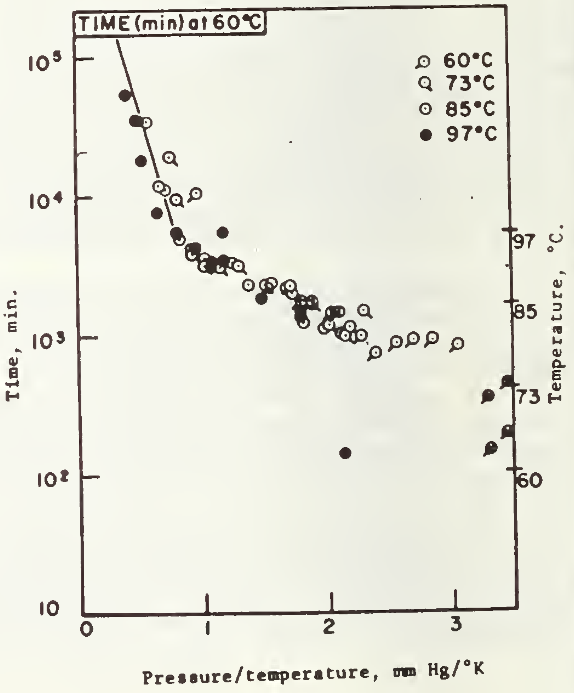

Figure 2.4 - Data of Figure 2.3 replotted in terms of reduced variables and superposed to 60 °C. Data of Fulmer [17] courtesy of the SPE Journal. The shift factors are indicated by the right vertical axis.

Another example of an effort to establish a master curve for a variety of stress-cracking agents is the work of Suezawa et al. [11]. Figure 2.5 shows their master curve for one high density polyethylene in the presence of four different stress-cracking agents.

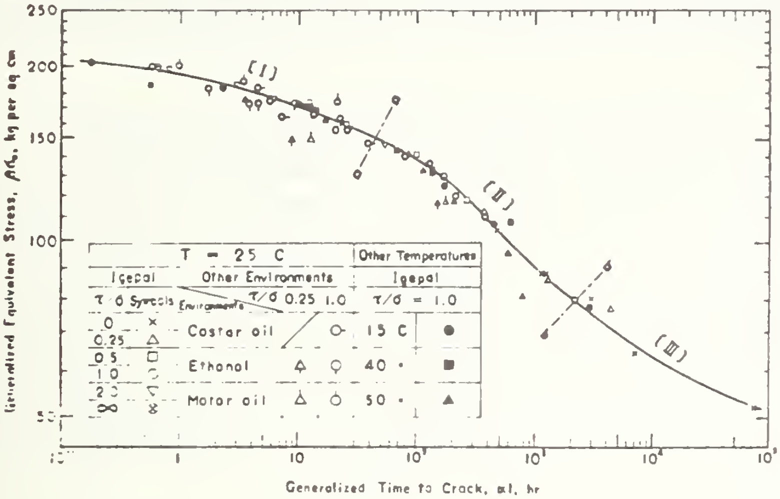

Figure 2.5 - Generalized master curve for environmental stress-cracking of high density polyethylene. Data of Suezawa et al. [11]. Courtesy of the Materials Research and Standards Journal of the ASTM.

In figure 2.5, αt represents a generalized time to crack and $\beta\sigma_0$ a generalized equivalent stress. In this work the biaxiality of the imposed stress was achieved by applying a torsional stress to the specimen (a cylinder) at the same time the specimen was loaded in tension. The ratio τ/σ represents the shear stress in torsion divided by the tensile stress. As is evident, a rather good superposition can be obtained for a wide range of conditions. In principle then, it should be possible from a master curve such as this to predict failure times for a nearly arbitrary state of stress, temperature, and stress-cracking agent.

3. Experimental Studies

In fiscal year 1976, under DOT contract AS-50074, the NBS Polymers Division initiated laboratory studies on damage in semicrystalline polymers. Much of this work was concerned with the time to fail for polyethylene as a function of applied stress in uniaxial extension under conditions of varied temperature, molecular weight, and environment. In addition, the idea of additivity of damage was examined for several simple loading histories. The work to be described in Section 3 of the present report represents a continuation and further extension of experiments begun in fiscal year 1976. As a matter of convenience, Section 3 has been subdivided into the following several headings:

(3.1) Time to failure for polyethylene in uniaxial extension in air.
(3.2) Stress cracking of polyethylene in uniaxial extension.
(3.3) Stress cracking of polyethylene subject to biaxial stress.
(3.4) Additivity of damage in polyethylene in the presence of an adverse environment.

The experimental procedures followed, unless otherwise specified, were the same as those described in reference [1]. New procedures or apparatus will be described in the text where appropriate.

3.1 Time to Fail for Polyethylene in Uniaxial Extension in Air

In reference [1], log time to break versus applied stress data (uniaxial extension) were shown as a function of temperature for three different molecular weight high density polyethylenes (figures 7.1, 7.2, and 7.3). Samples A and B were commercial linear polyethylenes, while sample C was the NBS Standard Reference Material (SRM) 1475 polymer. To better demonstrate the effect of molecular weight, we have replotted these data on log-log coordinates in figure 3.1.1.

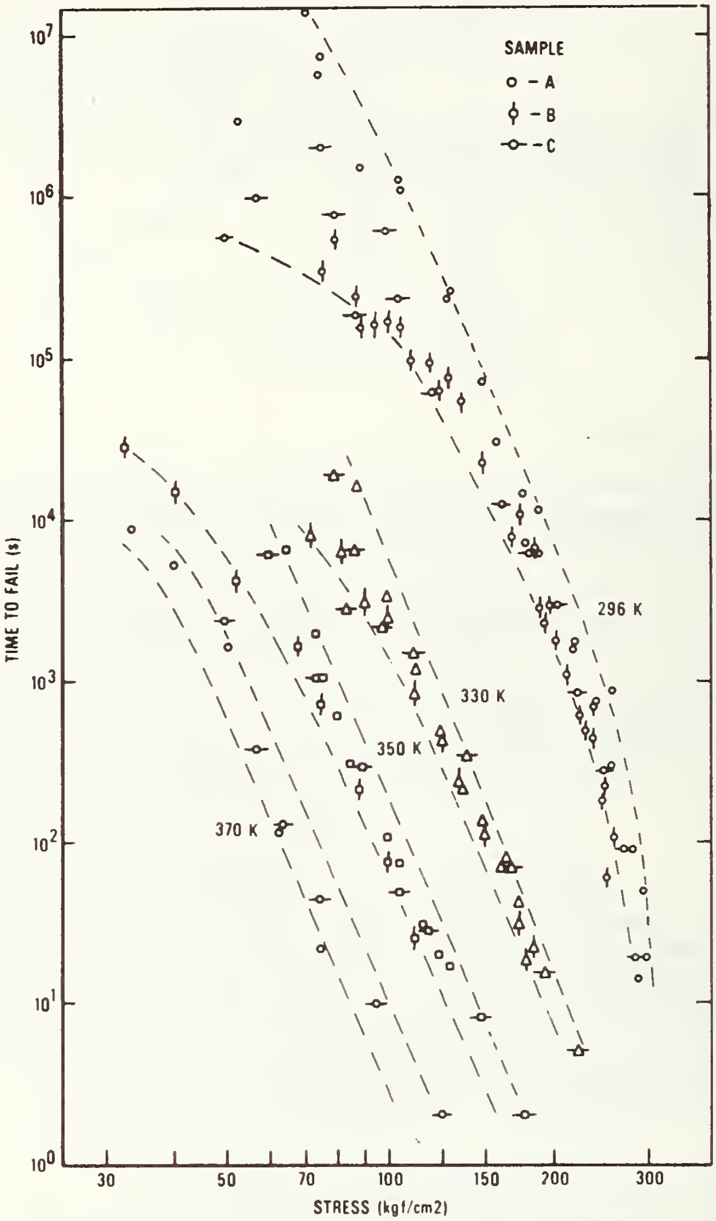

Figure 3.1.1 - Effect of molecular weight on time to fail versus applied stress in uniaxial extension for three samples of high density polyethylene in air.

A comment is appropriate here concerning the definition of breaking. In the previous report, breaking, or failure, was defined simply as the occurrence either of fracture (separation) or of neck formation followed by cold-drawing. By this definition, nearly all the specimens from each of the three samples (see figure 3.1.1) tested at room temperature (296 K) failed; only specimens from sample A actually cold-drew to any extent before breaking. At elevated temperatures, several specimens cold-drew, but did not fracture before the experiment was stopped. Therefore, in order to be consistent with the previous report, we shall continue to apply the term "failure" to describe the data, with the recognition that in many cases fracture did not occur.

To return to figure 3.1.1, it can be seen that for large stresses the behavior of all three samples is not dramatically different as a function of molecular weight; and the bounds determined by the experimental scatter in data points are reasonably narrow. However, as the stress decreases to small values, the divergence in lifetimes among the three samples becomes much more pronounced, an indication that a significant improvement in lifetime can be gained by increasing molecular weight (A > B > C). Note that at a given stress level (at small stresses), the scatter in the data point is less at the elevated temperatures than is the case at room temperature. This behavior may result in part from the difficulty encountered in maintaining a constant room temperature over long periods of time, whereas, the elevated temperatures were controlled to within about (0.05 °C). On the other hand, from the high degree of scatter in the data points and the rather pronounced bending over of the curves for the highly crystalline low molecular weight sample C, it is apparent that other factors, in addition to temperature, were important in determining lifetime.

More recently, experiments in uniaxial extension have been conducted on two additional commercial ethylene polymers, and much of the remainder of work to be described in this report will concern these two polymers. One sample, designated D, was selected because it was a linear high density polyethylene recommended for use in food packaging. This sample has material characteristics very similar to sample A used earlier. The second sample, designated E, was chosen because it is branched. This polymer was actually an ethylene-hexene copolymer recommended by the manufacturer for use in blow molded items, such as large shipping containers, gasoline tanks, and chemical tanks. Some of the pertinent material characteristics of both samples are given in Table 3.1.1.

Table 3.1.1 Polymer characteristics of two polyethylenes used in the present study.

Sample	Density (gm/cm^3)	Melt Flow[1] (gm/10 min.)	Structure	Environmental Stress-Crack Resistance[2] (Hours)
D	0.964	0.75[3]	Linear	15-20
E	0.950	10.0[4]	Branched	450

[1] - ASTM Test D1238-73
[2] - ASTM Test D1693-70
[3] - Condition E of 1
[4] - Condition F of 1

Experimental data for log time to fail versus applied stress in uniaxial extension are shown for sample D at several temperatures in figure 3.1.2. Here, the term "time to fail" implies separation, for most of the specimens, with the exception of several at the higher temperatures, broke almost immediately upon necking, or fractured prior to necking. In overall behavior, sample D appears very similar to sample A [1]. For comparison, the behavior of both is shown on log-log coordinates in figure 3.1.3. Overall, sample D is marginally superior in time to fail for a given stress and temperature, except at very long times at room temperature (296 K) where they are nearly equal. Since sample D had a higher melt index than did A, one main difference in character may be that sample D was more crystalline, which could account for the observed overall lifetime superiority. The higher molecular weight of sample A is reflected by the fact that for a given condition of stress and temperature, sample D did not draw to the same extent as A before fracture occurred.

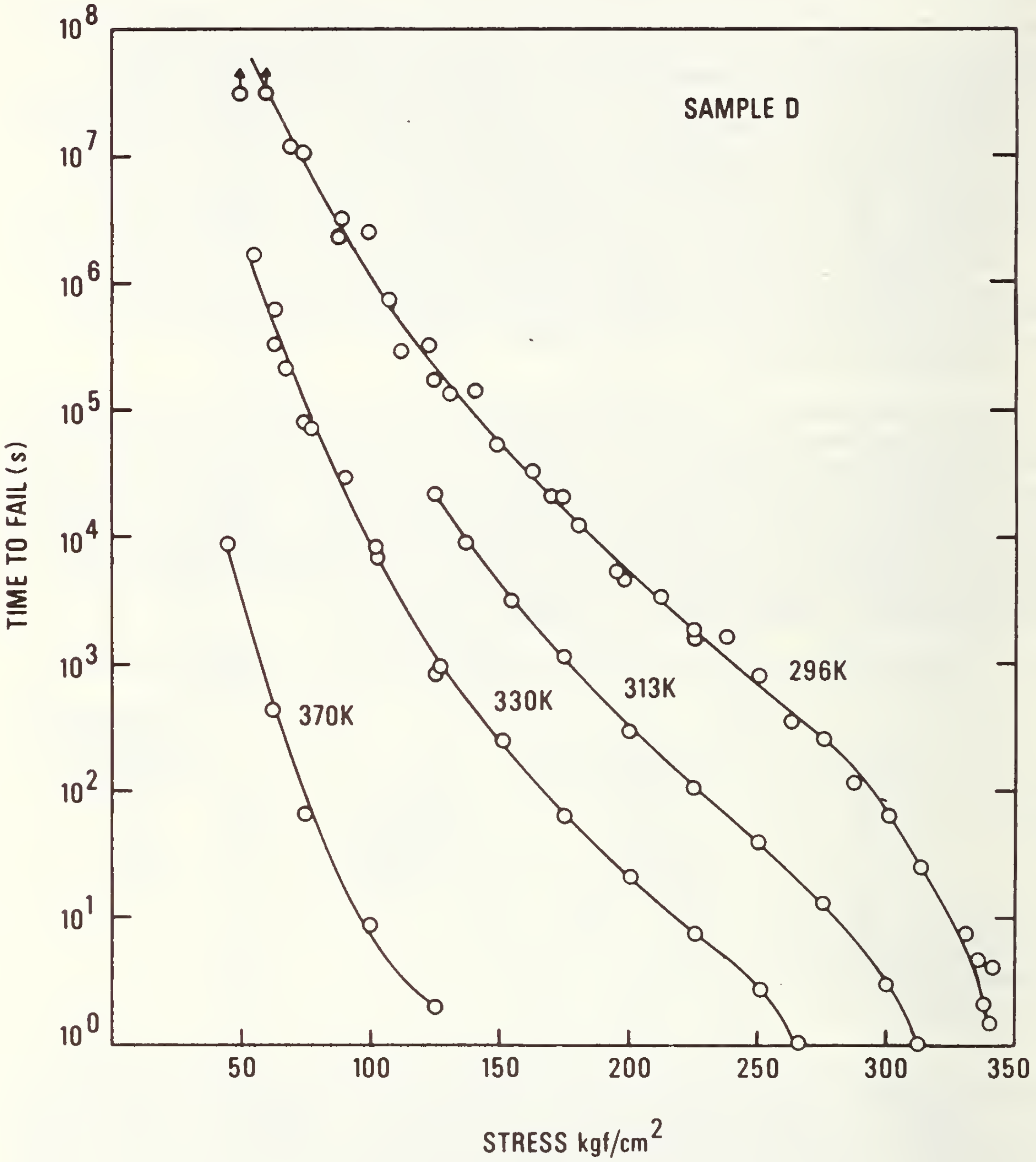

Figure 3.1.2 - Time to fail versus applied stress in uniaxial extension for a high density linear polyethylene (sample D) in air.

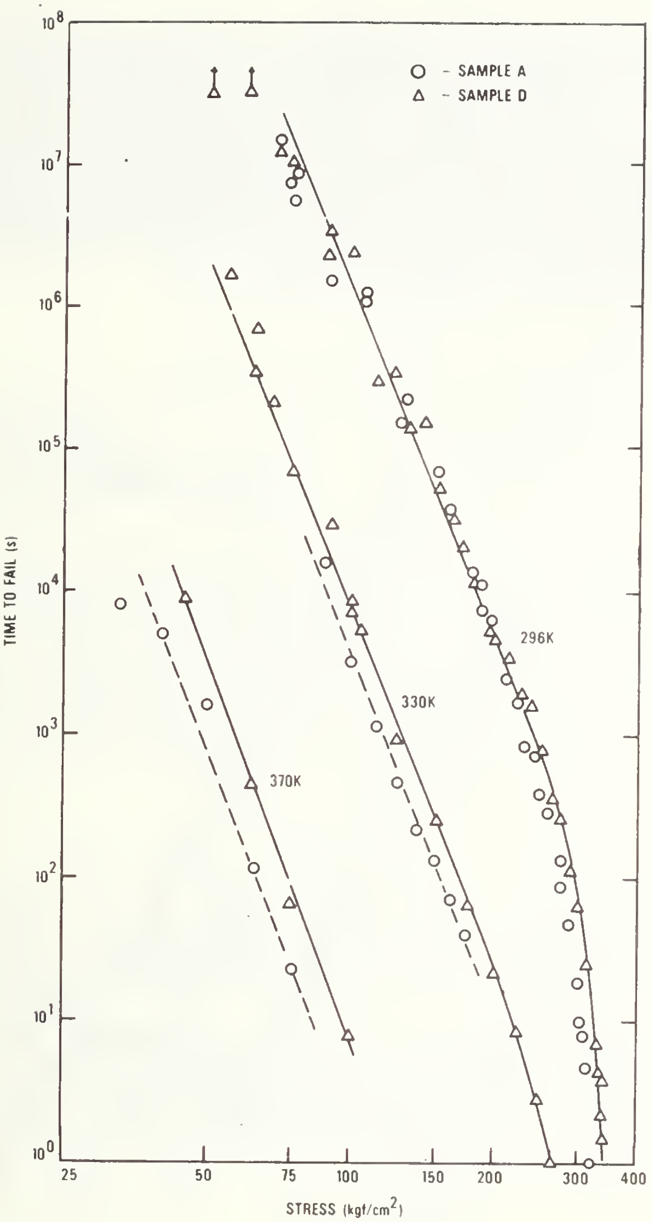

Figure 3.1.3 - Comparison of time to fail versus applied stress in uniaxial extension for two samples of high density linear polyethylene in air.

Another difference which should be noted is that both samples A and B used in the earlier studies had experienced rather long shelf lives prior to molding ($\simeq$13 years), whereas sample D had just recently been manufactured. Therefore, it was not certain to what extent, if any, shelf life may be influential with respect to the properties under investigation. Based upon the results indicated in figure 3.1.3, it would appear that age probably had little, if any, effect, and that the primary difference was one of crystallinity and/or molecular weight. Nonetheless, in what follows, we have chosen sample D for further discussion since the experimental work carried out on this sample was more extensive than for sample A.

For the case of creep to failure in uniaxial extension, the data in figure 3.1.2 have been replotted on log-log coordinates in figure 3.1.4. The initial observation is that at all four temperatures examined the data fall on a line that is very nearly linear. Two exceptions can be noted, (1) at very high stresses, and (2) at room temperature for long times to fail. With regard to the first exception, it was pointed out in the previous report [1] that in this load region the creep occurs so rapidly that sufficient heat is generated (of the order of several degrees Celsius) to effectively lower the modulus of the specimen resulting in earlier failure. At long times to fail at room temperature, there appears to be a slight tendency for the curve to bend over. A similar trend was found for the highly crystalline samples B and C even when plotted on semilog paper. Unfortunately, there are not yet enough data points at long times to tell whether a further erosion from linearity will occur as the loading becomes smaller and smaller. The reader is reminded that 10^8 seconds represents about 3.2 years. The two points with arrows correspond to specimens which have yet to fail.

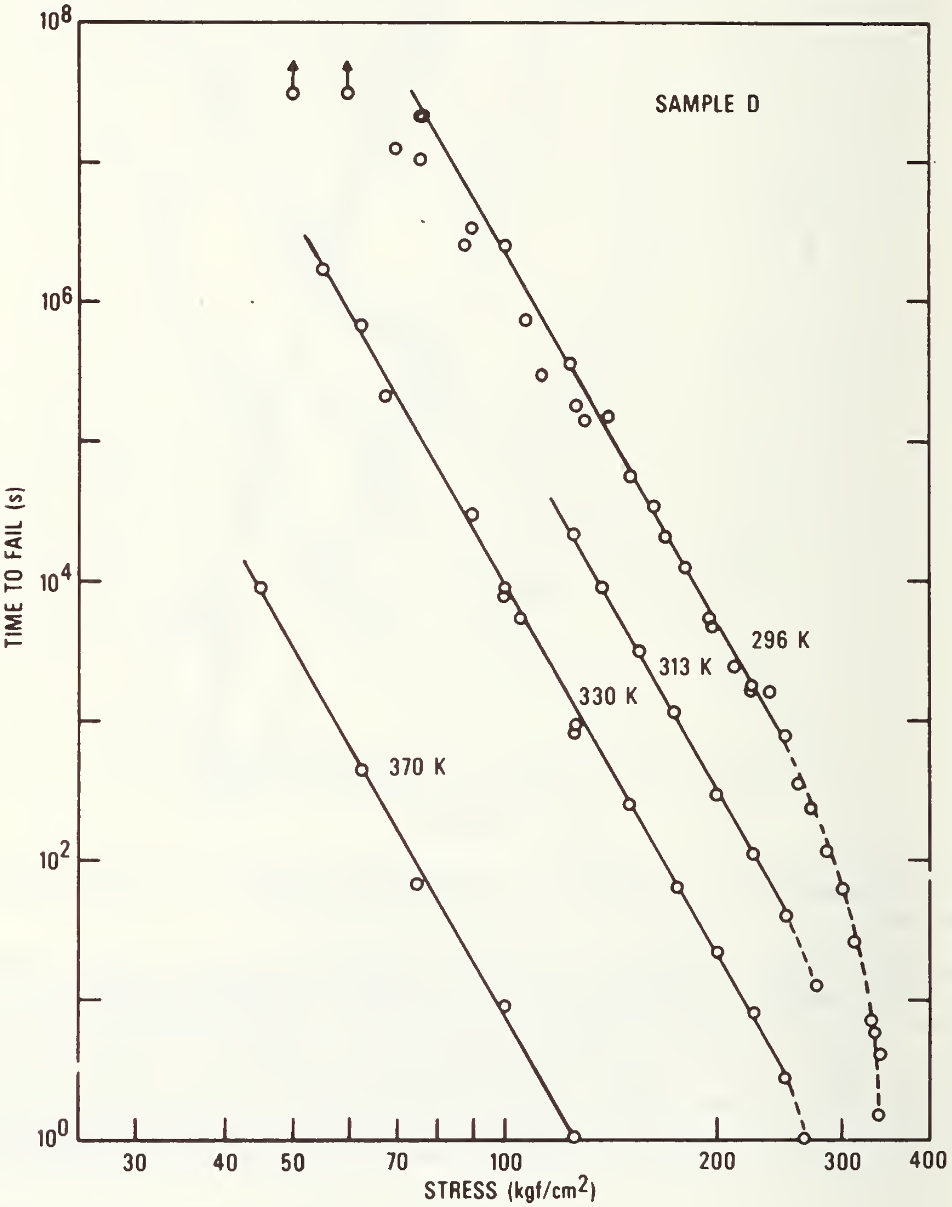

Figure 3.1.4 - Data of figure 3.1.2 replotted on log-log coordinates. Arrows indicate specimens still under test.

In addition to the high degree of linearity of the different curves in figure 3.1.4, a second major feature is that they are parallel to one another as well. In Section 2, the point was made, which is central to the issue of predicting lifetime behavior based on accelerated testing, is the assumption that test data obtained at different temperatures can properly be superposed to provide one master curve. This means that the functional form of the time to fail versus applied stress curves must not be substantively different at different temperatures. The linear and parallel nature of the curves shown in figure 3.1.4 suggest that on semilog paper the data for sample D might obey an exponential equation of the form

$$t_f = Ae^{B\sigma^{C}} \qquad (3.1.1)$$

where t_f = time to fail;
σ = applied stress;
A and B are material constants;
C = an exponent to be determined.

Using equation (3.1.1), we have fit all four curves shown for sample D in figure 3.1.3, and then, by shifting the curves obtained at each elevated temperature both vertically and horizontally, all the data now appear on one master curve which is shown in figure 3.1.5. The shift factors are shown by the crosses near the left ordinate axis, or time axis, in the figure, and have as their reference point zero stress and 1 second. With the exception of the high load range where the temperature rise during creep becomes a problem, the superposition is remarkably good over nearly 8 decades in time. The solid line represents a fit of the room temperature data to the equation

$$t_B = (2.1 \times 10^{14})e^{-3.6\sigma^{0.36}} \qquad \text{(sec.)}$$

where now the exponent of σ represents a best fit to the room temperature data. In terms of accelerated testing, say, for example, a test time of about 3 hours, an almost 6 decade saving in time required to conduct the tests has been accomplished by raising the temperature from room temperature to 370 K (97 °C).

Once a set of time shift factors ($a_t[T]$) has been determined, it is customary to plot the natural logarithm of the shift factors versus reciprocal absolute temperature (1/T). If the resulting line obeys a linear relationship, the behavior is said to be "Arrhenius" and from the slope of the line an apparent activation energy can be calculated from the expression

$$a_t[T] = Be^{\frac{\Delta H}{RT}} \qquad (3.1.2)$$

where $a_t[T]$ is the time shift factor, B is a constant, R is the gas constant (8.31 kJ/mole), T is absolute temperature (degrees Kelvin), and ΔH the apparent activation energy. For sample D such a plot is given in figure 3.1.6 where the shift factors are those employed in figure 3.1.5. It is clear that for this high density linear polyethylene the solid circles can be represented quite well by a straight line, the slope of which yields an apparent activation energy of 150 kJ/mole (36 kcal/mole). Here, then, is one instance where ΔH is constant over the entire range of temperature covered, which means that between room temperature and about 100 °C one should be able to predict from figures 3.1.5 and 3.1.6, failure times in uniaxial extension for any arbitrary stress and temperature, provided, of course, the conditions of specimen preparation are nominally the same.

Since the data in figure 3.1.2 were obtained from constant load experiments in creep, the same information should be available by examination of the respective creep curves. Therefore, creep data were obtained for a number of specimens at different temperatures at one level of stress in uniaxial extension (1.23 x 10^7 N/m^2 or 125 kgf/cm^2), and these results are shown in figure 3.1.7. In a similar fashion to that employed in figure 3.1.5

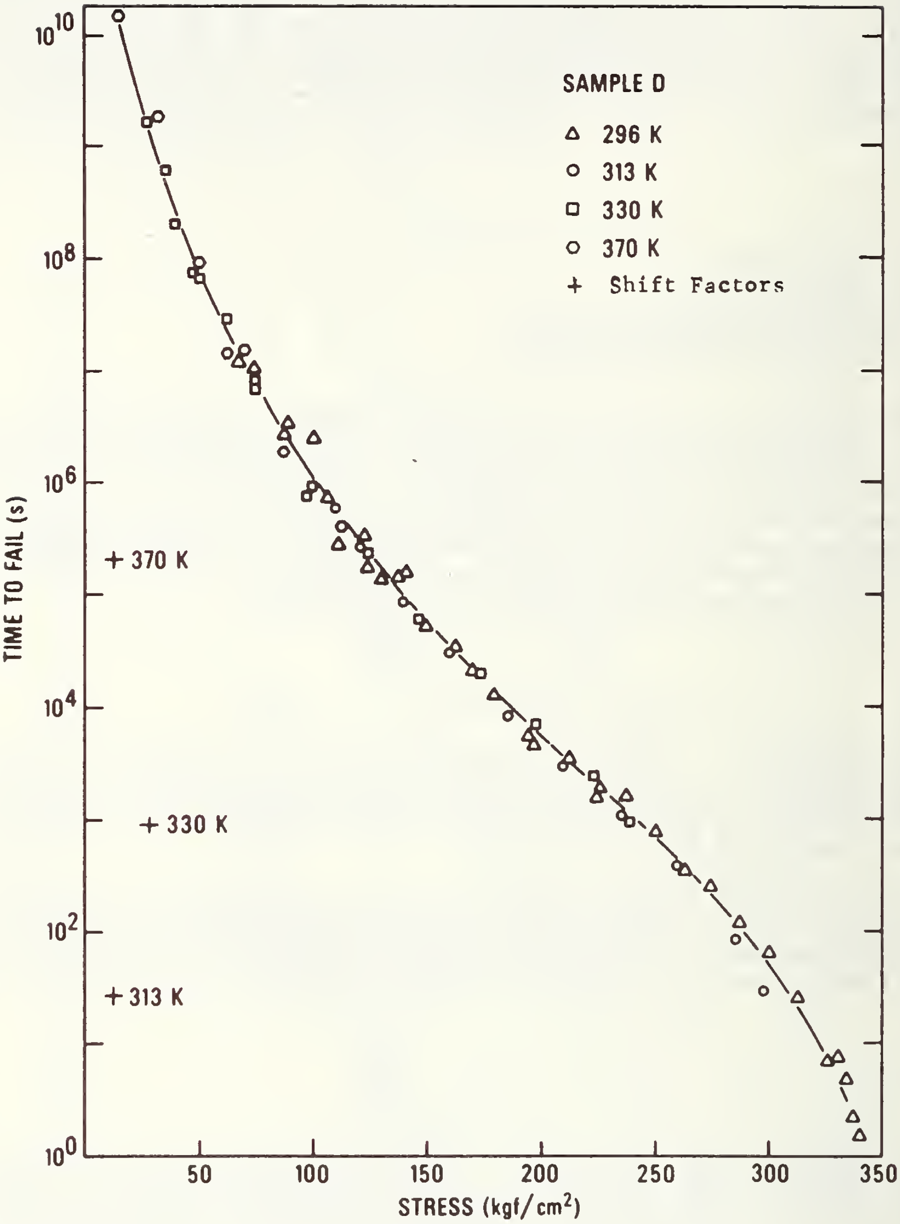

Figure 3.1.5 - Master curve for sample D in air obtained by superposing the data in figure 3.1.2 to 296 K (23 °C).

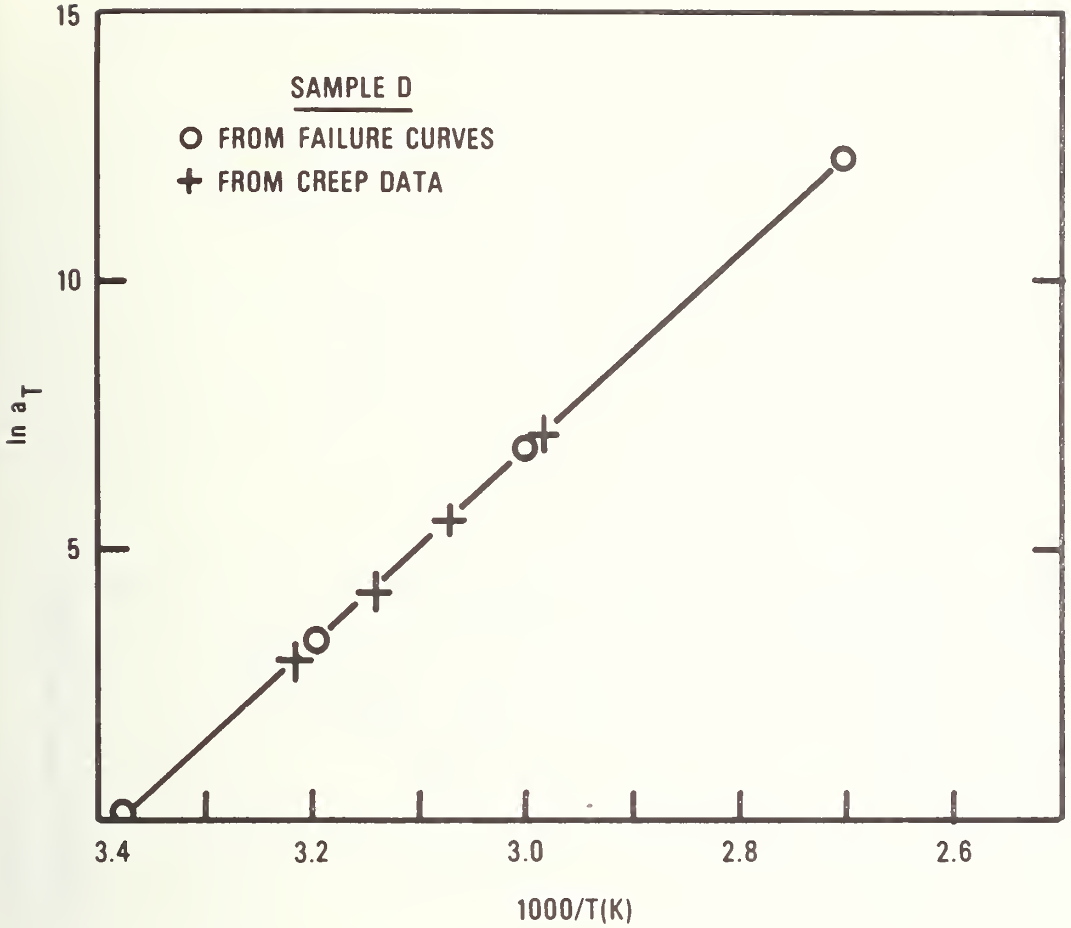

Figure 3.1.6 - Arrhenius plot of the shift factors determined from the master curve shown in figure 3.1.5 and from creep data obtained for sample D in air.

to superpose the data, the creep curves in figure 3.1.7 were superposed onto the room temperature (296 K) creep curve to yield the master curve given in figure 3.1.8. Again, the horizontal shift factors employed are those indicated along the time axis, and if plotted in figure 3.1.6 (crosses) yield the same straight line represented by the circles. Since both the lines shown are essentially superposed on one another, the same apparent activation energy is obtained by either method.

We turn now to a discussion of sample E, the branched ethylene-hexene copolymer. From the point of view of hazardous materials transportation, this polymer is of interest since it is recommended by the manufacturer as the base resin for large free-standing containers. Results of log time to fail versus stress in uniaxial extension are given for sample E in figure 3.1.9. Now, however, in the case of the branched polymer, by failure is meant the time to reach the onset of necking rather than actual fracture, since most specimens cold-drew, but did not fracture prior to removing the load. This difference in behavior will be shown presently for specimens tested to actual fracture at room temperature.

From a comparison of figures 3.1.2 and 3.1.9, it can be seen that for stresses above about 150 kg/cm^2, the branched polymer fails (necks) sooner at a given stress than does the linear polymer, but below 150 kg/cm^2 it rapidly becomes superior. This same behavior was observed previously [1] for sample A and the two commercial container materials which were branched. Since sample E was somewhat lower in density than D and contained branching, it almost certainly had lower crystallinity which could account for its poorer performance at very large stresses in uniaxial extension.

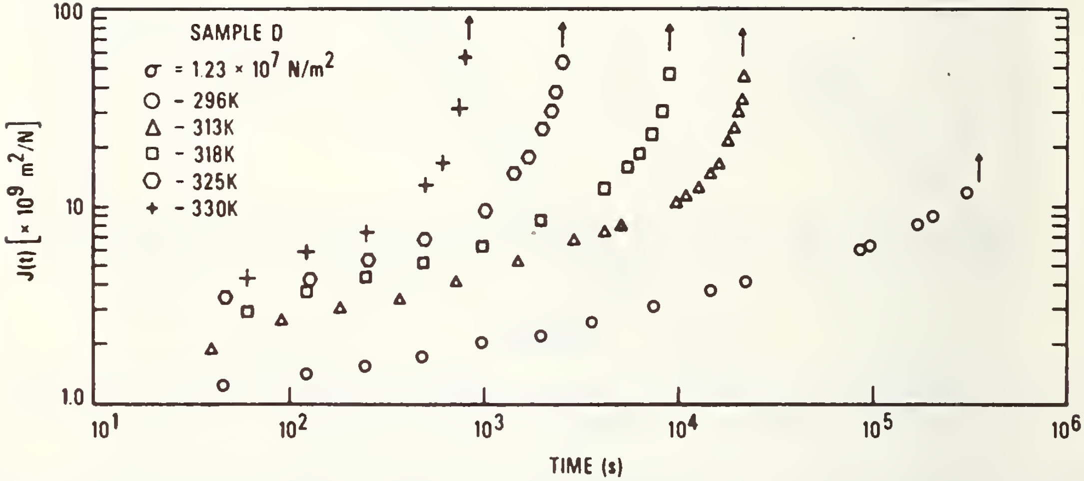

Figure 3.1.7 - Compliance J(t) versus time from creep to failure experiments on sample D. Arrows indicate the onset of cold-drawing.

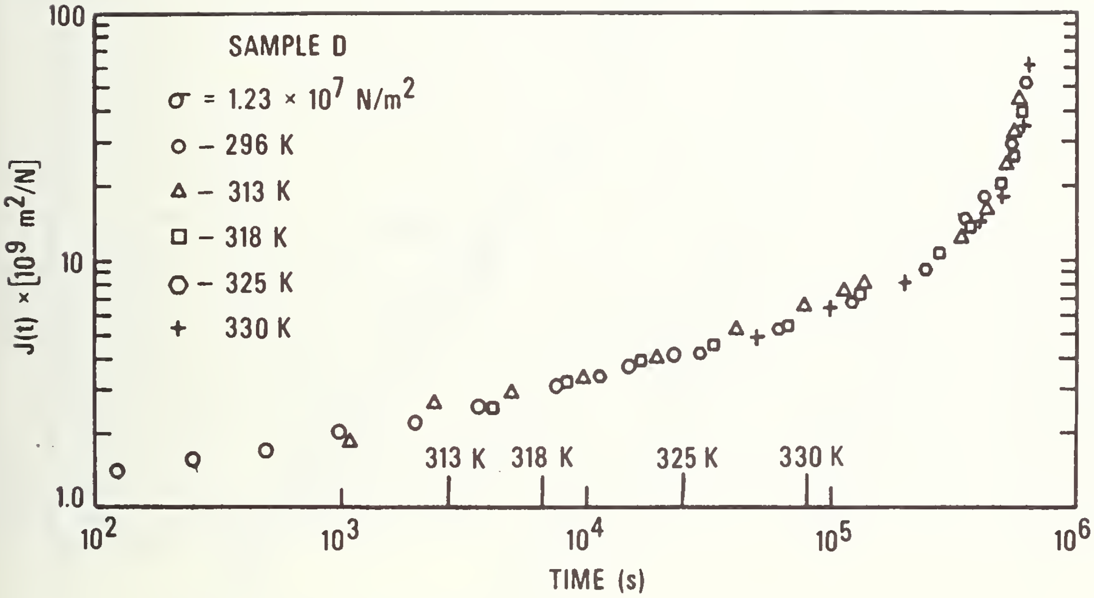

Figure 3.1.8 - Superposition of creep data shown for sample D in figure 3.1.7. Shift factors are indicated along the time axis.

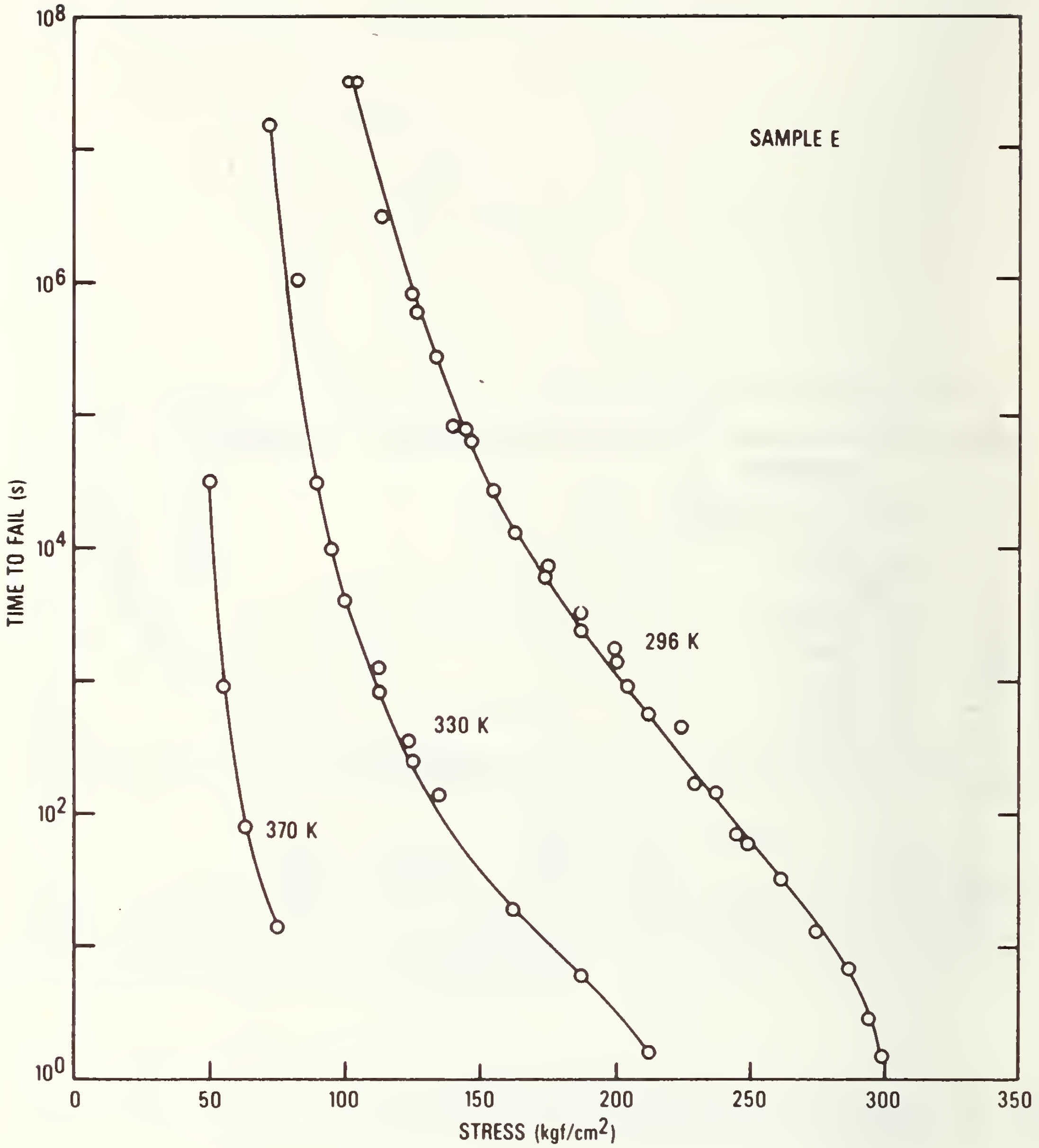

Figure 3.1.9 - Time to fail versus applied stress in uniaxial extension for an ethylene-hexene copolymer (sample E) in air.

The behavior of the copolymer perhaps can better be seen by replotting the data of figure 3.19 on log-log coordinates as in figure 3.1.10. Unlike sample D for which the data can be represented quite well by straight lines, such is not the case here for sample E. Even on log-log coordinates there is a sharp curvature upwards at all three temperatures, and it is clear that the data do not obey so simple a relationship as that for the linear polymer. In figure 3.1.10, the open symbols now correspond to the observation of necking or cracking, whereas the filled symbols represent actual fracture. At room temperature, observe that for a stress above about 200 kg/cm^2, the specimens necked and then fractured almost simultaneously. However, below 200 kg/cm^2, specimens first necked and then cold-drew to an extension ratio (λ) of about 7 or 8. It is interesting that the region of stress separating neck formation followed by fracture from that of neck formation followed by cold-drawing is exceedingly narrow. This transition zone also happens to coincide with the point at which the downward curvature appears in the failure curve. The several specimens which cold-drew without breaking were then maintained under the same load until fracture occurred. Note that for these specimens, fracture occurred approximately two decades in time later than the point of global instability (necking). Although the ultimate extension ratio reached before fracture depended upon the applied stress, it was generally between 12 and 14.

It is again useful, from the point of view of accelerated testing, to superpose the data in figure 3.1.9, in order to obtain a master curve from which the shift factors can be used to determine an apparent activation energy. However, after several attempts, it was discovered that, although superposition was possible which was reasonable in appearance (see figure 3.1.11), no suitable set of shift factors could be found which yielded a straight line on an Arrhenius plot. Therefore, as in the case of sample D, a series of creep curves were obtained for the branched polymer at different temperatures and same level of applied stress. Several results are shown in figure 3.1.12, where the data have been superposed onto the room temperature creep curve, and the horizontal shift factors are given on the Arrhenius plot in figure 3.1.13. It is immediately apparent that even the creep results do not yield a straight line and that this polymer, unlike sample D, cannot be characterized by a unique ΔH. Nevertheless, in figure 3.1.11, we have superposed the 330 K data shown in figure 3.1.9 onto the room temperature curve using the shift factor determined from the creep experiment. Since no creep data were available at 373 K (97 °C), those points were shifted in order to obtain the best fit in appearance, and for that reason, the shift factor shown in figure 3.1.13 is indicated by the solid circle. Unfortunately, it was also discovered that the very same data could be shifted to fit essentially the same curve equally well in appearance but with different shift factors. Therefore, an important point to be made here with respect to accelerated testing is that some care must be exercised in determining a master curve, especially for polymers such as sample D for which the time to fail versus applied stress curve becomes very steep, in particular at high temperature and/or long failure times. As we have seen before, this ambiguity emphasizes the necessity to have at least some long-time failure results in order to have a greater degree of confidence in predicting long time behavior.

3.2 Stress Cracking of Polyethylene in Unaxial Extension

One of the main objectives of this report is to examine the stress-cracking behavior of polyethylene under a variety of imposed conditions, a primary goal being to provide information which will be useful in the establishment of an improved stress-cracking test pertinent to the transportation of hazardous materials in large reusable plastic containers. From the discussion in Section 2, it is apparent that a large body of literature already exists on the subject, and in some instances attempts have been made to establish master design curves from which lifetime in the presence of a specified stress-cracking agent can be predicted for fairly arbitrary conditions of stress and temperature. Sections 3.2 and 3.3 will summarize the results of a number of experiments carried out in our laboratory, where both uniaxial and biaxial stresses have been employed in the presence of several known stress-cracking agents. Section 3.2 will be concerned with stress-cracking behavior under conditions of a uniaxially applied stress; experiments involving biaxial stresses will be discussed in Section 3.3.

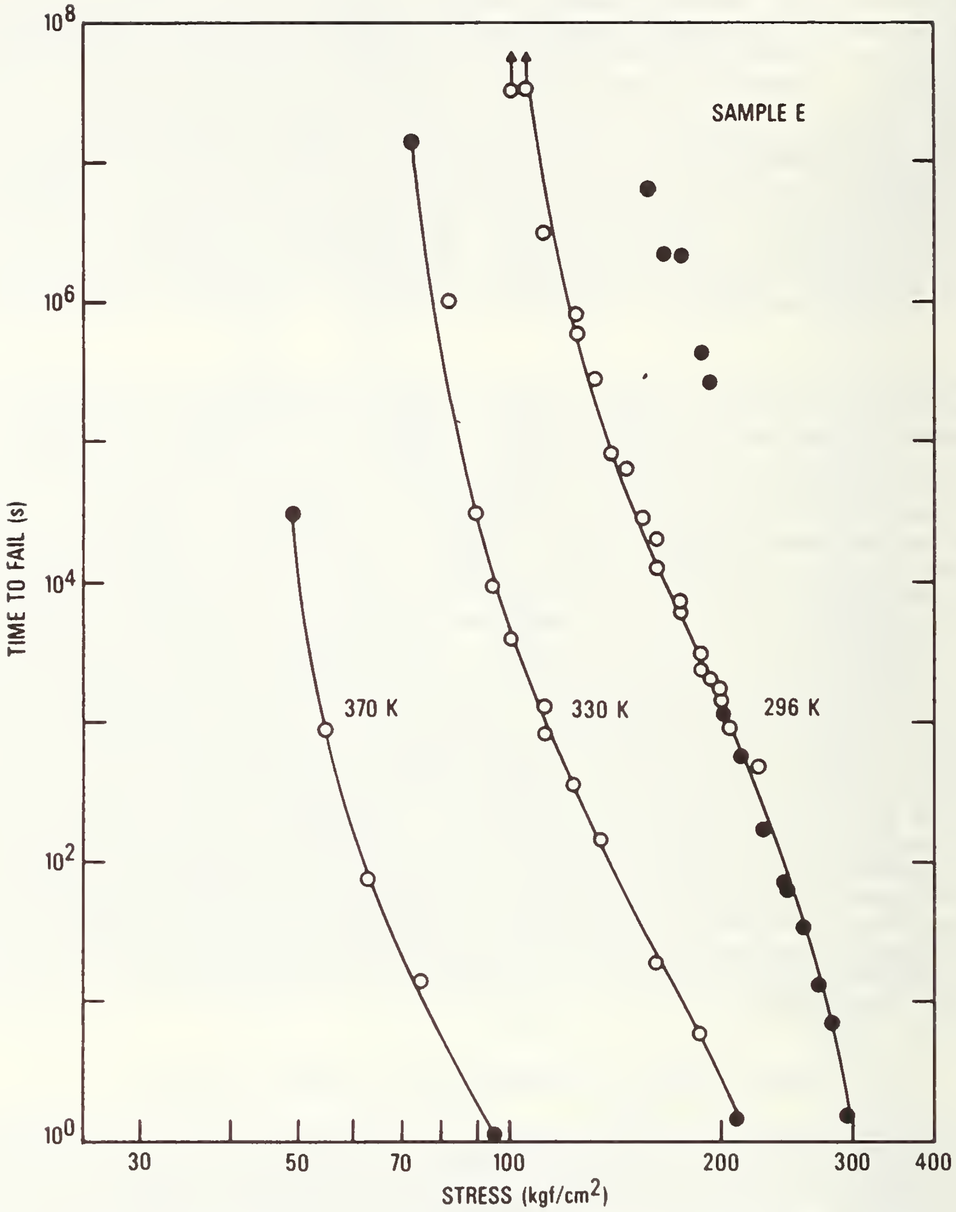

Figure 3.1.10 - Data from figure 3.1.9 replotted on lon-log coordinates. Open circles correspond to the time required to form a neck, filled circles to the time of actual fracture. Arrows indicate specimens still under test.

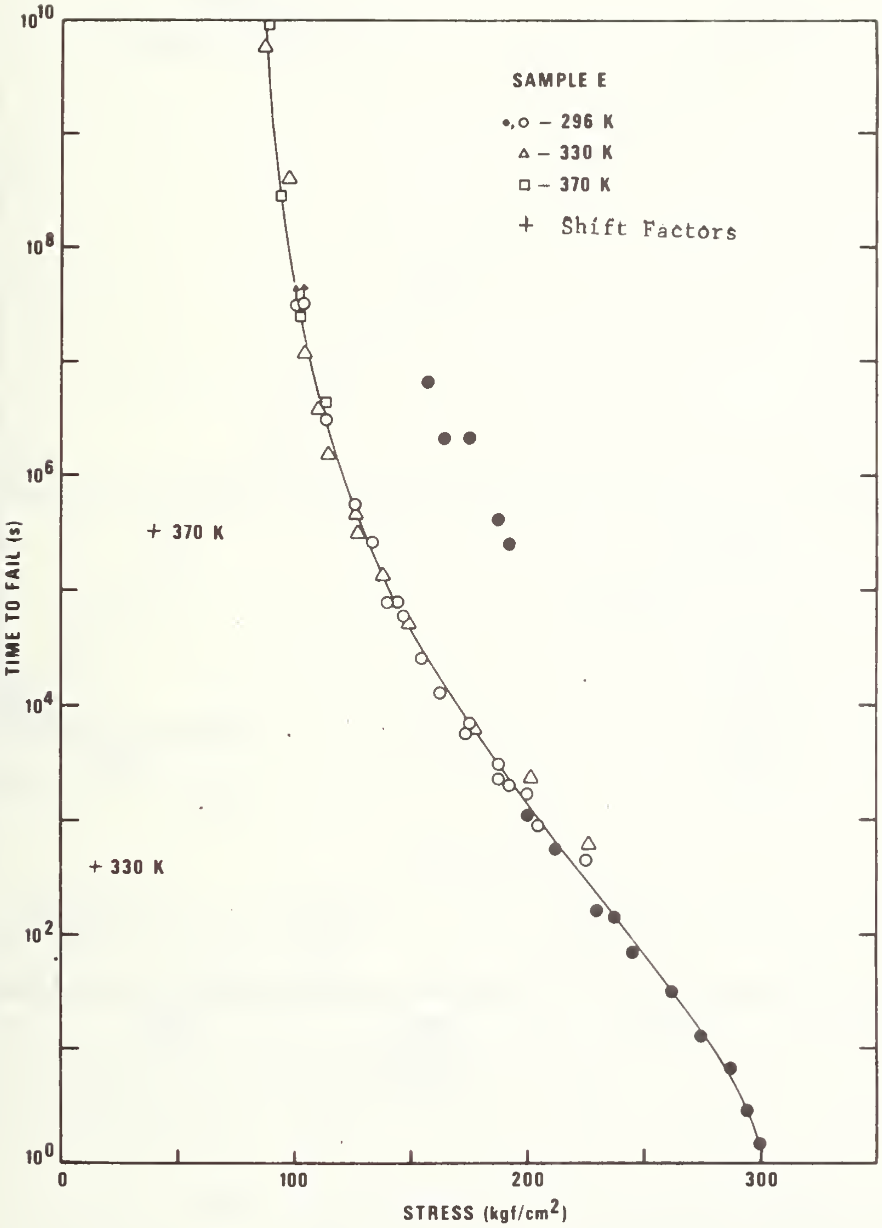

Figure 3.1.11 - Master curve for sample E in air obtained by superposing the data from figure 3.1.9 to 296 K (23 °C). Symbols the same as in figure 3.1.10.

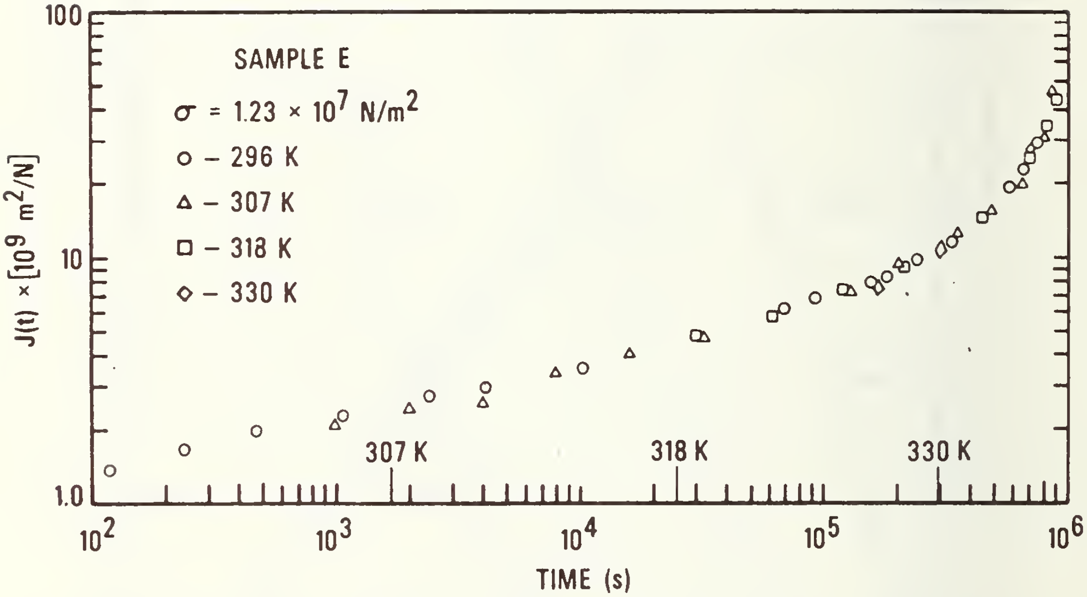

Figure 3.1.12 - Superposition of creep compliance data for sample E in air. Shift factors are indicated along the time axis.

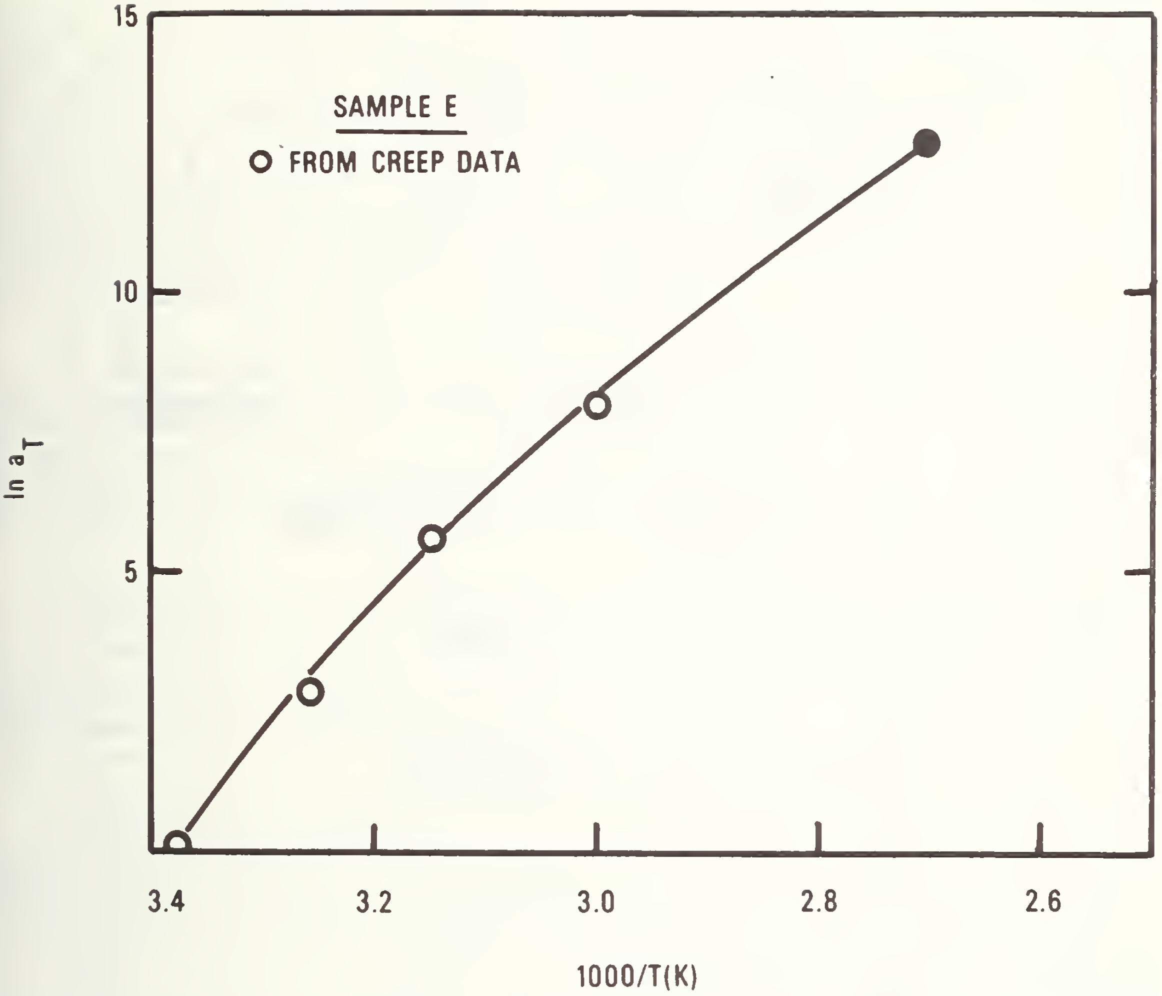

Figure 3.1.13 - Arrhenius plot of the shift factors determined from the master curve for sample E shown in figure 3.1.11.

Experiments similar to those described in Section 3.1 were carried out on the same two polyethylene samples (D and E), but in the presence of a stress-cracking agent. The experimental procedures employed here were essentially the same in principle as those described in reference [9], and a diagram of the apparatus used is shown in figure 3.2.1. The desired temperature was maintained by circulating a mixture of water and ethylene glycol from a controlled temperature bath through a double walled pyrex glass condenser surrounding the specimen.

The bottom was sealed with a rubber stopper to prevent leakage and the top covered with aluminum foil so that only a small opening was left to allow the support filament to move unimpeded. All of the experimental data were obtained with the specimen submerged in the stress-cracking agent rather than in the vapor, and the temperature was measured by placing a thermometer in the liquid next to the center of the specimens. It was found typically that a temperature gradient of from 0.1 to 0.2 K occurred between the bottom and top clamp. Fiducial marks were placed on the straight portion of the specimen in order to make creep measurements. It is worthy of note that most types of inks, one exception being India ink, and other types of marking substances tested turned out to be stress-cracking agents themselves, and even in air the specimens nearly always failed at one of the fiducial marks.

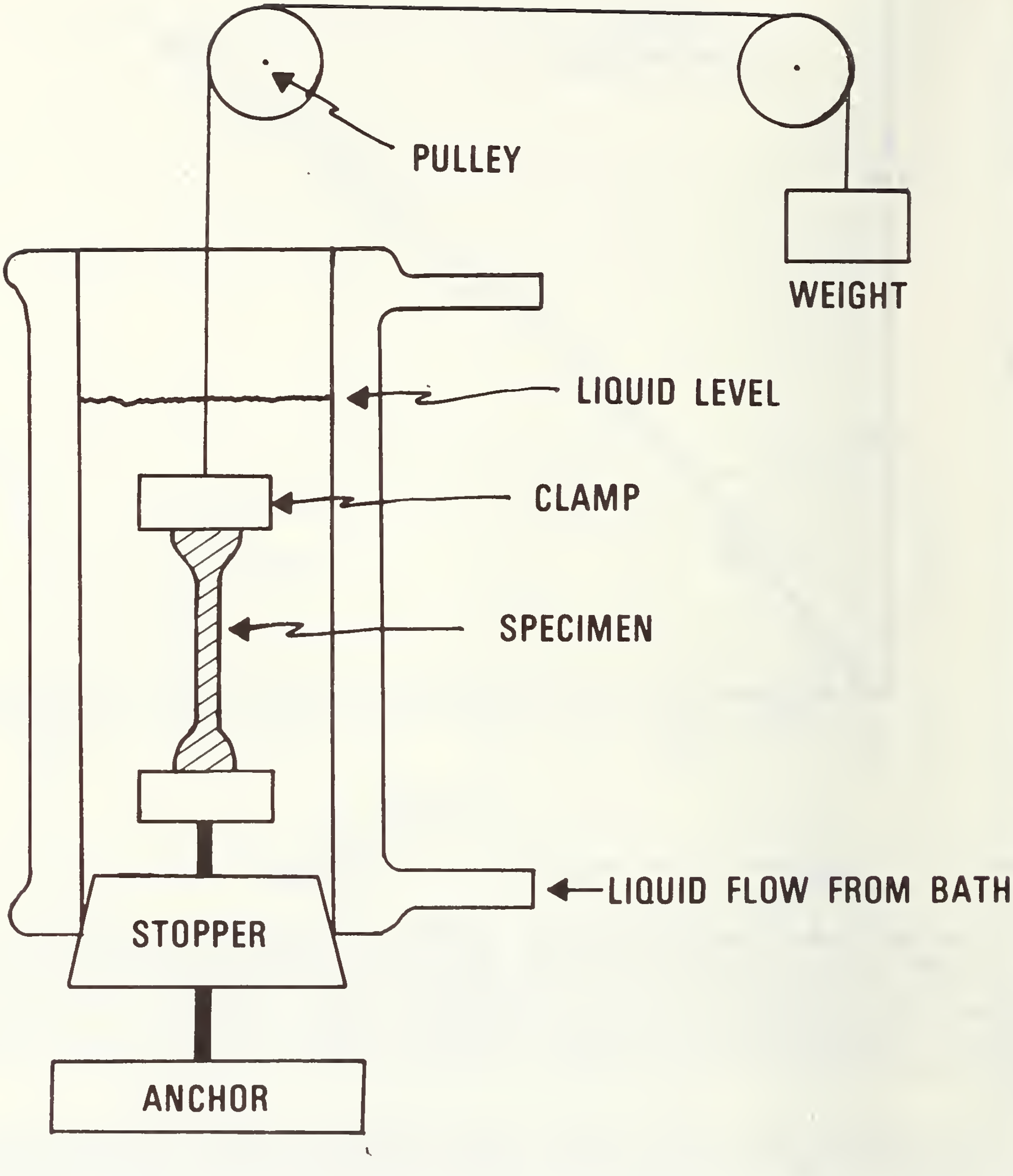

Figure 3.2.1 - Schematic diagram of apparatus for determining stress-crack resistance in uniaxial extension.

Shown in figure 3.2.2 are results for sample D in the presence of three known stress-cracking agents. Nonylphenoxypoly(ethyleneoxy)ethanol was chosen since it is generally regarded to be one of the most active of the so-called surface active stress-cracking agents and is in widespread use in present stress-cracking tests, including ASTM tests. Both n-hexane (C_6H_{14}) and n-dodecane ($C_{12}H_{26}$) are normal alkane solvents known to swell polyethylene. In all cases, the specimens were presoaked in the stress-cracking agent for at least 16 hours prior to loading. It has been reported in the literature that in the case of nonylphenoxypoly(ethyleneoxy)ethanol, presoaking the specimen has little, or no, effect on the lifetime behavior, as was found to be the case here as well. However, for the two solvents there was a pronounced difference in lifetime at the relatively large stresses depending upon the time of presoaking (up to times of about 16 hours). The same result was also found from weight gain measurements where after about 16 hours (overnight) the specimens apparently absorbed very little additional solvent.

The solid lines in figure 3.3.2 correspond to the same solid lines drawn through the data points shown in figure 3.1.2 for sample D at 296 K and 330 K in air. Observe first that at room temperature, the presence of nonylphenoxypoly(ethyleneoxy)ethanol has little or no effect on lifetime at stresses above about 150 kgf/cm^2; but below that value the lifetime becomes increasingly shorter until reaching a point at low stresses where the data points are displaced a nearly constant amount from the solid line. At the same time, the effect at 330 K (57 °C) is an approximately constant shift over the entire range of stresses tested, the amount of shift being about the same as that for the long times at room temperature.

By comparison, the two solvents which are readily absorbed into polyethylene accelerate failure much more rapidly. At a stress of 75 kgf/cm^2, the presence of hexane or dodecane has the same influence on time to fail at room temperature as it does running the same test in air at 330 K (57 °C). Also, at 50 kgf/cm^2, the presence of solvent at 330 K has decreased the lifetime by about four decades in time from that at room temperature in air, which demonstrates the highly disastrous effect of having both solvent and elevated temperature present at the same time the specimen is under stress.

Another point to be made here is the following. Although the presence of nonylphenoxypoly(ethyleneoxy)ethanol at 330 K decreased the lifetime at a stress of 100 kgf/cm^2 by a factor of nearly 1000 from that at 296 K in air, the overall effect is primarily one of temperature and not one of stress-cracking agent. Only a modest decrease in time to fail occurred due to the presence of nonylphenoxpoly(ethyleneoxy)ethanol. However, in the following section, we shall see that for biaxial stress conditions the effect can be much more dramatic. This is one reason why an effort is generally made in developing stress-crack tests to incorporate a biaxial stress component in order to enhance failure under conditions more realistic of in-use conditions.

Now according to the same procedures used in Section 3.1, the data in figure 3.2.2 have been superposed to yield the result given in figure 3.2.3. In figure 3.2.3 room temperature (296 K) has been chosen as the reference temperature and the shift factor for the 330 K (57 °C) solid line is the same as the employed in figure 3.1.5. The data for the three stress-cracking agents at 330 K have, in turn, been shifted correspondingly the same amount. As is evident, the stress-crack results obtained at 330 K correlate very well with the stress-crack behavior observed at room temperature. We point out that the shifting procedure followed in figure 3.2.1 is somewhat different from that employed in a number of previous studies, for example, references [11] or [17]. In those investigations, the superposition was carried out with respect to a reference state specified not by temperature alone, but also by adverse environment. One advantage in presenting the data as shown in figure 3.2.3 is that the relative severity of a given stress-cracking agent can readily be judged not only against other stress-cracking agents, but against the maximum lifetime possible in the absence of an adverse environment. It is interesting to observe from figure 3.2.3 that, to the extent lifetime behavior at room temperature can be predicted realistically based on a superposition of accelerated test data obtained at higher temperatures (330 K), even at very small stresses one must conclude that the presence of solvent will cause failure in a finite time.

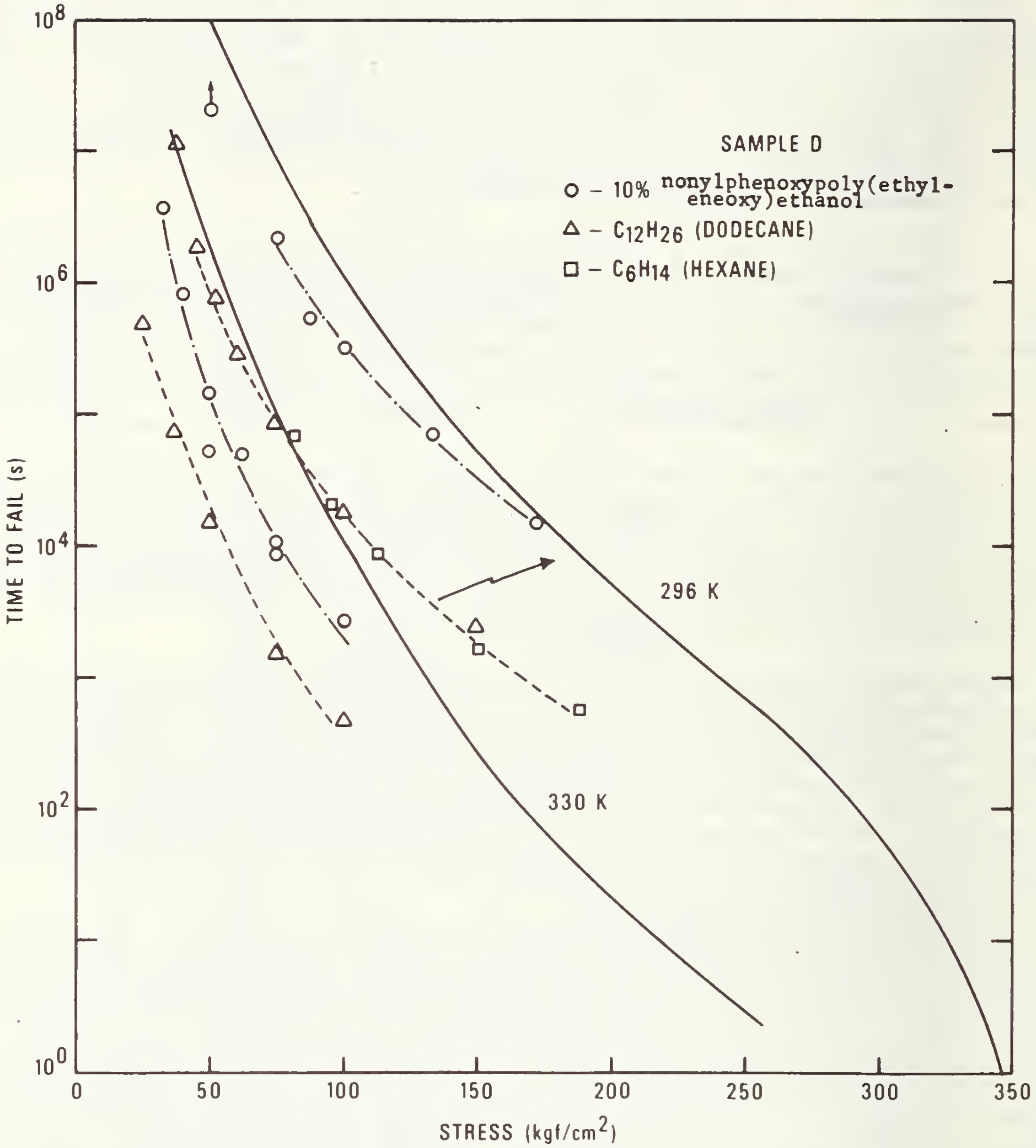

Figure 3.2.2 - Time to fail versus applied stress in uniaxial extension for sample D in various stress-cracking agents. The solid lines represent the data at 296 K and 330 K from figure 3.1.2.

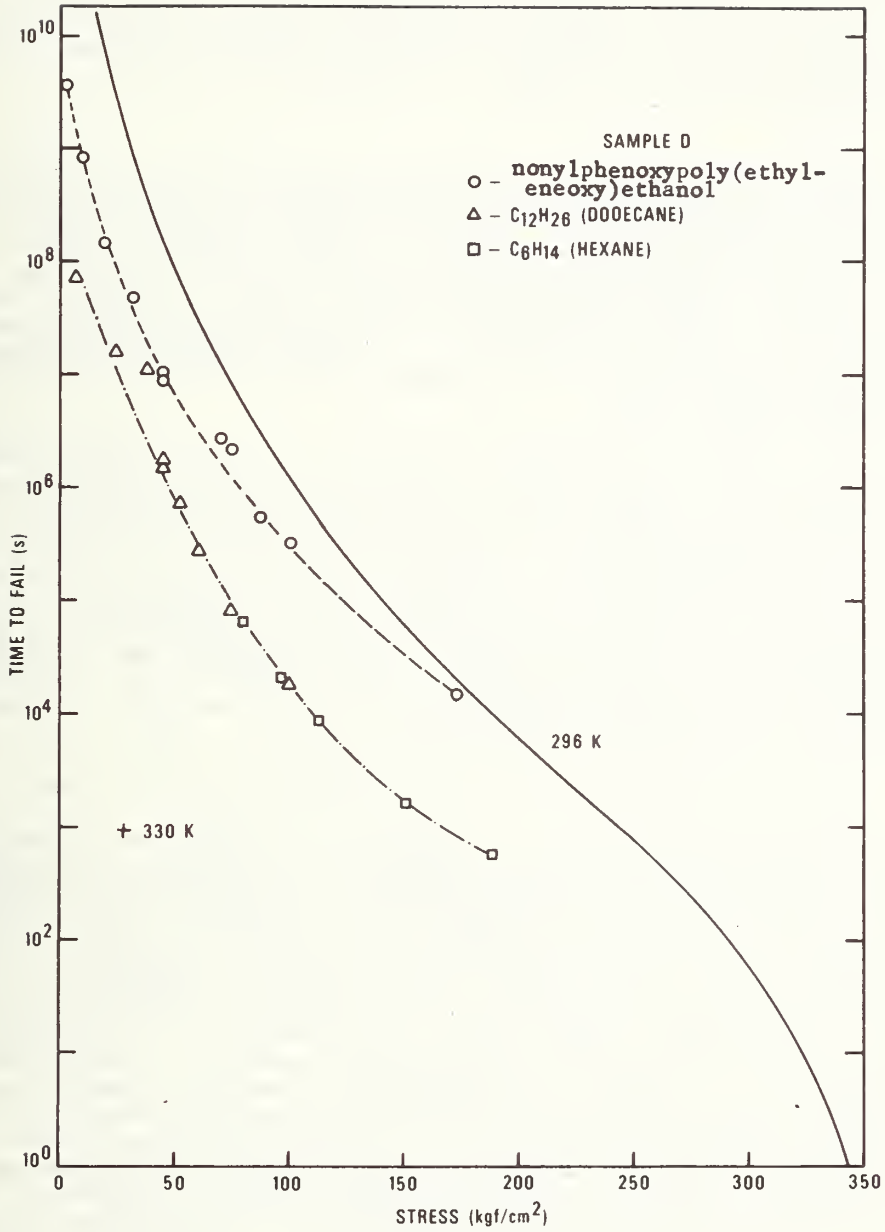

Figure 3.2.3 - Master curve for the stress-crack behavior of sample D at 296 K. The solid line represents the data from figure 3.1.5 and the shift factor for the 330 K data is indicated by the cross.

From the standpoint of a qualification test a more useful procedure may be to superpose the data not to room temperature as a reference temperature, but to a temperature corresponding approximately to the highest temperature expected in use. Such a procedure has been followed by Fulmer [17] in bottle tests where the reference temperature was chosen to be 333 K (60 °C). In figure 3.2.4, the same data presented in figure 3.2.2 are also shown superposed where the reference temperature is now 330 K (57 °C). The overall behavior is essentially the same as that seen in figure 3.2.3 except that the times to fail are now substantially reduced.

Analogous results to those shown in the previous three figures are presented in figures 3.2.5, 3.2.6, and 3.2.7 for Sample E, the branched copolymer. Whereas, in the case of the linear polymer (sample D), the presence of nonylphenoxypoly(ethyleneoxy)ethanol had a significant effect on lifetime in uniaxial extension at room temperature, based on only limited data there is no evidence that the nonylphenoxpoly(ethyleneoxy)ethanol had any influence on the branched copolymer at 296 K. It was pointed out in Section 2 that branching greatly improves stress-crack resistance. That this is true, can readily be seen by comparing the superposed data shown in figures 3.2.6 and 3.2.3. In fact, below about 150 kgf/cm^2, it is apparent that the branched copolymer in nonylphenoxypoly(ethyleneoxy)ethanol is superior even to the linear polymer in air.

As was true for sample D, the decrease in time to fail is more severe for the branched copolymer in the presence of solvent than in nonylphenoxypoly(ethyleneoxy)ethanol and, as was also true in the earlier example, the net effect is primarily one simply of shifting the entire curve from that expected in air. Note however that in figure 3.2.6, the curve for n-dodecane ($C_{12}H_{26}$) no longer coincides with that for n-hexane (C_6H_{14}), as was the case in figure 3.2.3. Due to its volatility, no experiments were carried out at 330 K (57 °C) using n-hexane, and no data are available for n-dodecane at 296 K. Nonetheless, it would appear that the molecular weight of the solvent may be an important parameter in determining the stress-crack behavior of the branched polymer. Similar behavior occurs in the presence of silicon oils of different molecular weights [20], where the lower the molecular weight is (higher viscosity), the more destructive the effect is.

3.3 Stress-Cracking of Polyethylene Subject to Biaxial Stress

In the two preceding subsections, experiments have been described in which specimens of polyethylene were stressed uniaxially at constant load in the presence of various stress-cracking agents. In the several paragraphs which follow, we shall further examine the stress-crack behavior of one type of polyethylene when the applied stress is essentially biaxial, as is more likely to be the case under actual in-use conditions. The method of investigation chosen here is very similar in principle to that employed by Rivlin and Saunders [27] to study the deformation of rubber. A diagram of the apparatus used is given in figure 3.3.1. The specimen, in the shape of a flat sheet or film, is clamped between a top plate and base piece. In the present case, a 15.25 centimeter diameter hole (6 inches) was cut in the top plate and the top and bottom edges of the hole perimeter rounded and tapered as shown in order to minimize curvature and eliminate sharp edges at the point of contact of the sheet with the top plate. An o-ring located very close to the clamping point was inserted to prevent loss of gas around the edge when the vessel was pressurized. The gas inlet was connected via a pressure reducing valve either to a cylinder of nitrogen gas or to an air line. Once the specimen was clamped in place, the system was pressurized and maintained at a constant pressure until failure occurred. In the present experiment, failure was detected generally either by sound or more often by the feel of escaping gas. A more refined version of this test method would require a highly sensitive pressure indicator installed in the gas line which, upon a slight decrease in pressure, would trigger a switch to shut-off the gas supply and record the time to failure. In experiments where a stress-cracking agent was present, failure was easily detected by the appearance of liquid or bubbles on the outer surface of the specimen. Initially a small amount of stress-cracking agent was placed in the bottom of the pressure reservior and the specimen then clamped in place. Once pressurized, the entire assembly was immediately inverted to insure that the stress-cracking agent remained near the center of the test specimen (at the lowest point of the bubble) and did not contact the specimen near the o-ring seal. In cases where liquid was allowed to contact the specimen at or near the clamping point, failure often occurred there rather than at the center of the bubble, an indication that the maximum stress may

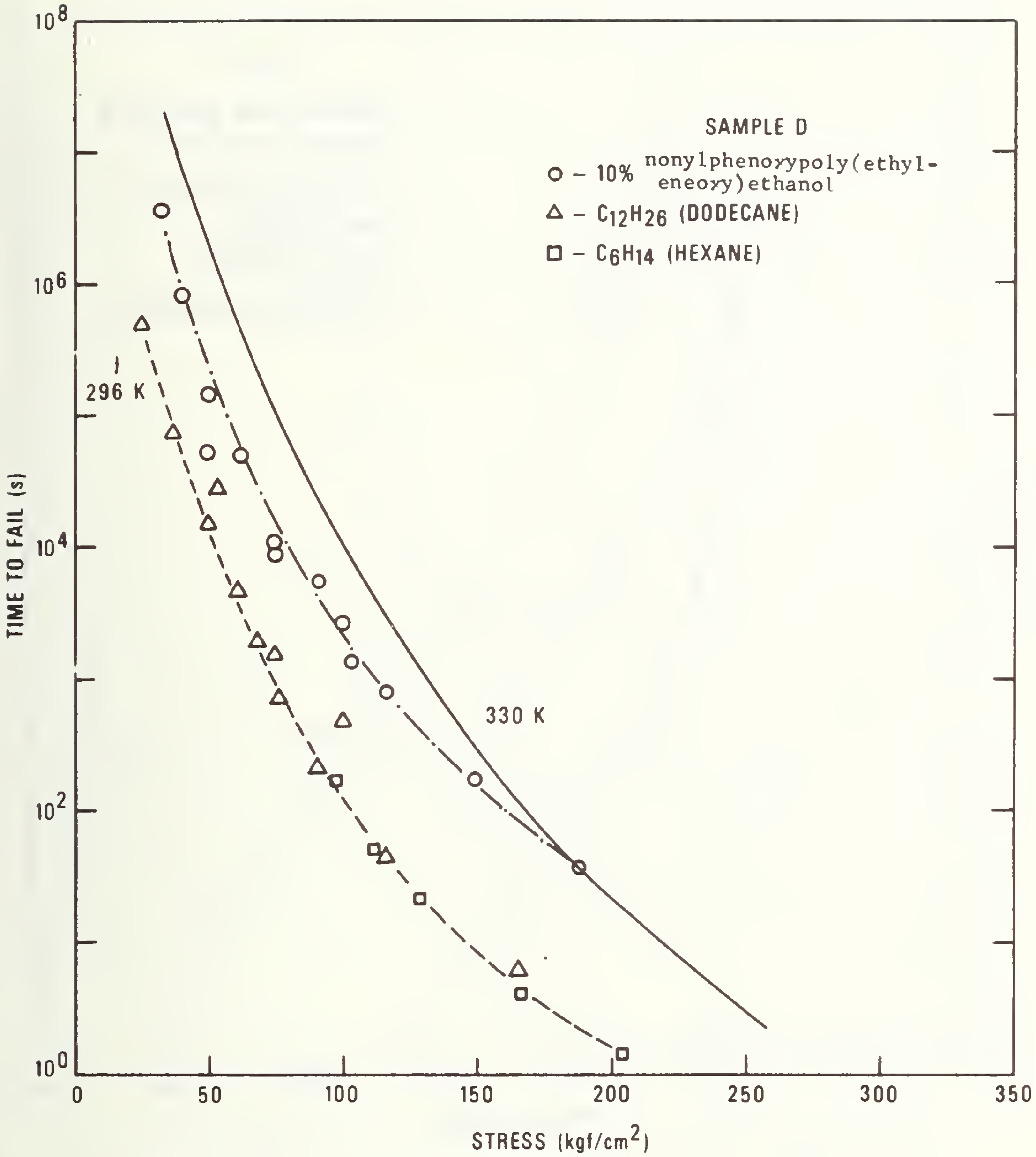

Figure 3.2.4 - Master curve for the stress-crack behavior of sample D at 330 K. The reference point for the room temperature shift factor indicated by the cross is the upper left corner of the figure.

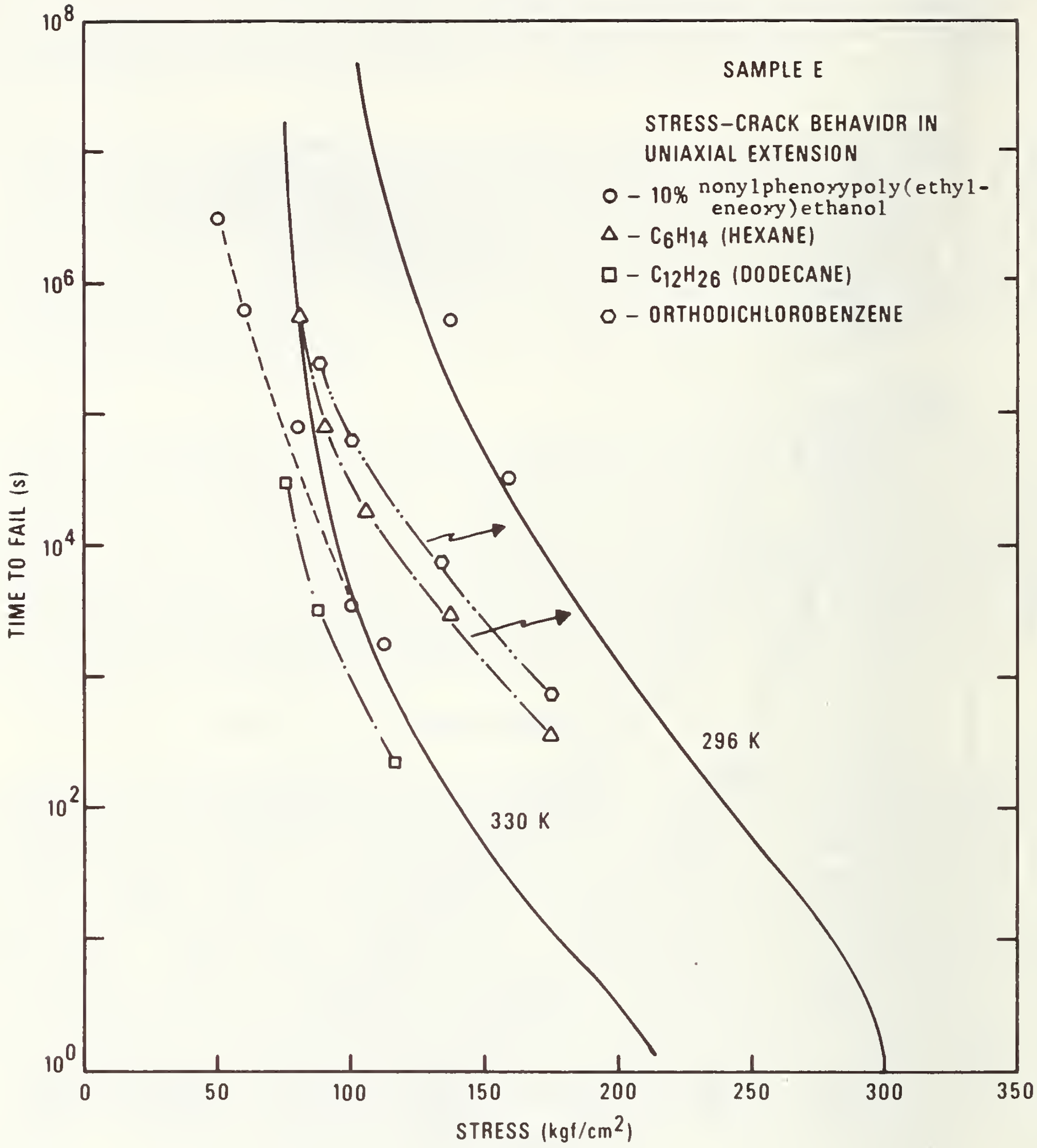

Figure 3.2.5 - Time to fail versus applied stress for sample E in various stress-cracking agents. The solid lines represent the data at 296 K and 330 K from figure 3.1.9.

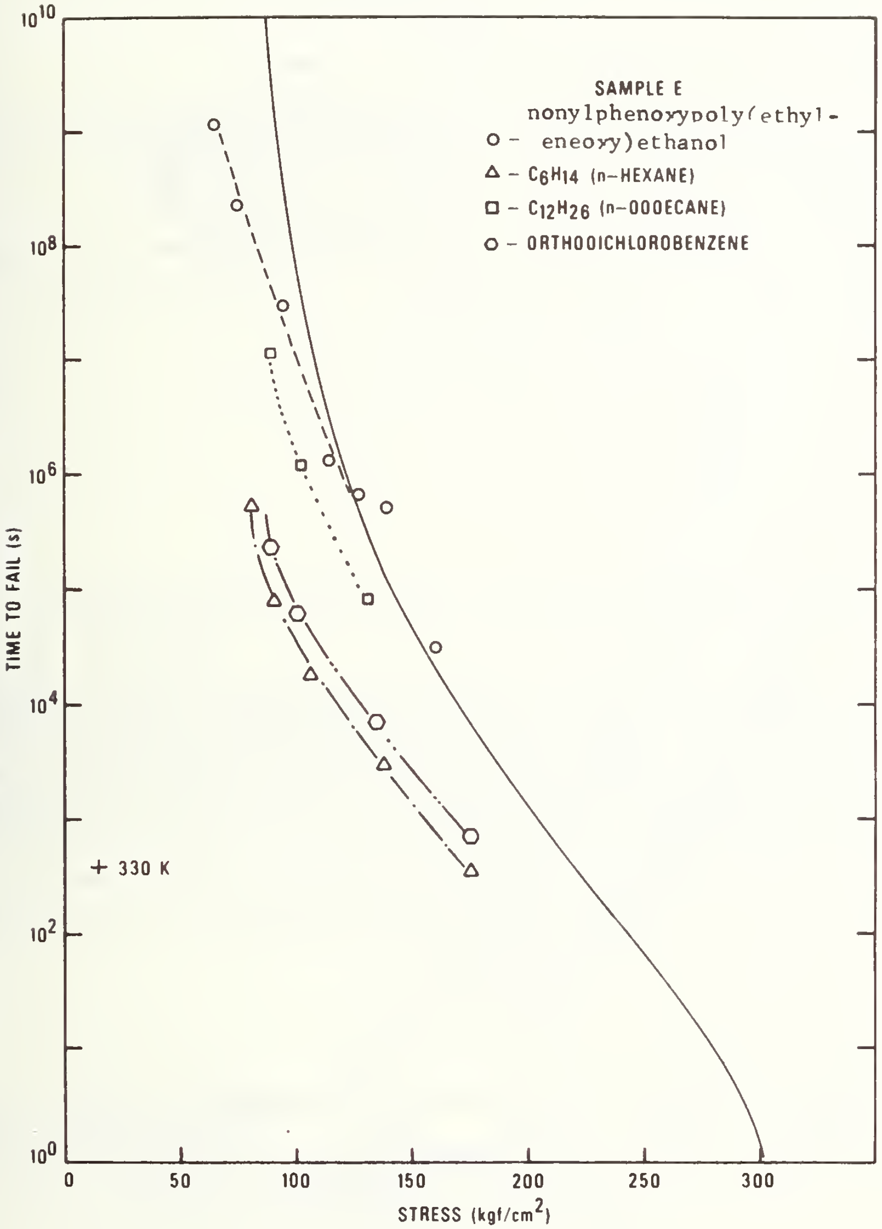

Figure 3.2.6 - Master curve for the stress-crack behavior of sample E at 296 K. The shift factor for the 330 K data is indicated by the cross.

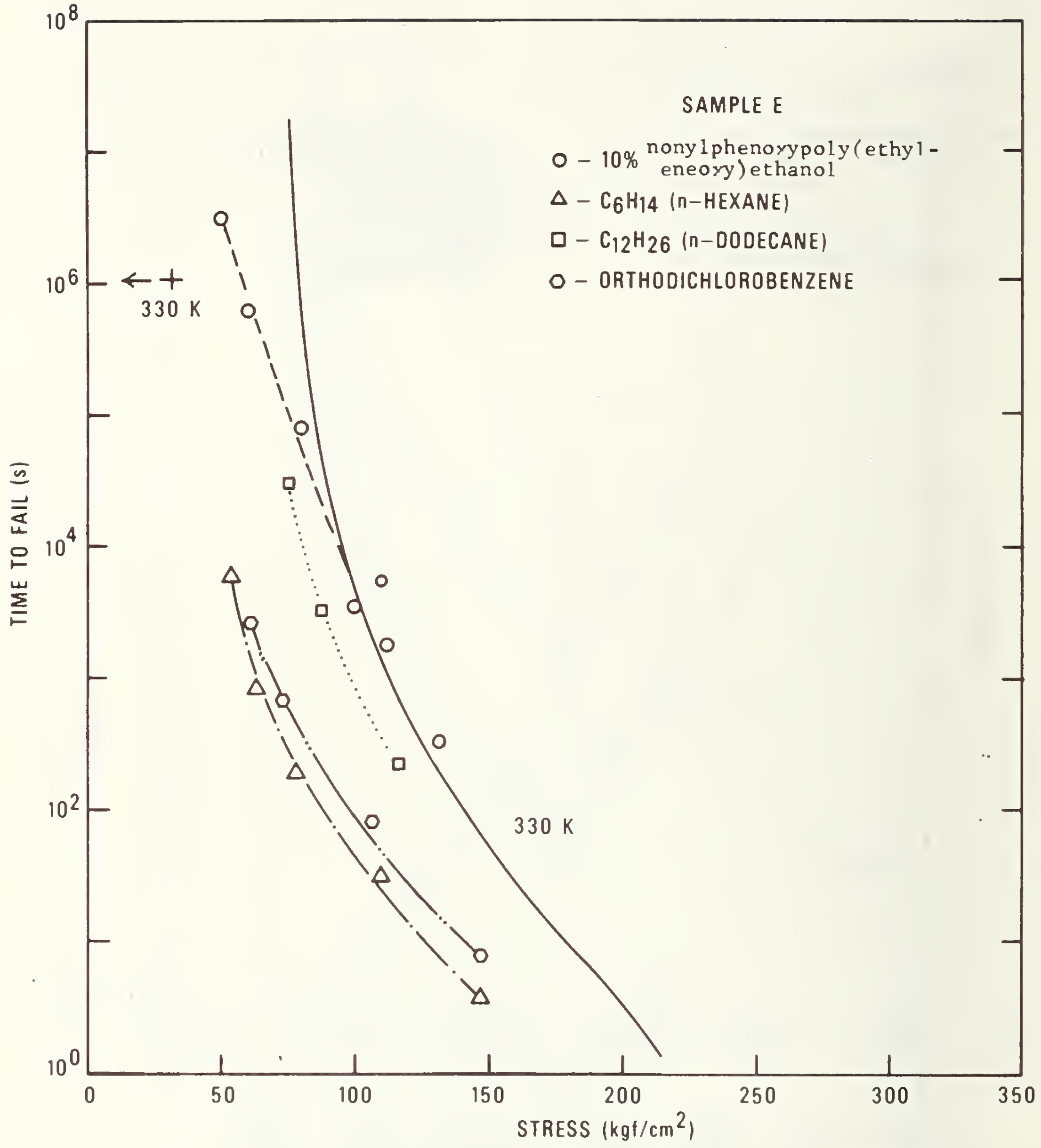

Figure 3.2.7 - Master curve for the stress-crack behavior of sample E at 330 K. The reference point for the room temperature shift factor indicated by the cross is the upper left corner of the figure.

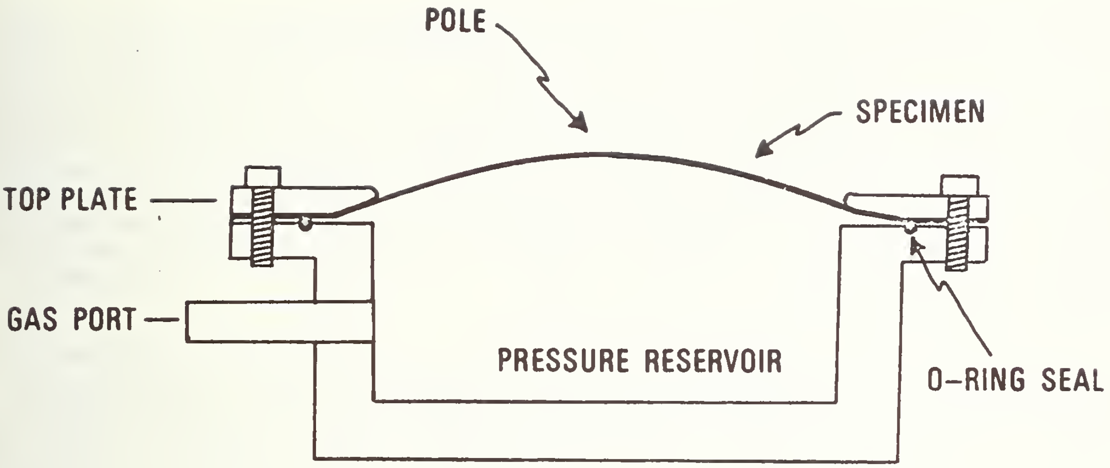

Figure 3.3.1 - Schematic diagram of apparatus for determining stress-crack behavior under biaxial stress conditions.

occur in the region near the point of clamping. Even in air, some difficulty was encountered in obtaining times to fail greater than about 10^6 seconds, since at the lower pressures nearly all of the specimens tested failed at the o-ring seal in times shorter than anticipated based on data obtained at the higher pressures. Since the specimens used in the present experiments were thin films, it is also possible that a small amount of unknown chemical leached out of the rubber o-ring which itself acted as a stress-cracking agent.

For the geometry shown in figure 3.3.1, an equivalent, or radial, stress can be calculated at the pole of the bubble from the expression

$$\tau = \frac{Pr\lambda^2}{2h} \qquad (3.3.1)$$

Where

τ = radial stress component;
P = internal pressure:
r = radius of curvature of the bubble at the pole;
h = initial thickness of the sheet; and
λ = extension ratio given by $1+\varepsilon$ where ε is the strain.

Equation (3.3.1) is valid only in the vicinity of the pole; therefore, when a stress-cracking agent is present, inverting the apparatus during testing is important in order to maximize the expectancy that failure will occur in the polar region. It can also be seen from equation (3.3.1) that in order to convert from internal pressure to an equivalent radial stress requires a knowledge of the radius of curvature as a function of internal pressure for each specimen thickness used.

In the present study the specimens were all cut from one sheet of high density polyethylene film obtained from a commercial source. This polymer, designated hereafter as sample F, had a melt index of 0.75 as determined by the manufacturer (ASTM D1238), and therefore, had the same value as that for sample D discussed earlier. The thickness of the film was approximately 0.025 mm (.001 inch) and as supplied was in the form of a biaxially oriented blown film with a blow-up ratio of 4:1.

Because the film was biaxially oriented, several specimens were cut parallel, perpendicular, and at 45° to the extrusion direction and tests made first in uniaxial extension. The results are presented in figure 3.3.2 and are drawn to the same log-log scale employed in figure 3.1.3 which compares samples A and D. Little or no difference in time to fail occurred for the specimens cut parallel and perpendicular to the extrusion direction, on indication that this particular film may be nearly equibiaxially oriented. The specimens cut at 45° to the extrusion direction did fail 2 or 3 times sooner than did the specimens cut along the orientation directions. When compared to the behavior of samples A and D in figure 3.1.3, the film actually is superior in terms of time to fail at stresses below about 150 kgf/cm^2. Whether or not this behavior reflects the orientation present or possibly differences in polymer composition between sample D and F is uncertain, but orientation may well be the predominent factor.

For the film specimens subjected to biaxial loading according to the procedure diagramed in figure 3.3.1, the experimental data are plotted in figure 3.3.3 (circles and triangles). In air, there appears two well defined regions for the specimens tested at room temperature. At the higher end of the pressure scale, the slope of the failure curve is quite steep and essentially linear on log-log coordinates. In this region, the film failed ductilly, that is, cold-drawing perpendicular to the extrusion direction occurred prior to the actual failure which was manifested in the form of cracks parallel to the extrusion direction. In the range of pressure below the break in the curve at times of about 10^4 seconds, there was no evidence of cold-drawing, but rather the appearance of crazes which eventually developed into a crack failure. The pressure at which the break in the curve occurs, and perhaps the fact that it occurs at all, will no doubt depend both on the amount of orientation initially present in the film and on the initial specimen thickness.

In the presence of a stress-cracking agent such as nonylphenoxypoly(ethyleneoxy)ethanol (solid circles in figure 3.3.3), the break in the curve becomes even more pronounced and occurs somewhat earlier in time (higher pressures). Interestingly enough, above a pressure of about 2×10^4 pascals, the nonylphenoxypoly(ethyleneoxy)ethanol no longer influences the time to fail, possibly because at times this short, the process becomes diffusion controlled. At lower pressures, the effect is much more dramatic. For example at a pressure of 0.86×10^4 pascals (1.25 psi), the time to fail is already shortened from that value in air by a factor of 40, and at 0.7×10^4 pascals (1.0 psi), the reduction is several decades. Again, however, it should be pointed out that these differences may well depend on both the extent of initial orientation and specimen thickness.

At 330 K, a similar behavior can be noted except that the time scale is significantly reduced. The shape of the curve in the case of the stress-cracking agent (solid triangles in figure 3.3.3) is the same overall as at 296 K. However, in air, the well defined break in the curve which occurs at 296 K does not appear at 330 K, at least within the range of pressures examined. Since in the presence of stress-cracking agent the shape of the failure curve is the same at both temperatures, the data can be superposed in a similar manner to that done earlier in Section 3.1 or that done by Fulmer [17] in his bottle experiment. The result is that if the natural logarithm of the shift factor is plotted versus the reciprocal absolute temperature, an activation energy of only about 43 kJ/mole (≈ 10 kcal/mole) is obtained, a value which is very low compared to that reported by Fulmer for blow molded bottles of branched polyethylene (≈ 22 kcal/mole). However, in the present case, there is insufficient data at other temperatures in order to place a very high degree of confidence in the calculated activation energy.

Now, for several of the specimens tested in air at room temperature, creep measurements were made as a function of time and these experiments are summarized in figure 3.3.4. The arrows indicate the point at which a crack opened allowing gas to escape. The strain, or elongation, was measured by placing fiducial marks of India ink about 1.5 centimeters on either side of the pole (center of the film), and marks were placed both parallel and

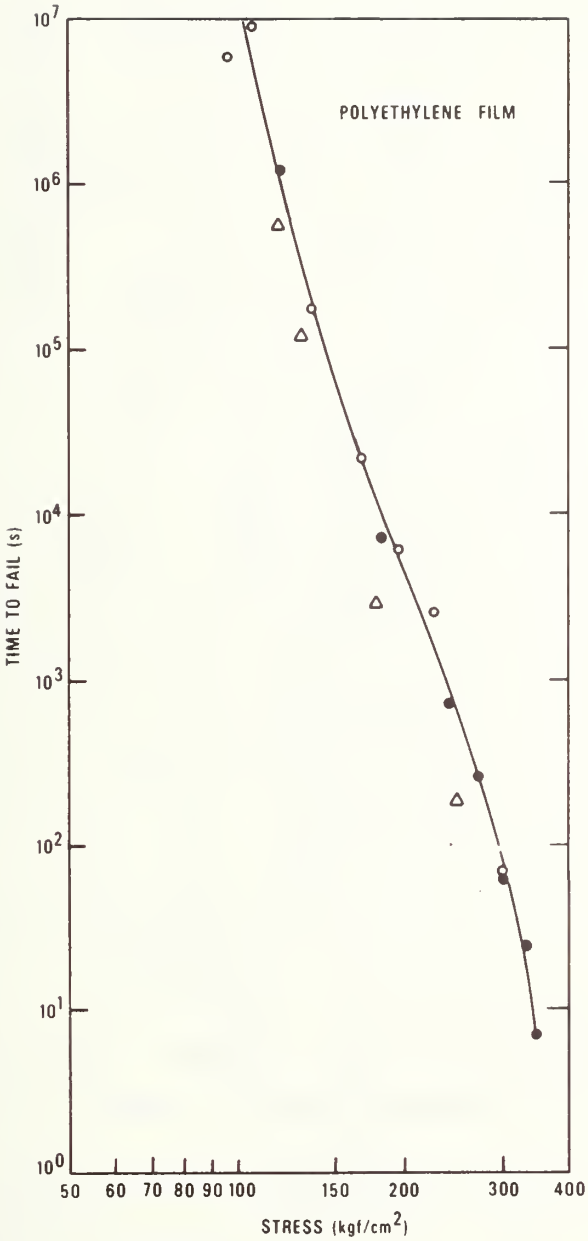

Figure 3.3.2 - Time to fail versus applied stress in uniaxial extension for a high density linear polyethylene film. Open circles correspond to specimens cut parallel to the extrusion direction, filled circles perpendicular, and the triangles 45° to the extrusion direction.

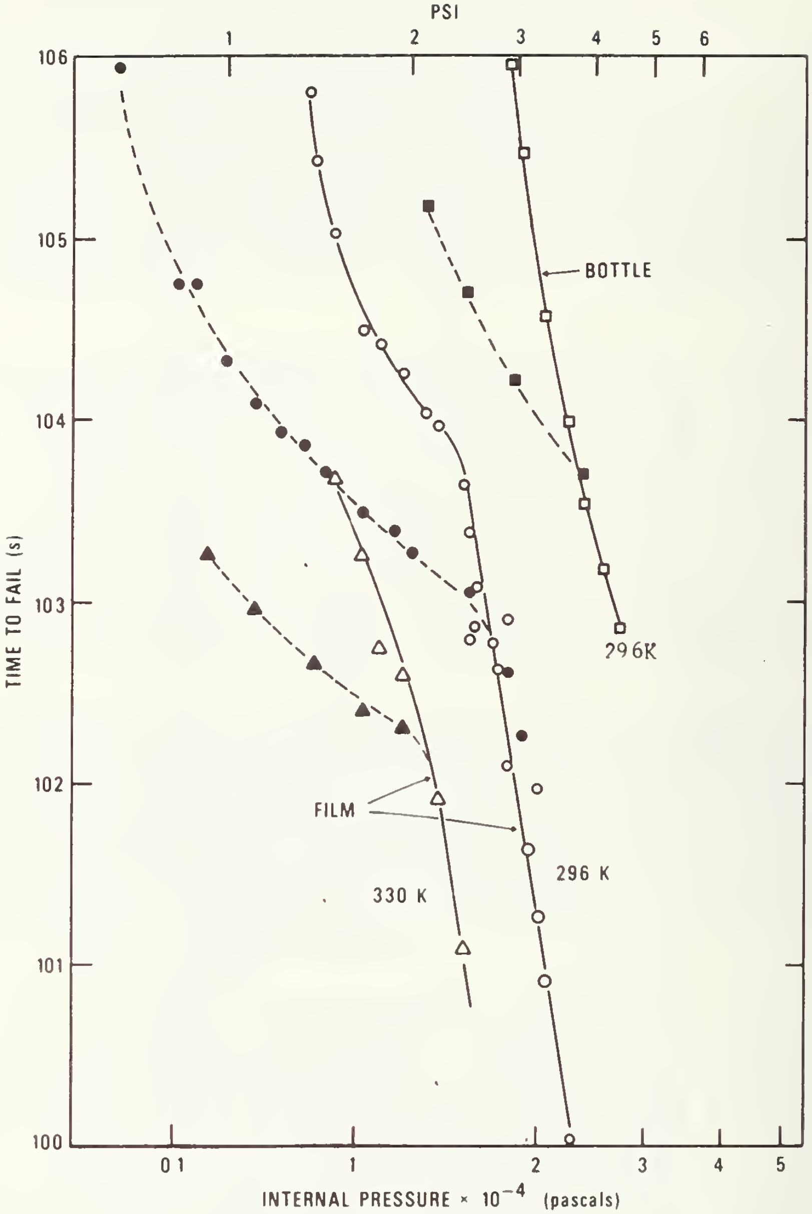

Figure 3.3.3 - Time to fail versus internal pressure for polyethylene film and bottles tested to failure under biaxial stress conditions in air and in igepal. Open symbols air, filled symbols igepal. The pressure scale for the bottles is 20 times that shown.

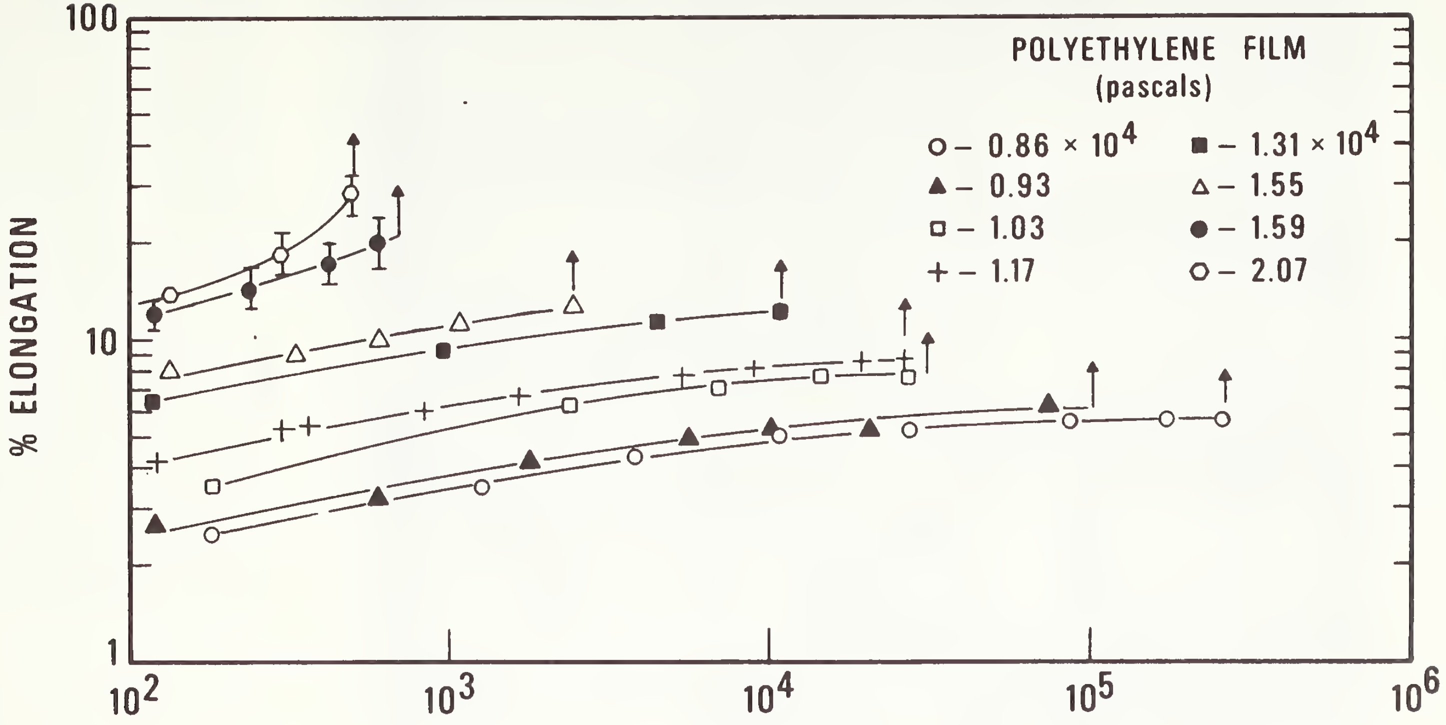

Figure 3.3.4. Creep to Failure Data for Polyethylene Film under Biaxial Test Conditions, Internal Pressures Are as Indicated and the Arrows Correspond to the Point of Failure.

perpendicular to the extrusion direction. The position of the marks was then followed in time with a traveling microscope. In most all cases, a difference in percent elongation was observed between the two directions, the percent elongation generally being greater in the direction parallel to the extrusion direction. It was also true that the amount of difference in percent elongation diminished with decreased pressure, as might be expected. In figure 3.3.4, the points shown represent the average percent elongation for the two directions and, except for the two specimens for which bars are shown, the extremes were at most only a small amount greater than the size of the data points themselves.

One interesting aspect to the creep data is that crazes first became visible at a strain of about 4-5 percent. This means that on a microscopic scale they must occur at even smaller strain. Also, it can be noted that as a general rule the crazes first appeared in time by a factor of from 10 to 100 earlier than the actual failure. Unfortunately, no creep data were obtained in the presence of nonylphenoxypoly(ethyleneoxy)ethanol due to the impracticality of making creep measurements with the apparatus inverted. The question then remains as to whether the effect of the stress-cracking agent is principly one of inducing the formation of crazes at an earlier stage (smaller strain), or is one of greatly reducing the time to failure after the crazes form. From the point of view of stress-cracking, one important consideration in container design, where reuse is intended, may be to reduce the maximum allowable strain expected under conditions where the container remains filled over a long period of time, to a level below that where crazes form easily.

Finally with respect to this film, it should be noted that in the presence of the solvents, n-hexane or n-dodecane, the permeation rate through the film was so great under even the smallest pressures applied that no failure occurred before all the liquid had passed through the film.

In another set of experiments, blow molded bottles (Boston Round) having a capacity of 227 cm^3 (8 oz.) and produced from the same polymer as sample D were tested to failure at 296 K containing either air or nonylphenoxypoly(ethyleneoxy)ethanol solution. These results are also presented in figure 3.3.3 (open and solid squares), where now a factor of 20 scale change has been applied along the pressure axis. Unlike the film, no break appears in the failure curve for the bottles in air at 296 K, whereas in the stress-cracking agent a similar break does occur which is also reminiscent of the behavior reported by Fulmer [17] for blow molded detergent bottles tested to failure in Igepal.

Some interesting comparisons can be made between the behavior exhibited by the bottles and that found from the bubble test on film. In the film, the location of the failure was more or less random with respect to the pole position; however, in the bottle test all the bottle failed at the same point regardless of whether or not the failure was ductile, or whether the experiment was done in air or in stress-cracking agent. An example of this is shown in figure 3.3.5 for several bottles of sample D tested to failure in air at different pressures. In each case the final crack opening occurred at the same point, near the midpoint of the bottle and along a seam parting line. This was true whether the bottle first cold-drew preceding failure (in a circumferential direction), or cracking occurred with no prior cold-drawing visible. Thus, a pressurized container test of this type may be advantageous from the point of view of container design, but from a material properties aspect is less so unless the container can be made highly uniform overall.

3.4 Additivity of Damage in Polyethylene in the Presence of an Adverse Environment

In Section 7.5 of reference [1], the concept of additivity of damage was introduced. For cases in which the environment is relatively inert, such as air, it was shown that the cumulative damage could be expressed simply as a sum of fractional times to failure, providing the stress and temperature histories were known. Further, it was demonstrated that information gained from experiments involving a constant rate of loading in uniaxial extension could be used to predict the time to fail for conditions of static loading. In transportation, where container reuse may be an issue, a cumulative damage criterion is of some interest; for, as it was suggested previously, if the average environment which a container experiences during normal in-use conditions can be reasonably estimated, then a qualification test for reuse based on a cumulative damage principle might be appropriate.

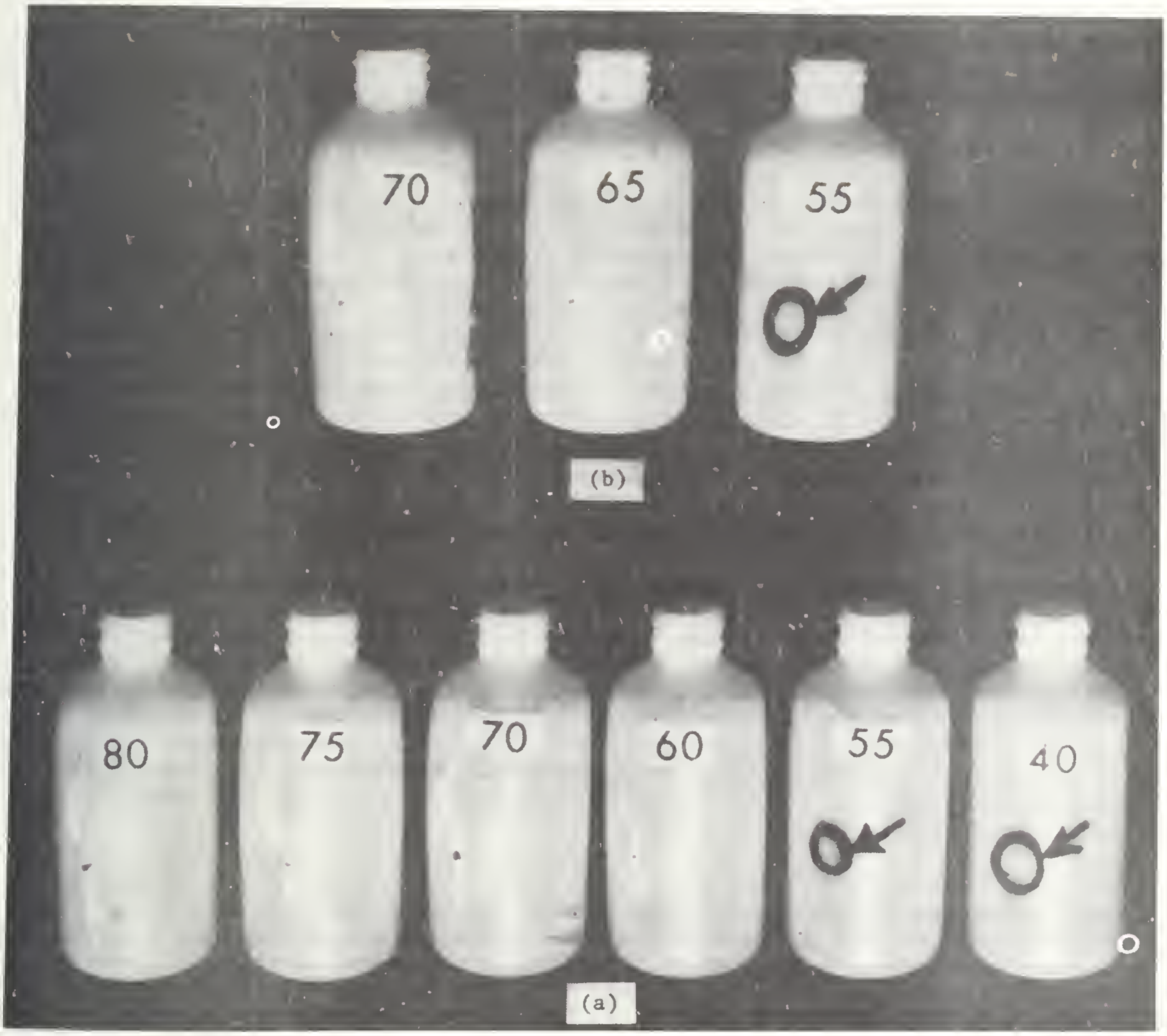

Figure 3.3.5 - Examples of polyethylene bottle failure in air and in igepal. (a) in air, (b) in nonylphenoxypoly(ethyleneoxy)ethanol. Numbers shown indicate internal bottle pressure in psi.

However, in the previous work both the temperature and environment (air) were held fixed, and whether or not additivity of damage remains a valid concept in the presence of an adverse environment, which possibly may change with time as well, is yet to be resolved.

We shall report here the results of experiments in which a series of very simple stress, temperature, and environmental histories have been applied to specimens of polyethylene. Sample D, the linear high density polyethylene, was chosen since the effect of stress-cracking agents on this polymer was found to be more dramatic than was the case for the branched polymer. As will be seen, the behavior of this polymer becomes more difficult to predict based on additivity of damage when the additional parameter of an adverse environment is added.

In one set of experiments two specimens were heated to 330 K (57 °C) and then loaded in uniaxial extension to a stress of 75 kgf/cm^2 for a length of time equal to about one half the expected total time to failure as determined from the 330 K data given in figure 3.1.2. At that point, the load was removed and a solution of nonylphenoxypoly(ethyleneoxy)ethanol in water was added to one specimen and n-dodecane to the other. Both specimens were held overnight at 330 K in the liquid before the load was reapplied and the time from that point on to the actual failure was recorded. In this case, the fractional time to failure is defined simply as time to failure in stress-cracking agent after reloading divided by the time to failure determined for the same stress from figure 3.2.2. The result was that the total fractional time for the specimen loaded in air and then in nonylphenoxypoly(ethyleneoxy)ethanol was 0.93, and correspondingly for the specimen first loaded in air and then in n-dodecane, it was 1.2. According to the additivity of damage criterion employed earlier, the fractional times to failure should sum to unity at the time of actual failure.

For a second set of specimens the reverse procedure was followed, that is the initial portion of the experiment was done in stress-cracking agent and the final portion in air. However, one important difference in the later set of experiments was that after the initial loading period in stress-cracking agent, each specimen was cleaned as thoroughly as possible and then allowed to dry overnight at 330 K before being reloaded. In the case of the nonylphenoxypoly(ethyleneoxy)ethanol, the specimen was scrubbed in distilled water with a medium bristle brush prior to drying, whereas the specimen exposed to n-docecane was first washed in a mild soap and water solution and then rinsed in distilled water. For these specimens, the total fractional time to failure with the nonylphenoxypoly(ethyleneoxy)ethanol was 0.71 and 0.69 for the n-dodecane.

Since only one specimen was tested for each set of conditions imposed, no meaningful statistical analysis is possible. However, for the first two specimens with total fractional times of 0.93 and 1.2, their departure from unity must be considered within expectation when account is taken of the scatter typical of the data points shown in figures 3.1.3 (330 K) and 3.2.2 (330 K). On the other hand, for the latter two specimens, the fractional times to failure observed during the second portion of the experiment are quite short (0.21 for the specimen initially in nonylphenoxypoly(ethyleneoxy)ethanol and 0.19 for that initially in n-dodecane compared to the expected value of 0.5). In fact, based on the results in figure 3.2.2 (330 K), one would conclude that removing the specimen from the nonylphenoxypoly(ethyleneoxy)ethanol and then washing and drying it had little, if any, effect since the total time to failure was about what it would have been if left in the nonylphenoxypoly(ethyleneoxy)ethanol from the outset. For the specimen tested initially in n-docecane, a similar statement applies except that the effect is less severe. Therefore, we can infer, albeit based on rather limited data, that it may be difficult, if at all possible, to remove completely material adsorbed or absorbed while under stress simply by washing and drying the specimen. Essentially this same conclusion was reached in reference [9], where particular reference was made with respect to the presence of nonylphenoxypoly(ethyleneoxy)ethanol. As a result, it may be true that an additivity of damage criteria will at best provide a bound, either upper or lower, to lifetime prediction whenever environmental factors in addition to temperature and stress are important. Of course, as a predictive tool, or in terms of qualification procedures, the knowledge of an upper bound is of little, or no, practical value.

Another area of concern, where the reuse of shipping containers may be involved, is the possibility that the adverse environment may change as a function of time. One can envisage situations in which a container designated for reuse is exposed to more than one type of lading, either accidentally or otherwise, and the effects due to stress-cracking may be compounded, thus further eroding its useful service life. As an example of this possibility, two specimens of sample D were presoaked, one in nonylphenoxypoly(ethyleneoxy)-ethanol and the other in n-dodecane, for a period of one day at 330 K. Each specimen was then loaded to 75 kgf/cm^2 for a length of time corresponding to one half the expected time to failure. The load was then removed and both specimens cleaned as before. They were then presoaked overnight at 330 K, but in the reverse sense from before (n-dodecane and nonylphenoxypoly(ethyleneoxy)ethanol, respectively), and again reloaded at the same stress until failure occurred. The resulting total fractional times to failure were respectively 1.3 and 1.1. Therefore, it would appear that for the two combinations tested no further degradation in mechanical integrity occurred over and above that expected for either stress-cracking agent separately. This is not to say that for other combinations of surface active stress-cracking agents or solvents an effect will not appear.

4. Summary and Recommendations

In Part I of the previous Final Report [1], the specifications and qualification tests contained in paragraph 178.19 of 49 CFR (Specification 34) were reviewed, the result being that several areas were identified where, insofar as mechanical properties are important, the present test requirements were judged to be inadequate. Specific recommendations were made to upgrade several of the qualification tests, primarily by redesigning them to provide more quantitative information. Among the several recommendations made were: (1) the necessity for container manufacturers and/or shippers to carry out performance tests on specimens taken from the finished container; (2) incorporating into qualification tests the idea of a test to failure; and (3) the establishment of retest procedures. Also noted was one important area not addressed in Specification 34, namely that of stress-cracking.

The principle focus of the present report has been directed toward the problem of stress-cracking in polyethylene, and an effort has been made to delineate the more important parameters influencing stress-cracking and to provide an indication of the directions previously taken to establish test methodology for determining stress-crack resistance. Section 1 dealt with a brief review of stress-cracking tests presently in common use, and these were found to be primarily the tests included by the ASTM as standard test methods or recommended practices. Section 2 was intended to provide the DOT Office of Hazardous Materials Operations with general background information on the subject of stress cracking, and to point out several of the more important parameters which influence stress-crack resistance. Section 3 presented a summary of experimental work carried out in the NBS Polymers Division during the contract period. This work included time to fail experiments carried out under both uniaxial and biaxial stress conditions in both air and known stress-cracking agents.

In the final section several recommendations are made covering two areas not presently addressed in 49 CFR 178.19, namely stress-cracking and reuse.

As already noted, DOT regulations do not currently require a test for stress-crack resistance. From discussions with industry personnel and a survey of the recent technical literature (see Section 2), it is clear that stress-cracking remains a problem of concern to industry. Furthermore, based on existing data available in the technical literature and on experiments conducted in our own laboratory (see section 3), it appears that the greatest utility to conducting tests for stress-crack resistance lies in: (1) the selection of a polymer resin with good stress-crack resistance, and (2) establishing the relative severity of different products as stress-cracking agents by comparing them to a known stress-cracking agent. From a practical viewpoint, one of the most obvious and fruitful approaches to minimizing failures in the field due to stress cracking is to optimize stress-crack resistance at the outset by proper testing at the time of manufacture. Therefore, as a qualification procedure, the DOT should require under 49 CFR 178.19-7 a test for stress-crack resistance. Test data should be submitted to the DOT indicating stress-crack resistance of the container material to a prospective lading and to a known stress-cracking agent. Such tests should be carried out at the time of initial production and whenever any change is made in the material or processing technique.

We interject that the simple knowledge that a substance is a stress-cracking agent should not necessarily exclude it from shipment in a particular container (a stress-cracking agent being defined here as any substance when in contact with the polymer causes failure in a time shorter than that in air, all other factors being equal). If it can be demonstrated that the failure time in the presence of a particular lading and under relatively severe environmental conditions is much longer than any expected service life or time in transportation, then there would appear to be no strong justification for rejection on that basis alone. At some point, however, a judgment has to be made as to the suitability of shipping the product in a given container. The criterion to be invoked in such a decision can only be made based on a knowledge of industry wide experience and from evaluation of the expected transportation environment. From the standpoint of the DOT Office of Hazardous Materials Operations, two valuable aids in this regard should be: (1) the information available through the submission of test data on stress-crack resistance, and (2) an up-to-date, complete as possible, record of field failures. We note parenthetically that the DOT Hazardous Materials Incident Report (Item F) makes provision for the reporting of at least 16 different types of packaging failures. None of these pertain specifically to failure due to stress-cracking, yet nearly all of them can either be a result of, or be accelerated by, exposure to a lading which at the same time is a stress-cracking agent. Cumulative damage to a container caused by a stress-cracking agent will, in general, not be visible even by careful visual inspection. However, the container may have been sufficiently weakened at some point that it will fail under conditions which normally would not cause failure. In most instances, the man in the field who observes the failure will not be in a position to judge whether or not the failure was a result of prior internal damage due to stress-cracking. However, in cases where the incidence of field failures with a particular lading, or type of lading, falls well outside any statistically likely incidence rate for the industry as a whole, a knowledge of the severity of a lading, or type of lading, as a stress-cracking agent may be valuable in re-evaluating the suitability of transporting that lading in the container in question.

Now as to just which stress-cracking test is the proper one for inclusion in DOT regulations remains open to discussion. In Section 1 of this report, it was observed that the most often used tests for stress-crack resistance are those currently included in the ASTM Book of ASTM Standards [4]. It was further noted that considerable criticism has been directed toward several of these tests, and recent discussions with members of the plastic container industry further substantiates the general viewpoint that even the most widely accepted tests are not considered to the wholly satisfactory. Clearly, there remains a need to develop a performance oriented stress-cracking test which can be carried out in the laboratory on specimens taken directly from a finished container. Much of the work described in Section 3 of this report was undertaken to establish a data base from which such a test can be developed. However, further work is required in several areas in order to ascertain which type of test is the most appropriate. For example, it has been suggested [17] that a scaling may be possible between results obtained from tensile tests in uniaxial extension and comparable data obtained from actual container tests. If true, then the actual testing can be greatly simplified from that required under conditions of biaxial stresses. However the evidence that such a scaling exists between the two types of tests is not well documented.

In spite of their apparent shortcomings it is recommended that until a new test for stress-crack resistance becomes available, DOT regulations should include one of the presently accepted test methods for determining stress-crack resistance. As a polymer resin test, one intended to aid in the selection of a polymer to optimize stress-crack resistance and for determining the relative severity of various products as stress-cracking agents, tests such as ASTM 2561-70 and ASTM 2648-70, or a test similar to that described in Section 3.3 of this report appear to be the most appropriate. In order to provide more quantitative information, a test such as ASTM 2561-70 should be carried out at more than one internal pressure.

Where reuse is a primary concern, it is recognized that the requirement of a stress-cracking test on a continuing basis to a given production lot of containers may be impractical since: (1) the retest procedures may become sufficiently costly that the entire operation becomes uneconomical, and (2) not all of the containers may be returned to the shipper at the same time. From the same production lot one container may experience a much shorter time in the field than another, possibly under unknown conditions, so that the difficult question arises as to just how the containers should be chosen for retesting and at what intervals they should be retested. Presumably, a deterioration in the performance characteristics of a container (cumulative damage) due to exposure to a lading which is a stress-cracking agent, if sufficiently severe, will be reflected upon subsequent testing by an inability to meet the minimum retest specifications. It is, therefore, recommended that some provision be made in DOT regulations for retesting of containers on a periodic basis. A retest procedure can be established by choosing a subset of tests contained in 49 CFR 178.19-7 and requiring that containers: (1) be selected at random from a given production lot that has been returned after some specified number of trips, and (2) be submitted to the chosen tests. The three most relevent tests would appear to be a drop test, hydrostatic pressure test, and a static compression test.

We know also from experiments carried out in our laboratory that the application of only a small stress over a very long period of time can result in failure, and that in the presence of stress-cracking agent, the amount of deformation (strain) in the container can be very small at failure (5 percent or less). Therefore, it is important that the dimensions of the container remain constant, or nearly so, over the expected service life of the container. By placing fiducial marks near the top, center, and bottom of the container, and on opposite sides, the circumference of the container can easily be monitored periodically with a tape measure. If a container has been subjected to either a large internal pressure or compressive force for any length of time, damage done to the container may be reflected by an irreversible increase in the circumference of the container. Further exposure to even moderate environmental conditions may then be sufficient to cause failure, especially if the lading is known to be a stress-cracking agent. Periodic inspection of the container dimensions should provide one relatively easy and non-time consuming method for detecting potentially hazardous situations. For example, a container which is found to have increased irreversibly in circumference by, say, 5 percent or more will probably have difficulty passing the qualification tests required under specification 34. Such a test does not insure that a container will not fail as a result of stress-cracking, or otherwise, since the failure may occur at the chime or near a closure, but does provide a means of screening lots of containers which may have experienced unusually severe conditions resulting in incipient damage.

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16. Abstract

This report is Part III of a series prepared for the Office of Hazardous Materials Operations under Research Contract No. AS-50074. Parts I and II dealt with mechanical properties and permeation aspects of the performance of plastic packaging for the transport of hazardous materials. Part III describes studies carried out in the NBS Polymers Division during fiscal 1977. The emphasis of this work has been directed toward providing background information and laboratory studies on the subject of stress-cracking, the results of which will be pertinent to the establishment of performance criteria.

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