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PERFORMANCE OF PLASTIC PACKAGING FOR HAZARDOUS MATERIALS TRANSPORTATION

PART I. MECHANICAL PROPERTIES

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16. Abstract

This report, prepared for the U. S. Department of Transportation, contains background information useful in evaluating the performance of plastic packagings for hazardous materials transportation, insofar as mechanical properties are concerned. Current DoT regulations and test methods are reviewed, as well as testing procedures from other organizations and countries. Also included are recommendations to modify current DoT regulations to make test methods more quantitative. Finally, experimental data are presented which represent the initial stage of a study it is hoped will ultimately lead to the establishment of criteria upon which the long time behavior of plastic containers can be predicted based on short time tests.

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PREFACE

This Report is Part I of a series prepared for the Office of Hazardous Materials Operations under Research Contract No. DOT AS-50074. Part I is concerned with mechanical properties aspects of the performance of plastic packagings for the transport of hazardous materials. The authors gratefully acknowledge the assistance and cooperation of the following organizations: the Office of Hazardous Materials Operations Staff, in particular, Mr. Mario Gigliotti, for his guidance throughout this project; members of the Plastic Drum Institute of the Society of the Plastics Industry; members of the Manufacturing Chemists Association; and Mr. P. E. Campbell of the Phillips Petroleum Company.

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1. INTRODUCTION

The hazardous materials regulations embodied in the "Code of Federal Regulations, Title 49 - Transportation, Parts 100 to 199" (Title 49 CFR) are published and maintained by the Office of Hazardous Materials Operations (OHMO). Within these regulations are specifications for plastic containers used in the transportation of hazardous materials. These specifications require, among other things, that the plastic containers be compatible with the lading and that the plastic containers should not be permeable to the lading to an extent which could create a hazard. There are, however, no standards on which one can base decisions as to whether a plastic container, selected for a particular use, is or is not in conformance with either aspect of the regulations. A similar situation prevails in the specifications for reuse of plastic containers.

In addition to its role in protecting the public interest through the formulation of specifications and regulations, the OHMO must frequently rule on requests for exemptions which allow the shipment of hazardous materials in packages which have not yet come within the purview of the regulatory system. A significant number of these exemptions are for use of plastic containers. Decisions on these containers are difficult to render in the absence of data on their material properties as they relate to the intended use.

In the light of the National Bureau of Standards (NBS) legislative mandate for "...development of methods for testing materials, mechanisms, and structures...." and for "...cooperation with other Government agencies and with private organizations in the establishment of standard practices, incorporated in codes and specifications," the NBS is uniquely suited to assist the OHMO in the solution of the problems outlined above. The position of the NBS, as a party accountable only to the public interest, aids materially in maintaining equity in the process of formulating specifications and regulations by diminishing the possibility of conflicts of interest. The role of the NBS in obtaining and evaluating critical data on materials properties is well-established.

In fiscal year 1976 under Department of Transportation (DOT) contract AS-50074, the 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 the tests given in 49 CFR, a survey of other test methods, and laboratory studies on damage in polyethylene (PE).

The findings of all these investigations are presented in detail in this final report for Contract DOT AS-50074. Briefly stated, our findings are that: (1) performance criteria regarding permeation of lading materials should be developed for use by DOT, and (2) additional performance criteria should be implemented in the area of mechanical properties. The latter criteria should address the issues of failure due to stress cracking and failure due to long-time, low-level applied stresses encountered in the shipping and storage of the container.

All of the above areas, permeation performance, stress crack resistance, and long-term mechanical integrity, are particularly relevant in situations where the containers are expected to be reused. The trend toward reusable containers is a result of the widespread use of Specification 34 (paragraph 178.19 of 49 CFR) as the basis for exemptions.

There have been a number of developments with regard to plastic containers in the packaging industry in recent years which have subjected the regulatory system to increasing pressure. Container fabricators have found ways to make sturdy, chemically resistant, industrial containers in a wide range of styles and sizes. Resin producers have developed materials which result in improved impact resistance, stress-crack resistance, and barrier performance. Shippers have found that significant economies can be realized by use of the lighter weight plastic containers. The net result has been that plastic containers have been removed from the sphere where they were regarded as useful only for situations in which metal or glass containers did not provide adequate protection, and now compete in many areas both on economic and performance grounds with other types of containers.

From the standpoint of the OHMO these innovations have been reflected in the increasing numbers of requests: (1) to expand the scope of exemptions to include new commodities, (2) to determine new specifications covering new container configurations, or (3) to change existing specifications to encompass modifications in container design.

In part, these pressures arise from the nature of the Hazardous Materials Regulations themselves. Within the Regulations (49 CFR), the following two lists appear: (1) a list of commodities, and (2) a list of container specifications. Packages are selected from the container list on a commodity-by-commodity basis. There has long been a recognition that such a system can be (and is) unwieldy and that a performance-oriented approach should be developed [1][1]. The Naval Surface Weapons Command (NSWC) has been attempting to devise such an approach with respect to barrels, drums, and packs [2].

Plastic containers present special problems of their own and the OHMO has determined that there is a need for studies of plastic materials properties which can be used as input in formulating performance-oriented specifications.

In this report, three potential approaches are considered as possible solutions to the problems of developing adequate specifications for plastic containers used in shipping hazardous materials. First, the important physical parameters relating to the mechanical or permeation failures of plastic containers will be discussed. Second, from a general knowledge and understanding of the permeability of polymeric materials and related failure modes, the validity and usefulness of the present DOT tests, as well as the usefulness of tests from other organizations, ASTM, ISO, etc., will be analyzed. Finally, areas where new tests are necessary will be suggested and baseline data necessary to the establishment of such tests will be presented.

Laboratory studies to date in the NBS Polymers Division have been concerned primarily with the creep failure, in extension, of polyethylene over a wide range of stress levels. Experimental and theoretical work have demonstrated that the assumption of additivity of damage as a result of various stress and temperature histories is valid for polyethylene in a normal environment (absence of a stress-cracking agent). Using the assumption of additivity of damage as well as data on time-to-break versus applied stress at different temperatures, specimen lifetimes have been predicted for several different simple stress histories.

2. POLYETHYLENE - THE PLASTIC FOR CONTAINERS

In confronting the materials science questions which bear on shipping containers, the first step in determining what materials are being used was to examine the materials properties given in the specifications found in 49 CFR. Table 2.1 is a list of all the specifications listed in paragraph 173 of 49 CFR which deals with plastic containers. Table 2.1 does not include all of the references found in paragraph 173 of 49 CFR for special uses of polyethylene in non-specification packages for use with specific ladings. When allowance is made for the frequency of use of these specifications, it becomes clear that polyethylene is the principle material used in fabricating nonmetallic containers for the shipment of hazardous materials.

As will be shown later, "polyethylene" is not one substance but covers many different materials under one name. In an attempt to further delineate the limits of the NBS investigations, inquiries were directed to the OHMO, resin suppliers, container manufacturers, and shippers to ascertain which forms of PE are in common use in the manufacture of containers for hazardous materials.

This informal survey revealed a consensus that the most critical applications were those involving free-standing containers, and, of the various resins in use, high-molecular-weight polyethylene was the most important resin.

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

TABLE 2.1
LIST OF PLASTIC SPECIFICATION CONTAINERS FOUND IN 49 CFR

SPEC	PARA	DESCRIPTION	OVPK[1]	CAP[2]	UNIT
1H	178.13	POLYETHYLENE CARBOYS IN LOW CARBON STEEL OR OTHER EQUALLY EFFICIENT METAL CRATES	YES	13	GAL
43A	178.18	RUBBER DRUMS	NO	30	GAL
34	178.19	REUSABLE MOLDED POLYETHYLENE CONTAINER FOR USE WITHOUT OVERPACK. REMOVABLE HEAD NOT AUTHORIZED.	NO	30	GAL
2T	178.21	POLYETHYLENE CONTAINER	YES	13	GAL
2U	178.24	MOLDED OR THERMOFORMED POLYETHYLENE CONTAINERS HAVING RATED CAPACITY OVER ONE GALLON. REMOVABLE HEAD CONTAINERS OR CONTAINERS FABRICATED FROM FILM NOT AUTHORIZED.	YES	55	GAL
2E	178.24A	INSIDE POLYETHYLENE BOTTLE	YES	5	QTS
2TL	178.24	POLYETHYLENE CONTAINER	YES	14	GAL
2S	178.35	POLYETHYLENE CONTAINER	YES	55	GAL
2SL	178.35A	MOLDED OR THERMOFORMED	YES	55	GAL
44P	178.241	ALL-PLASTIC BAG	NO	81	LBS

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[1] A "YES" MEANS THAT THIS CONTAINER IS MEANT TO BE USED WITH ANOTHER CONTAINER AS AN OVERPACK.

[2] THE NUMBER GIVEN IS THE MAXIMUM PERMITTED VALUE EXCLUSIVE OF AGE.

A further review of the plastics industry trade journals led to the same conclusion. For example, in the December 1975 *Modern Plastics* (page 10), it was estimated that 11,000 to 12,000 metric tons of high molecular weight polyethylene (HMWPE) would be used in 1976 in the production of 30 to 55 gallon drums to be used in all forms of transport. It was predicted that by the mid-1980's, 200,000 metric tons of HMWPE would be consumed annually by this market with plastic drums taking over 50 percent of the total drum market.

According to the *Plastics World* of February 16, 1976, HMWPE shipping containers and utility pails are taking 30 percent of the market away from steel in 1975-76.

It should be noted that evolving technology is rapidly placing new materials into contention as container resins.

3. GENERAL CHARACTERISTICS OF POLYETHYLENE

This report deals with tests and experiments on polyethylene because of the preeminence of this polymer in the plastics packaging industry. A brief description of the significant properties of polyethylene which control its mechanical and permeation properties will be given here. A number of terms which are widely used in the plastic container industry will be introduced and defined.

Polyethylene is obtained by the polymerization, or linking together, of numerous ethylene, $CH_2 = CH_2$ molecules. Polyethylene may vary according to: (1) average size of molecules or molecular weight, (2) distribution of size of molecules within the product, and (3) extent of branching of these molecules. (Branching describes the incorporation of short aliphatic side chains onto the long polyethylene molecules.) All of these characteristics affect the physical and chemical properties of the solid polymer.

3.1 Characterization of the Polymer

The determination of the molecular weight, its distribution and the degree of branching is usually categorized as the characterization of the polymer. Molecular weight and molecular weight distribution are usually determined by solution properties of the polymer. Light scattering, osmometry, ultra centrifugation, and dilute solution viscosity are some classical methods to obtain various measures of molecular weight. Gel Permeation Chromatography (GPC) is a more recent method to determine molecular weight and molecular weight distribution. All of these tests for molecular weight, except for GPC, are rather tedious and expensive to perform and are, therefore, not widely used in industry.

For these reasons, industry has turned to simpler methods of characterizing polyethylene resins. ASTM Method of Test D-1248-74[2], Standard Specification for Polyethylene Plastics Molding and Extrusion Materials, provides for five categories of polyethylene distinguished by the flow rates of polymer melts as measured by ASTM D-1238-70, Test for Measuring Flow Rates of Thermoplastics by Extrusion Plastometer. Results of this test are usually stated in terms of the melt index.

The flow rate obtained with the extrusion plastometer is not a fundamental polymer property and should not be so regarded. It is an empirically defined parameter critically influenced by the physical properties and molecular structure of the polymer and the conditions of measurement. The rheological, or flow, characteristics of polymer melts depend upon a number of variables. In general, however, the higher the molecular weight, the lower the melt index. Thus, one may use the melt index as a comparative measure of molecular weight.

The melt index is useful to polymer resin manufacturers as a method of controlling material uniformity. While the data from this test are not directly translatable into relative end-use processing characteristics, the melt index is nonetheless strongly indicative of relative "flowability" of various kinds and grades of PE. However, the melt index

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[2] All ASTM tests and specifications referred to in this Report can be found in the *ASTM Annual Book of ASTM Standards*, Parts 35 and 36 (1976).

of one manufacturer's resin may not be equivalent to that of another's with respect to its processing characteristics. The "property" measured by this test is basically the melt viscosity.

It should be pointed out at this time that the melt index of material taken from the final product may not be the same as that of the base resin, that is the melt index may be modified by the processing itself. For example, a polyethylene resin held at a high temperature (in the melt) for a substantial time may undergo degradation, thus increasing the melt index.

The mechanical properties important to use of the polymer in container applications are generally correlated to the melt index. In Table 3.1 some of these properties and their relation to variations in melt index and molecular weight are shown.

ASTM D-1248-74 also provides for four types of polyethylene, as distinguished by their density as determined by ASTM D-1505, Test for Density of Plastics by the Density Gradient Technique. In specification D-1248-74:

Type I is polyethylene in a density range of 0.910 to 0.925 g/cm^3. This is termed "low-density" or "branched" polyethylene, or LDPE.

Type II is polyethylene in a density range of 0.926 to 0.940 g/cm^3. This is termed "medium-density" or "linear" polyethylene or HDPE.

Type III is polyethylene in a density range of 0.941 to 0.959 g/cm^3. This is termed "high-density" or "linear" polyethylene or HDPE.

Type IV is a polyethylene of density 0.960 g/cm^3 or greater. This type is termed "high-density" also.

In general, density is a measure of both degree of branching and degree of crystallinity. Type I polyethylene is highly branched and contains moderate crystallinity while Type IV polyethylene has little branching and is highly crystalline.

"Degree of Crystallinity" is here used to indicate that the molecular ordering in polyethylene can vary from a random configuration analogous to a bowl of spaghetti to an ordering where nearly all the volume is filled with crystallites. The extent to which the polymer exhibits ordering (crystallinity) is mainly influenced by molecular weight, thermal history, and degree of branching.

A number of other properties roughly correlate with density. In Table 3.2 variation in several properties among different polyethylene types are shown. The chief differences among these types of polyethylene are in rigidity, heat resistance, and resistance to loading. Generally, increased density results in greater stiffness, strength, and heat resistance, while resulting in lower impact strength and resilience.

The physical and mechanical properties of polyethylene are not determined entirely by the manufacturer of the resin. For a fixed molecular weight plastic, the process associated with forming the resin into a container can result in modifications to the physical and mechanical properties of the containers as a result of the stresses and temperatures applied during processing.

For example, a container rapidly cooled from the melt will have a somewhat lower density and crystallinity than one slowly-cooled. At the same time, quenching, or rapid cooling, may lead to much greater "residual" stress than will slow cooling. On the other hand, a polymer melt held at a too high temperature for some length of time can undergo degradation of the resin.

TABLE 3.1

RELATIONSHIP OF MECHANICAL PROPERTIES OF POLYETHYLENE TO VARIATIONS IN MELT INDEX AND MOLECULAR WEIGHT

Property	As Average Molecular Weight Increases (Melt Index Decreases)	As Molecular Weight Distribution Broadens
Melt Viscosity	Increases	-
Tensile Strength at Rupture	Increases	No Significant Change
Elongation at Rupture	Increases	No Significant Change
Resistance to Creep	Increases	Increases
Impact Strength	Increases	-
Resistance to Low Temperature Brittleness	Increases	Increases
Environmental Stress Cracking Resistance	Increases	Increases
Softening Temperature	-	Increases

TABLE 3.2
PHYSICAL PROPERTIES OF TYPICAL POLYETHYLENE RESINS

PROPERTY	ASTM TEST METHOD	ASTM TYPE I	ASTM TYPE II	ASTM TYPE III	ASTM TYPE IV
Density, gms/cc	D 1505-68	0.910-0.940	0.926-0.940	0.941-0.959	0.960+
Environmental Stress Cracking, F_{30}, hrs.	D 1693-70	<1 ->1000	<1 ->1000	<1 ->1000	<1 -1000
Tensile Strength, 2"/min., psi	D 638-68	1000-1900	1200-3500	3000-4000	3800-4700
Elongation, 2"/min., %	D 638-68	>800	135-800	50-900	10-900
Modulus of Elasticity, psi	D 638-68	8M-25M	25M-55M	60M-150M	110-150M
Modulus in Flexture, psi	D 790-66	8M-60M	60M-115M	125M-210M	240-260M
Vicat Softening Temp., °F	D 1525-65T	185-214	210-255	235-260	250-260
Brittleness, Temp., °F	D 746-64T	<-180	<-180	<-180 to -35	<-180 + 70
Heat Distortion Temp., °F 66 psi	D 648-56	110-115	130-150	160-170	165-170
Coefficient of Linear Expansion, in/in/°C	D 696-70	1.0×10^{-4}	—	1.3×10^{-4}	1.3×10^{-4}
Thermal Conductivity, Btu-in/ft^2	C 177-63	3.7	3.7	3.7	3.7
Specific Heat, cal/gm	—	0.458	0.458	0.458	0.458
Taber Index (mg lost/1000 cycles)	Taber Abraser	10-15	6-10	2-5	2-5
Hardness, Shore D	D 2240-68	44-48	45-60	55-66	65-70

3.2 Mechanical Properties of Polyethylene

A variety of mechanical tests and measurements may be made on polyethylene. However, since the main thrust of this report with respect to mechanical properties is in the area of mechanical failure of the material, those properties and tests which lead to some understanding of mechanical failure will be emphasized.

A common mechanical measurement made on materials is the elastic modulus or "stiffness." For all materials there is a region where doubling the applied stress doubles the strain and visa versa. This is referred to as the linear region of the material. In the linear region the ratio of the applied stress to strain is called the elastic modulus.

For polyethylene, the linear region occurs only for strains of 10^{-4} or smaller. By way of comparison, in the case of rubber this region occurs for strains of 10^{-1} or smaller, whereas in some metals it occurs for strains of 10^{-6} or less. At higher strain, stress and strain are not connected by a linear relationship; then the description of the mechanical properties become more complex. Figure 3.1 is a typical stress strain curve for a polymer. The modulus is commonly taken to be the initial slope of the curve.

Other features derived from stress-strain curves are the yield point, tensile strength, and elongation. They represent, respectively, the maximum elastic strength, the ultimate strength, and the amount that the polyethylene can be drawn before it breaks. These mechanical properties are especially important in practical applications.

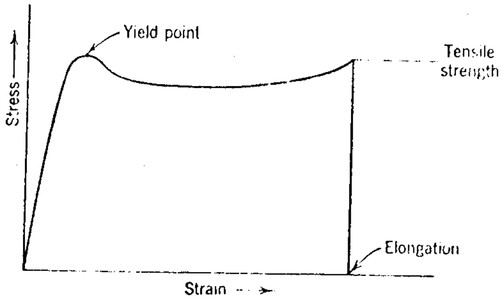

Fig. 3.1. Idealized Stress-Strain Curve for a Typical Crystalline Olefin Polymer

Most mechanical properties depend on the state of the resin. For example, the tensile strength decreases with increased temperature. Increased density results in an increase in tensile strength, as does an increase in molecular weight. Furthermore, these properties depend on the rate at which the material is strained. Figure 3.2 is a stress-strain curve for two representative grades of polyethylene at two different strain rates. The yield point, tensile strength, and elongation depend not only on the density of the material, but also on the rate at which the experiment was done.

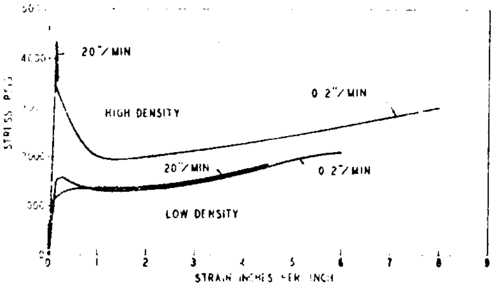

Fig. 3.2. Stress-Strain Curve Showing Dependence of Stress on Rate of Strain and Density

The variation of the yield point of one particular sample as a function of rate of strain and temperature is shown in figure 3.3. From these examples, it is clear there are strongly time-dependent phenomena influencing the mechanical properties of polyethylene. As will be shown later (Section 7), at high levels of stress the failure times (time-to-break or time-to-fail) for polyethylene A can be much larger than for polyethylene B, but at a low level of stress the reverse may be true.

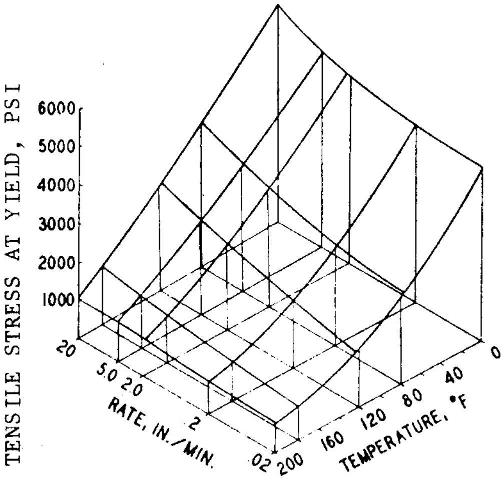

Fig. 3.3. Effect of Temperature and Rate of Loading on Tensile Stress at Yield Point for 0.3-M.I. 0.950 Density Copolymer

Two other often discussed material properties related to failure of the polymer are impact strength and brittleness temperature. Impact strength is a measure of the polymer's ability to withstand high stresses for short times without failure. Impact strength is affected by molecular weight and, to a lesser extent molecular weight distribution. As molecular weight increases, impact strength increases. A commonly used measure of the impact strength is the IZOD impact test (ASTM 256-72a).

The IZOD impact test indicates the energy required to break notched specimens under standard conditions. It is calculated at ft-lb/in of notch and is usually calculated on the basis of a 1 inch specimen, although the specimen used may be thinner in the lateral direction. The IZOD value is useful in comparing various grades of a plastic. However, some materials are notch-sensitive and derive stress concentrations from the notching operation. Furthermore, the test is open to much criticism as it shows different results depending on whether or not the sample had been notched. For example, in the notched IZOD impact test conducted over a wide temperature range, low-and high-density polyethylenes react differently [3]. Between 0 °F and 20 °F, low-density polyethylene goes through a sharp transition point where the impact strength increases from less than one ft-lb/in of notch to 18 ft-lb/in. On the other hand, high-density polyethylene shows a gradual increase in impact strength as the temperature is raised. Data on unnotched specimens are quite different. The transition point for low-density polyethylene does not appear and the two curves nearly superpose.

The brittleness temperature is of some use in judging the relative merits of various materials for low-temperature flexing or impact. It can be measured by an ASTM test (ASTM D-746-73). As is pointed out in paragraph 3 of this test, it is specifically relevant only for the materials and conditions specified in the test, and the values cannot be directly applied to other shapes and conditions. The brittleness temperature does not put any lower limit on service temperature for end products, but this property is sometimes used in specifications.

The effect of different environments on the mechanical properties of polyethylene has not been discussed so far. Materials which swell, soften, or which chemically react with the polymer will change its failure properties. In addition, other ladings which show no appreciable chemical or physical effect on the polymer in the absence of stress can, under the influence of internal or applied stresses, accelerate the failure. These materials are categorized under the general heading of stress-cracking agents. Stress-cracking is the appearance of cracks, internal or external, and thus, failure of the polymer at times earlier (or lower stresses) than the polymer would have failed in an inert environment.

Depending on the manner of its initiation, the resulting failure may be recognized as environmental, thermal, fatigue, solvent, or oxidative. Elevation of temperature usually heightens stress-cracking activity. At the same time, environmental stress-cracking resistance generally improves as the melt index decreases. Broadening of the molecular-weight distribution with low molecular weight material (<30,000) decreases stress-cracking resistance, whereas broadening with high molecular weight material can increase stress-cracking resistance. However, during processing at high rates of shear the high molecular weight components can be broken down so that it is important for stress-cracking tests to use test specimens obtained from the final product.

ASTM-2561-70 and ASTM-1693-70 provide various tests to determine the effects of environmental stress-cracking agents on blow molded polyethylene containers.

There are also other forms of stress-induced failure involving no chemical changes. For example, in solvent-cracking the liquids which induce failure apparently do so by weakening the surface layers of the material through solvation and swelling. Another example is thermal stress-cracking which is brought about through internal physical changes as a result of heating prestressed polyethylene; it is to be distinguished from thermal embrittlement which can occur in unstressed material. Thermal stress-cracking is a weakness primarily of the higher density polyolefins. For polyethylenes, it is enhanced by increasing the melt index. Molecular-weight distribution also remains important, particularly in the more highly crystalline polymers. Static fatigue, or brittle creep failure, is closely related to thermal stress-cracking. ASTM-2951-71 provides a test method for thermal stress-crack resistance of Types III and IV polyethylene plastics.

Other types of stress failure involve chemical alteration of the polymer. Beyond the initiation step, which consists of an irreversible oxidative damage, oxidative stress-cracking is mechanically indistinguishable from the others. Catalyst residues in the polymer, or certain additives, can be oxidation promoters. Therefore, antioxidants must be added in order to minimize this type of failure.

3.3 Chemical Resistance

Polyethylenes have excellent chemical resistance to many chemicals and solvents. At ambient temperature, they are resistent to acids and alkalies except for oxidizing acids such as nitric, chlorosulfonic, and fuming sulfuric. They are unaffected by hydrofluoric acid. The polyethylenes are generally insoluble in organic solvents at temperatures below 50 °C (122 °F). However, at higher temperature they are soluble to varying degrees in hydrocarbons and halogenated hydrocarbons. They are appreciably affected by chlorinated solvents, aliphatic and aromatic hydrocarbons, certain esters, and oils. Polyethylene can be dissolved at temperatures greater than 71 °C (160 °F) in toluene, xylene, amyl acetate, trichloroethylene, petroleum ether, paraffin, turpentine and lubricating oils.

3.4 Permeation

Polyethylene is permeable to gases, vapor, and liquids. The permeation rates depend not only on the nature of the permeant, but also on the physical state of the polymer. Material permeating into the polymer may change the polymer's physical and mechanical properties.

3.5 Surface Cleanability

Polyethylene, being generally chemically inert and essentially non-polar, shows low adhesion, i.e., little tendency to bond to materials. Thus one might expect it to be easily cleaned. However, the characteristic of being permeable to many materials means that although the surface may be "clean," substances absorbed in the container walls may be removable only with difficulty.

4. DEVELOPMENT OF STANDARDS AND SPECIFICATIONS FOR PLASTIC CONTAINERS

The problem of setting up specifications and tests to insure safe transport of hazardous materials in plastics containers is a complex one. For normal transportation use, it is known that there are plastic materials which should not be used for packaging because packages made from these materials are too fragile, too hard to handle, too expensive, would not afford the required protection, or some combination of these. In general, people who work in the packaging industry are able to predict whether a given package will be satisfactory or not on an empirical basis derived from past experience, knowledge of materials properties, and economic factors. Furthermore, if a new package fails it is simply pulled off the market with no major adverse consequences to the public.

When dealing with packages for hazardous materials ladings, however, more sophisticated methods must be brought to bear because the risks associated with a trial and error approach are generally regarded as unacceptable. Furthermore, setting down specifications for each lading and each container on a case-by-case approach is rapidly becoming impractical in the face of the proliferation in the number of commodities and package types moving in commerce. Under these circumstances, what is needed is a set of criteria based on standards which a reasonable person can interpret and apply to assess the level of risk associated with a particular combination of package and lading.

Standards or regulations are generally either specification-oriented or performance-oriented, and a clear distinction exists between them. The specification-oriented approach is typified by many building codes. There are a myriad of details as to construction materials, and configuration which go into constructing a building to meet the specifications. It is not uncommon, under this system, for an innovative, improved solution to a problem to sit in limbo until codes are amended to permit the use of the new approach. After enough such modifications have been made, however, the code may no longer be interpretable by everyone who needs to comply with it.

In performance-oriented approach, the person who wishes to demonstrate compliance with a set of regulations needs only to submit test data in support of his contention that his product meets or exceeds certain levels of performance. As long as the given product meets these criteria, there is no need to specify the color, or weight of the product, nor the material from which it is made unless, of course, compatibility with a lading is to be a problem. It is possible and most often, desirable to combine the two approaches in order to arrive at the most equitable set of regulations.

To insure that a set of tests and specifications will minimize the number of failures, it is necessary to consider all situations which can lead to failure of the container. In so doing, methods must be established whereby the in-use history of the container can be approximated by a sequence of laboratory tests. Listed below are a number of factors which appear governing the use of plastic containers. Solely for convenience sake, they have been divided into two categories--those dealing with the container itself and those dealing with the interaction of the lading and container. In reality, the distinction between the two may not be clear-cut because of interdependencies.

1) Container Use Conditions

a) Temperature history

The maximum and minimum temperatures the container will experience in service and the maximum time a container is likely to be subjected to the maximum temperature must be determined. The effect of cycling temperature on the material properties will also be an important factor. For example, it is shown in Section 7 that a 34 °C rise in temperature can, for identical stress histories, cause a 1000-fold decrease in time-to-fail for polyethylene under the conditions of an applied uniaxial stress.

b) Stress history

Both the maximum stress and the time the container is at maximum stress should be established. Again, the effect of various stress histories, including cycling the stress, will be important. For example, the question arises as to whether a given container is more likely to fail as a result of a high stress occurring for a short time, such as might be experienced in dropping, or fail as the result of a low stress sustained over a long time period, as may occur in stacking and/or vapor pressure increase of the lading if the container is unvented. Again, it will be demonstrated in Section 7 that the results can be greatly different depending upon the polymer resin type.

c) Useful lifetime

Containers designated for one trip use (not reusable) should be designated with the above mentioned factors in mind. However, if the container is to be reused, additional factors such as the maximum number of trips and/or maximum length of service must be determined as well. Stated another way, what is the maximum allowable period in service before retesting is required? These times or periods shall be referred to as the *lifetime or useful lifetime.*

2) Effect of Lading

a) Chemical attack

Some ladings may soften, swell, or react chemically with polyethylene. Two questions which arise in this connection are: (i) should ladings known to interact with polyethylene be allowed to be shipped in polyethylene containers (for example nitric acid or mixtures containing nitric acid), and (ii) if so, how does one determine that such an interaction has taken place?

b) Stress-cracking

A variety of chemicals are known to stress crack polyethylenes to varying degrees. What is needed in this case is to determine which ladings are stress cracking agents and what level of stress-cracking agent is acceptable to be shipped and for how long or often. Thus, a test to determine if a lading is to be judged a stress-cracking agent and, if so, a scale of severity needs to be established.

c) Permeation

Many liquids and gases permeate polyethylene, some may go through the polymer leaving it unchanged. Others may change its mechanical or other physical properties. Tests need to be established to determine the permeability of the polymer to its lading, and to what degree a change in mechanical or other physical properties of the container due to permeant is acceptable.

Special problems may exist with respect to containers designated as reusable. Ladings from an earlier use which have permeated the container may at a later time diffuse back out into a subsequent lading, thus contaminating it.

d) Product alteration

Similar to c), the lading may be contaminated by the extracting from the polymer of additives (antioxidants, etc.).

5. REVIEW OF PRESENT DOT SPECIFICATIONS AND TESTS AND OTHER TESTS FOR POLYETHYLENE CONTAINERS

The present DOT specifications and tests for polyethylene containers are contained in Part 49 of the Code of Federal Regulations (49 CFR). These address specifications on material properties of the resins used to manufacture the containers as well as qualification tests on actual containers. In this section, these tests will be reviewed in the light of the discussions in Section 4. Comments on the current requirements used by DOT for acceptance of plastic containers used under exemptions will also be given.

Also reviewed in this section are tests and standards from sources other than 49 CFR. An effort has been made to broadly cover the standards literature. In so doing, the following publications have been searched.

1) *American National Standards Catalogue*, 1975 catalog and 1976 supplement.

2) *World Index of Plastic Standards*, NBS Special Publication No. 352 (December 1971).

3) *An Index of U.S. Voluntary Engineering Standards*, NBS Special Publication No. 329.

4) *An Index of U.S. Voluntary Engineering Standards*, Supplement 1 and 2, NBS Special Publication No. 329/1 and 329/2.

5) *Transportation of Dangerous Goods* (1970), and Supplement (1973), Part II. Recommendation prepared by United Nations Committee of Experts on the transport of dangerous goods.

This survey has uncovered standards from sources such as International Standards Organization (ISO), ASTM, Department of Defense (DOD), Japanese Standards Association, and British Standards Association, etc.

In order to clarify the kinds of materials and what one is dealing with, all of the specifications in Part 178 of Title 49 CFR for free-standing polyethylene containers or for plastic containers intended for use with overpack are listed in Table 2.1. Table 5.1 lists the materials properties required of the resins used to manufacture the containers and also summarizes which tests are required on which container. Table 5.2 gives a partial list of allowed ladings for plastic containers. Those familiar with DOT tests will recognize many similarities to tests from other sources. However, a number of interesting differences occur and some of these will be mentioned at the appropriate point.

5.1 Comments on Resin Specifications

1) Melt Index (ASTM 1238-62T)

The melt-index test is primarily useful to polymer manufacturers as a method of controlling material uniformity. While the data from this test are not directly translatable into relative end-use processing characteristics, the melt-index value is nonetheless strongly indicative of relative "flowability" of various kinds and grades of polyethylene. The "property" measured by this test is basically the melt viscosity, or "rate of shear." In general, the materials that are more resistant to flow are those of higher molecular weight so that the melt index is useful in determining the approximate molecular weight.

However, polymers, such as polyethylene, in the amorphous state (melts) and above a molecular weight of about 30,000 show a non-newtonian behavior when they are sheared; that is to say, the viscosity depends on the rate of shear. In the limit of zero shear, the viscosity depends on the weight average molecular weight to the 3.4 power. At higher rates of shear, the non-newtonian viscosity depends not only on the molecular weight, but also on the molecular weight distribution. Although the designers of this test tried to simulate a viscometer which extrudes the material at low rates of shear, the rates attained are mostly in the non-newtonian region. Furthermore, the short capillary used in the test introduces difficulties due to end effects, which depend highly on the "elasticity" of the material which, in turn, depends on the molecular weight distribution. As a result, one can obtain the same melt index from materials which have different weight average molecular weights. Thus, this test is acceptable only to the extent that one is comparing materials which have, similar molecular weight distributions. Since most resins produced commercially have approximately log-normal molecular weight distributions, resins having the same density, the same melt index, the same tensile strength, and same percent elongation should not show significant differences in their general performance.

TABLE 5.1

LIST OF RESIN SPECIFICATIONS AND CONTAINER TESTS FOR DOT APPROVED CONTAINERS

	Resin Specification					Drop Test					
Specification Number	Melt Index	Density		Tensile Strength (psi)	Elongation (%)	Height	Temp.	Place	Vibration Test	Compression Test	Hydrostatic Test
		Min.	Max.								
1H	2.5[1]	N.S.[2]	N.S.	N.S.	N.S.	4	• F	ANY	No	No	No
43A	N.A.	N.A.	N.A.	N.S.	N.S.	6	N.S.	CHIME	NO	No	Yes
						4	N.S.	CLOSURE			
34	<1.2	.941	.965	1500	75	4	N.S.	WEAKEST	YES	Yes	Yes
						4	• F	ANY			
2T	<2.6[1]	.910[1]	.925[1]	1500	400	6	• F	ANY	Yes	No	No
						4	• F	ANY			
						4	N.S.	ANY			
2U	<2.6[1]	.910[1]	.925[1]	1500	400	4	N.S.	ANY	Yes	No	No
	(TYPE III P.E. MAY BE USED FOR <6 GAL)					4	• F	ANY			
2E	BLOW MOLDING GRADE CAPABLE OF HOLDING SHAPE WHEN STANDING EMPTY AND OPEN.					4	N.S.	WEAKEST	No	No	No
						4	• F	ANY			
2TL	<2.6[1]	.910[1]	.925[1]	1500	400	6	• F	ANY	Yes	No	No
						4	N.S.	WEAKEST			
						4	• F	ANY			
2S	2.6[1]	.910[1]	.925[1]	1500	400[1]	6	• F	ANY	Yes	No	No
						4	• F	ANY			
						4	N.S.	ANY			
2SL	<2.6[1]	.910[1]	.925[1]	1500[1]	400	6	• F	ANY	Yes	No	No
						4	N.S.	ANY			
						4	• F	ANY			
44P	< .6			2100[3]	350[3]	6	N.S.	6 DROPS	No	No	No

[1] DENOTES TEST METHOD ACCEPTABLE TO BUREAU OF EXPLOSIVES.

[2] NOT SPECIFIED.

[3] DENOTES ELONGATION AND TENSILE STRENGTH TESTED ACCORDING TO ASTM 882-73; ALSO, DROP TEST ACCORDING TO ASTM 1709 62T, AND TEAR TEST AS MEASURED ACCORDING TO ASTM D1922-61T.

2) Tensile Strength and Percent Elongation (ASTM D638)

Tensile properties are an indication of strength in a material. The force necessary to pull the specimen apart is determined along with prebreak stretch. The elastic modulus ("modulus of elasticity" or "tensile modulus") is the ratio of stress to strain in the limit of very small strain. The tensile strength is a useful value because parts should be designed to accommodate stresses to a degree well below this value.

For some applications where almost rubbery elasticity is desirable, a high ultimate elongation may be an asset. For rigid parts on the other hand, there is little benefit in the fact that they can be highly stretched.

There is benefit in moderate elongation, however, since this quality permits absorbing rapid impact and shock. The total area under a stress-strain curve is a measure of overall toughness. A material of very high tensile strength and little elongation would be brittle.

The above test may distinguish between two materials of the same melt-index and density but different molecular weight distributions. This may not be true of materials with bimodal distributions, or different densities.

3) Density (ASTM D1505-63T)

The density of the resin is a rough measure of the crystallinity and the branching of the polymer (see table in Section 3). As such, it gives another measure of the polymer's ability to perform.

5.2 Review of Container Tests

For ease of identification we shall give names to the tests.

1) Drop Tests (tests similar to 178.19-7 (a) and (b))[3]

The drop tests as presently used appear to be tests for failures which occur during handling. DOT regulation 178.19-7 (b) requires that a minimum of three containers taken at random from each continuous production lot be drop tested according to paragraph 178.19-7 (a) (2). There is no requirement that a single container shall be expected to withstand more than one test.

By way of comparison the SPI test for drop-impact resistance of plastic containers (Technical Bulletin PBD-4-1968) specifies that a minimum of twenty (20) randomly selected containers are required for testing, and the Japanese Industrial Standard for blow-molded containers from polyethylene (JIS Z0202-1962) requires that each container for special use (hazardous materials) be dropped 10 times. The Japanese test further specifies the order of drops in such a way that each edging is subjected to a direct impact. In each of these tests including the DOT test, the test temperature and drop height are not substantially different.

The ASTM Drop Test (ASTM D2463-74) contains a variety of procedures for making drop tests on containers. The static Drop Height Method (procedure A) is similar to the SPI test for drop impact in that it requires a minimum of 20 containers to be dropped.

Apparently, ASTM and SPI feel that 20 containers represent an appropriate sample size. In procedure B, a concept not incorporated into DOT tests is introduced. This is the idea of a test to failure. In this procedure (referred to as the "Bruceton Staircase Method"), the mean failure height of the test specimens is determined. It consists of dropping a set of test specimens from various heights, the drop height being raised or lowered depending on the result obtained on the specimen most recently tested. That is, if the previous

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[3] Citations of this type refer to paragraphs in *Code of Federal Regulations*, Title 49, Transportation, Parts 100 to 199. The revision date applicable to citations in this report is October 1, 1975.

specimen failed, the drop height is lowered; if the previous specimen did not fail, the drop height is raised. Such a procedure provides a more quantitative estimate of the strength of the container under drop conditions and allows for two types of containers to be quantitatively compared under drop conditions.

2) Vibration Test (tests similar to 178.19-7(c)(1))

This test appears to be directed at testing container closures. Since tests for closures are beyond the scope of this report they will not be discussed further.

3) Compression Test (tests similar to 178.19-7 (c)(2))

The Compression Test presumably is a means to determine the effects related to stacking or storage of containers for relatively short periods. The DOT test 178.19-7 (c)(2) specifies (as does the Japanese Industrial Standard Test Z 1706-1966 (7.4)) that the container must be maintained in the load-bearing condition (compression) for 48 hours at room temperature. On the other hand, the U.N. Committee of Experts recommends that the compression test should be carried out at 40 °C (104 °F) for a period of 28 days.

The SPI Column Crush Test (Technical Bulletin PBD-3-1968) is essentially a short time test insofar as the container is deformed in compression at a rate of one inch per minute, and it is not clear what relevance, if any, this test bears to stacking or storage over any realistic time period.

Compression tests such as the DOT, SPI, and Japanese Industrial Standard Tests mentioned above are very difficult to evaluate since it is not clear just how the information gained from the test relates to in-use behavior. For example, since the container is filled only to 98 percent of its capacity, the specified load may not be sufficient to cause an increase in the hydrostatic pressure on the water. The result in this case will be different than if an increase in hydrostatic pressure does occur.

4) The Hydrostatic Pressure Test (similar to 178.19-7 (a)(3))

Presumably, this is a test to determine the effectiveness of the closure and presence of cracks in the container. Tests at room temperature for such a short time can give no indication of efficacy for a long term stress situation.

5) Stress-Cracking Test

An important area which most testing procedures and regulations, including DOT regulations, do not address in any meaningful way is stress-cracking. The Japanese Industrial Standard does include a stress-cracking test which is similar to the ASTM test ASTM D2561-70 (procedure B). This is one instance where most test procedures for plastic containers are deficient, particularly where reuse is concerned.

5.3 Compatability Requirements

As required by 49 CFR, only certain ladings may be carried in specified containers. Table 5.2 provides lists by container type of the various ladings which may be carried in different allowed DOT specification containers. The range of materials allowed is enormous and varied. Corrosive liquids, oxidizing materials, and organic peroxides are most evident. For these, it is possible to determine their compatibility with polyethylene as long as the industrial grades of the materials do not vary. However, a large group of allowed materials do not have a clear chemical composition. They are: Class B poisonous liquids, nos (not otherwise specified) cleaning compounds; liquid organic peroxides nos; acids, nos; flammable liquids, not specifically provided for. There are a variety of materials which are additives, which in themselves may not be dangerous but may be incompatable with the polyethylene. The various additives may result in early failure, thus allowing leakage of the lading. The only requirement is that use of containers is "authorized only for materials that will not react with polyethylene and result in container failure." Further, there are no tests or criteria for container reactivity or failure in these terms. This would seem to be a serious deficiency in 49 CFR.

TABLE 5.2

PARTIAL LIST OF ALLOWED LADINGS FOR PLASTIC CONTAINERS

SPEC 34 - REUSABLE MOLDED POLYETHYLENE FOR USE WITHOUT OVERPACK

ACIDS OR OTHER CORROSIVE LIQUIDS NOS	173.245
HYDROCHLORIC (MURIATIC) ACID, ETC.	173.263
SULFURIC ACID	173.272
HYPOCHLORITE SOLUTIONS	173.277
HYDROFLUOSILICIC ACID	173.265
HYDROGEN PEROXIDE SOLUTION IN WATER	173.266

SPEC 2S - POLYETHYLENE DRUMS

FLAMMABLE LIQUIDS NOS	173.119
ALCOHOL	173.125
ACIDS OR OTHER CORROSIVE LIQUIDS	173.245
CLASS B, POISONOUS LIQUIDS, NOS	173.346
ARSENIC ACID	173.348
CARBOLIC ACID (PHENOL) LIQUID	173.346
DINITROBENZOL	173.371
HYDROGEN PEROXIDE SOLUTION IN WATER	173.266
FLAMMABLE LIQUIDS NOT SPECIFICALLY PROVIDED FOR	173.119
HYDROCHLORIC (MURIATIC) ACID, HYDROCHLORIC (MURIATIC) ACID MIXTURES, HYDROCHLORIC (MURIATIC) ACID SOLUTION, INHIBITED SODIUM CHLORITE SOLUTION, AND CLEANING COMPOUNDS, LIQUID, CONTAINING HYDROCHLORIC (MURIATIC) ACID	173.263
HYDROFLUOSILICIC ACID	173.265
HYPOCHLORITE SOLUTIONS	173.277
PROPELLANT EXPLOSIVES (SOLID) FOR CANNON, SMALL ARMS, ROCKETS, GUIDED MISSILES, OR OTHER DEVICES, AND PROPELLANT EXPLOSIVES (LIQUID)	173.93
HYDROBROMIC ACID	173.262
HYDROFLUORIC ACID	173.264
HYDROGEN PEROXIDE SOLUTION IN WATER	173.266
SULFURIC ACID	173.272
ETCHING ACID LIQUID, NOS	173.299
TRIS-(1-AZIRIDINYL) PHOSPHINE OXIDE	173.299A
RADIOACTIVE MATERIALS	173.393
LIQUID ORGANIC PEROXIDES, NOS, AND LIQUID ORGANIC PEROXIDE SOLUTION NOS	173.221
BENZENE PHOSPHORUS DICHLORIDE AND BENZENE PHOSPHORUS THIODICHLORIDE	173.250A

SPEC 2SL - MOLDED OR THERMOFORMED POLYETHYLENE CONTAINER

Flammable liquids	173.119
Peracetic acid	173.223
Acids or corrosive liquids	173.245
Hydrochloric acid	173.263
Hydrofluoric acid	173.264
Hydrofluosilicic acid	173.265
Sulfuric acid	173.272
Hydrogen peroxide solution in water	173.266
Hydrochloric (muriatic) acid, hydrochloric (muriatic) acid mixtures, hydrochloric (muriatic) aicd solution, inhibited sodium chlorite solution and cleaning compounds, liquid, containing hydrochloric (muriatic) acid	173.263
Hypochlorite solutions	173.277
Hydrofluoric acid	173.264
Hydrofluosilicic acid	173.265
Hydrogen peroxide solution in water	173.266
Allyl chloroformate, benzyl chloroformate, etc.	173.288
Etching acid liquid, nos	173.299
Tris-(1-aziridinyl) phosphine oxide	173.299a
Radioactive materials	173.393
Liquid organic peroxides, nos, and liquid organic peroxide solutions, nos	173.221
Benzene phosphorus dichloride and benzene phosphorus thiodichloride	173.250a

SPEC 21P - FIBER DRUM

Flammable liquids nos	173.119
Acids or other corrosive liquids nos	173.245
Compounds, cleaning liquid	173.256
Hydrochloric (muriatic) acid, etc.	173.263
Hydrofluosilicic acid	173.265
Hydrogen peroxide solution in water	173.266
Sulfuric acid	173.272
Low specific radioactive materials	
Radioactive materials	173.393

SPEC 2U - MOLDED OR THERMOFORMED POLYETHYLENE CONTAINER

Class B, poisonous liquids, nos	173.346
Carbolic acid (phenol) liquid	173.349
Dinitrophenol solutions	173.362a
Dinitrobenzol	173.371
Acids or other corrosive liquids not specifically provided for	173.245
Compounds, cleaning liquid	173.256
Hydrochloric (muriatic) acid, hydrochloric (muriatic) acid, mixtures hydrochloric (muriatic) acid solution, inhibited sodium chlorite solution and cleaning compounds, liquid, containing hydrochloric (muriatic) acid	173.263
Hydrofluosilicic acid	173.265
Alcohol	173.125
Liquid organic peroxides, nos and liquid organic peroxide solutions, nos other than acetyl peroxide solution, acetyl benzoyl peroxide solution, cumene hydroperoxide, dicumyl peroxide, hydrogen peroxide, peracetic acid, and tertiary butylisopropyl benzene hydroperoxide	173.221
Acids or other corrosive liquids, nos	173.245
Sulfuric acid	173.272
Hypochlorite solutions	173.277
Poisonous liquids, nos	173.346
Flammable liquids, nos	173.119
Acetyl peroxide and acetyl benzoyl peroxide solution	173.222
Tris-(1-aziridinyl) phosphine oxide	173.299a
Hydrogen peroxide solution in water	173.266
Liquid organic peroxides, nos, and liquid organic peroxide solutions, nos	173.221
Benzene phosphorus dichloride and benzene phosphorus thiodichloride	173.250a

SPEC 6D - CYLINDRICAL STEEL OVERPACK, STRAIGHT SIDED FOR INSIDE PLASTIC CONTAINERS

Propellant explosives (liquid) for cannon, small arms, etc.	173.93
Flammable liquids, nos	173.119
Alcohol	173.125
Liquid organic peroxides, nos and liquid organic peroxide solutions nos other acetyl peroxide solution, etc.	173.211
Acids or other corrosive liquids, nos	173.245
Electrolyte (acid) or corrosive battery fluid	173.257
Hydrobromic acid	173.262

Hydrochloric (muriatic) acid, hydrochloric (muriatic) acid mixtures, hydrochloric (muriatic) acid solution, inhibited, etc.	173.263
Hydrofluoric acid	173.264
Hydrofluosilicic acid	173.265
Hydrogen peroxide solution in water	173.266
Sulfuric acid	173.272
Hypochlorite solutions	173.277
Poisonous liquids, nos	173.346
Tris-(1-aziridinyl) phosphine oxide	173.299a
Compounds, cleaning liquid	173.256
Radioactive materials	173.393
Benzene phosphorus dichloride and benzene phosphorus thiodichloride	173.250a

SPEC 37M - CYLINDERICAL STEEL OVERPACK STRAIGHT SIDED FOR INSIDE PLASTIC CONTAINER

Flammable liquids, nos	173.119
Liquid organic peroxides, nos, and liquid solutions etc.	173.221
Peracetic acid	173.223
Acids or other corrosive liquids, nos	173.245
Electrolyte (acid) or corrosive battery fluid	173.257
Hydrochloric (muriatic) acid, hydrochloric (muriatic) acid mixtures, hydrochloric (muriatic) acid solution, inhibited, etc.	173.263
Hydrofluoric acid	173.264
Hydrofluosilicic acid	173.265
Hydrogen peroxide solution in water	173.266
Sulfuric acid	173.272
Etching acid liquid, nos	173.299
Tris-(1-aziridinyl) phosphine oxide	173.299a
Radioactive materials	173.393
Benzene phosphorous dichloride and benzene phosphorus thiodichloride	173.250a

6. DISCUSSION AND TENTATIVE RECOMMENDATIONS

The first four sections of this report were concerned primarily with delineating the more important resin characteristics and physical properties of polyethylene as they relate to the manufacture of plastic containers. Section 5 presented a review of several of the present DOT specifications and test methods as well as test procedures used by other countries and organizations such as ASTM, SPI, and the U.N. Committee of Experts. This survey, along with studies in our laboratory, have led to the conclusion that inadequacies exist in the present DOT specifications and test methods. Viewed overall the recommendations of the U.N. Committee of Experts on the transport of dangerous goods and the Japanese Industrial Standard for blow-molded containers of polyethylene appear to be more comprehensive than do the DOT regulations.

The present section is intended to provide preliminary recommendations whereby present DOT specifications and test methods can be modified to yield more quantitative results with greater predictive value. In Section 7, work will be described which may possibly aid in the establishment of test methods relevant to the reuse of containers. However, further experimental and theoretical work is necessary in the areas of mechanical properties in order to determine the validity of the assumptions made. Such work may require experimentation on actual containers under a variety of conditions simulating transport.

6.1 Resin and Materials Properties Tests

In general, DOT regulations presently require that materials properties be run on the resin prior to processing. Although these properties are important from a practical point of view, they are not as important as the material properties of the finished container. For example, if one assumes that melt index is an important material property affecting the performance of a finished container (see the discussion of melt index under Section 3), then the fabricator should be required to keep the melt index below some acceptable limit throughout his process to the finished container. Changes in the melt index are accompanied by changes in tensile properties, crystallinity, and molecular orientation which may have an adverse effect on container performance. In the case of steel cylinders for compressed gases, the regulations already require data from materials tests on finished containers. It should be possible to devise similar criteria for plastic containers. Furthermore, in the absence of such data it is not possible to correlate failures in the field with suspected defects in container design or industrial forming processes.

6.2 Test on Actual Containers

It should be apparent from the discussion in Section 5 that most of the test method procedures concerned with the mechanical integrity of the container could be improved by the incorporation of the idea of a test to failure. For example, the present DOT Drop Test for Specification 34 containers is based on a pass-fail criteria at fixed levels of performance determined from statistical samples of doubtful meaning. The importance of this statement is underscored by the fact that failures in drop tests have provided most of the clear indications that some manufacturers have been experiencing difficulty in making containers that meet specifications. ASTM test D-2463-74 provides a clear example of how the drop test procedures can be modified to provide a more quantitative result with greater statistical validity. An important point to be made here is that it is not sufficient to base acceptance upon a pass-fail criteria determined at only one drop height. More extensive test data should be required which provide information about the breadth of the pass-fail distribution curve.

Similar statements apply to the vibration test, hydrostatic pressure test, and static compression test. The importance of running the hydrostatic pressure test to failure will be of particular value in determining the weak point of a new container design. In the case of the compression test, current DOT tests do not require that the applied stress necessarily be large enough to cause yield. Such data should be required to insure that safe stress levels, well below the yield point, will not be exceeded during normal transportation or storage usage.

Although modifications to these or any of the other mechanical tests to yield more quantitative measures of the failure in these modes would be valuable in showing differences in effectiveness of container manufacturers' container design, none of these mechanical tests face the questions of long-time failure in polyethylene containers.

As was discussed in Section 3, polyethylene is known to fail as a result of the application of low stresses for long times. This is a well known phenomenon and is documented in Section 7. Thus, it is possible that a container which passes the drop test (a short-time, high-stress test) may fail upon being shipped for many days under conditions which will lead to an increase in vapor pressure of the material. This problem is more serious in the case of a container to be reused. A container may experience several drops as well as long-time, low-stress situations. The cumulative damage caused by these varied incidents could lead to failure during the next shipping. Just which test will assure that failure is unlikely to occur is currently under investigation.

None of the tests surveyed from other sources face this problem. There exist few, if any, retest procedures. Perhaps this is primarily a reflection of the fact that most container specifications, which have been surveyed, do not specifically address reuse. The one test which possibly comes closest to considering the question of long time failure is the stacking test, specified by the U.N. Committee of Experts on the transport of dangerous goods. In their test, the container must be capable of withstanding a predetermined applied stress for a period of 28 days at 40 °C (104 °F).

From the discussion above, it seems that two kinds of lifetime tests are needed. One type is needed to determine whether or not a new container will be able to withstand the various temperatures and stress histories which are likely to be experienced under extreme shipping conditions. A second category of tests, or retests, is needed to determine whether a container intended for reuse can be used for another extended period of use. Both types of tests would be expected to give an estimate of the lifetime of the container.

Two sets of data are necessary to determine how these tests may be established. First, estimates of the stress-temperature history the container sees during a year's use need to be established. Secondly, it is necessary to determine how failure of a polymer depends on its previous stress-temperature history. For example, are many high-stress, short-time occurrences (resulting from drops) more likely to cause failures than a long-term, low-stress situation resulting from stacking?

The first question falls within the realm of study of the transportation process itself. The second question can only be answered by a study of the failure mechanisms of the polymer. Studies with this intent in mind have been initiated and the results to date are reported on in Section 7. In fact the experimental studies reported in Section 7, although, as yet, far from complete, have led to suggestions for some general tests on lifetime of containers. The general scheme of the tests would be:

(1) In order to make meaningful lifetime tests for a container, measurements should be made on polymer specimens obtained from an actual container. To do this, pieces should be cut from an actual container and cut into tensile specimens. The specimens are then subjected to high temperatures (i.e., 77 °C) for a number of different tensile loads. The time to break as a function of tensile load is then determined. From these data and baseline data on polyethylene, similar to that provided in Section 7, the lifetime of the container can be estimated. *However, it must be recognized that the data supplied in Section 7 do not represent the whole picture, since the data were obtained for uniaxial stresses only. In actual use, materials nearly always experience biaxial, or multiaxial stresses which may significantly alter the lifetime behavior.*

(2) A test-to-failure with known hydrostatic pressure should be applied to a container of new design or made by a new process or new processor. The time-to-fail and the weak spot of the container design is thus determined. From the total container data and material data from (1) above, a better estimate of the lifetime of containers, made in the same way, can be obtained.

In this manner, one would have an estimation of failure times for a given container design from the second test discussed above and a control on the effect of materials or processing changes from the first test.

6.3 Tests Relating to Interaction of the Container and the Lading

There is little or nothing in the present DOT requirements concerning the interactions of the container with its lading. For containers made of polymeric materials, this is a major problem as was indicated in Section 3. The DOT requirement 49 CFR only requires that the lading and the material of the container be compatible. It was pointed out in Section 5, there is not a sequence of tests which define compatibility. In the case of exemptions, compatibility is better defined in terms of a sequence of tests and observations. This sequence of tests tries to establish quantitatively permeation loss, stress-cracking, and chemical attack, but even here quantitative requirements are not required. More quantitative tests appear to be necessary. In the following, several approaches to quantitative requirements will be proposed.

1) Stress-Cracking Tests

a) Lifetime tests in the presence of lading materials

The following proposed tests depend on, as yet, unconfirmed assumptions. The usefulness of the tests as measures of lifetimes (especially for reuse) in the presence of lading depends on research proposed to be done.

All containers of new design, made by a new processor, or made from a new polyethylene should be tested to failure at high temperatures and applied pressure with a known stress-cracking agent, for example, Igepal solution. This test could replace test number 2 discussed in the previous subsection. The time-to-fail and weak point of the container, with a known stress-cracking agent, should be determined.

From time-to-fail with a known stress-cracking agent, container lifetime with different ladings can be estimated. This would be done in the following manner: a scale of the stress-cracking ability would be established for the various ladings by determining the time-to-break versus stress curves for these various ladings materials on laboratory specimens of polyethylene. The time-to-break curves would be scaled to the time-to-break curves on specimens stress-cracked with the known stress-cracking agent. From these data, the lifetime of the container with the lading could be estimated.

The validity of the scaling procedure depends on the assumption that the time-to-break curves of various ladings are of the same functional form. Research aimed at improving the experimental underpinnings of these assumptions is proposed for next year.

b) Reuse criteria

Any of the above tests to determine the lifetime of the container could be used for retests to determine available further lifetime of the containers after an extended period of use. The success of such a procedure depends on the assumption that damage due to stress cracking and/or permeation induced moduli changes is additive for different ladings. It is proposed (in future work) to search for additivity or superposition criteria.

7. LABORATORY STUDIES OF MECHANICAL PROPERTIES LEADING TO THE FAILURE OF POLYETHYLENE

In this section the laboratory work carried out to date in the NBS Polymers Division pertaining to mechanical properties will be summarized. The present studies were undertaken with the goals of: (1) determining certain baseline data relevant to the failure of polyethylene under adverse and nonadverse conditions, and (2) exploring concepts which might prove useful in establishing procedures whereby plastic containers can be tested for reuse. The point should be made that in order to accomplish (2) a knowledge of (1) is required. What one is particularly looking for in (1) are insights which will lead to the estimation of long-term behavior based on relatively short-time tests.

7.1 General Introduction

The main problem associated with the reuse of plastic packaging for hazardous materials ladings lies in predicting the lifetime of the container. In actual use, a container may be subjected to a wide range of mechanical and environmental histories. Its lifetime will depend not only upon the present state of stress (or strain) and environment, but on the past stress (or strain) history and environment as well. By environment, we mean both physical and chemical, including temperature and type of lading. As described in earlier sections, when different resins from which the containers are made are compared, the life time will further depend on molecular factors such as chemical composition, molecular weight distribution, impurities, and architectural make-up (morphology). Another variable which can influence lifetime is that of the processing itself. It is entirely possible for two manufacturers of a similar type of container, using the same polymer resin, to produce containers of markedly different mechanical properties, including lifetime, due simply to differences in the operating procedures of processing.

It is known further from earlier work in our laboratory that even the simplest equation capable of describing the mechanical behavior of polymers is complicated due to the dependence of the material's "memory" on previous strain history. It is also known that the memory is dependent on temperature, swelling agents, and oxidative degradation. Because the stress applied on a material at any time depends on all these factors in a rather complex way, the status of a container in reuse cannot be specified without a knowledge of its previous in-use history.

To date, the information available in the open literature concerning ultimate properties of polymeric materials is fragmentary, and no study concerned with lifetime has addressed itself to all of the important factors. The initial task requires considerable groundwork in the form of experiments to determine how polymeric materials behave under conditions involving even simple histories. Such experiments can provide the basis upon which an understanding of the more complex histories likely to be encountered in actual container performance can be built.

Of concern here are several rather specific aspects of the overall problem and the present work represents an attempt to establish some of the more important experimental and theoretical parameters involved. Section 7, which is divided into four subsections and two appendices will deal exclusively with polyethylene since the great majority of commercial plastics containers in use today are fabricated from polyethylene.

1. Experimental Procedures
2. Time-to-Break Study
    (i) Under conditions of static loading to air
    (ii) Under adverse chemical environment
3. Description of Failed Samples
4. Assumption of additivity of damage

    Appendix A - Constant Rate of Loading Experiments

    Appendix B - Comment on Viscoeleastic Properties

1) Experimental Procedures

a) Samples

Linear polyethylenes (PE) of three different molecular weights were used to obtain time-to-break data. Some of the pertinent sample characteristics are summarized in Table 7.1. The two polyethylenes labeled A and B were from a commercial source and had weight average molecular weights, as determined by light scattering, of 160,000 and 90,000, respectively. Both polymers contained Ionol and dilaurylthiodipropionate as thermal stabilizers and had relatively little branching. However, it should be pointed out that both resins had experienced rather long shelf lives prior to molding and it is not clear to what extent the thermal stabilizers remained operative. Sample C, which had a weight average molecular weight of 50,000 as determined by Gel Permeation Chromatography, was the NBS Standard Reference Material (SRM) 1475. Additionally, samples were cut from two commercial PE containers, namely a cider and bleach bottle.

For the time-to-break study, molded specimens of all three molecular weights were prepared as follows. Since each resin was in the form of pellets, a flat sheet 15 x 15 x 0.15 cm was molded first. The pellets were melted in a heated press at the temperature specified in Table 7.1 and a pressure of approximately 3.8×10^6 pascals (556 psi) then applied. Each sheet was allowed to cool under pressure in the press to a temperature below 80 °C before being removed. Each sheet was then remolded in a "picture-frame" type mold under the same conditions outlined above to obtain a more bubble free and thinner sheet 15 x 5 x 0.1 cm in dimensions. In order to relax each sheet at a temperature higher than any to be employed in the breaking experiment, each sheet was heated in an oven at 115 °C in air for a period of 72 hours.

Individual specimens were cut from each sheet by first cutting the sheet into 0.635 cm wide strips which were then recut with a die into the shape of a "dog-bone." The final gauge length of the thin section was approximately 3 cm long and 0.32 cm in width. For purposes of area determination, each specimen was measured along its entire gauge length with a dial gauge in order to establish the minimum thickness. For the molded specimens, the maximum variation in thickness for a given sample was in all cases less than 0.01 cm. (10 percent).

In the case of the commercial container materials, the bottles were blow-molded, and variations in thickness over the length of the specimen were in some cases as great as 30 percent. In all cases, the areas used for calculation of the load per unit area were the minimum measured values.

The densities quoted in Table 7.1 were determined by hydrostatic weighing in boiled distilled water. For samples A, B, and C, the values shown represent averages based on measurement of specimens from four different sheets of each molecular weight, whereas for the two commercial containers, the values are based on only a single determination. In the case of samples A, B, and C, the largest deviation from the average was 0.001 g/cm^3, which based on analysis of the measurement technique also represents the estimated error.

7.2 Apparatus

For the time-to-break study, the specimens were clamped in aluminum clamps designed so that they hung vertically with little or no bending of the specimen while under load. Under the conditions of static loading, the time-to-break varied from 1 second to approximately 145 days. In cases where the specimen was subjected to a constant rate of loading, a light weight plastic bucket was attached to the lower clamp and water allowed to flow in at a predetermined constant rate until the specimen broke. Such an arrangement is convenient in that the bucket could either be preloaded statically for a predetermined period of time before superimposing a constant rate of loading, or not, depending upon the experiment. This method also has the added advantage that the specimen always broke with little, if any, cold-drawing.

In addition to the experiments at room temperature, data were also collected at 330 K (57 °C), 350 K (77 °C), and 370 K (97 °C). In these instances, the breaking experiment was done in an oven which could be controlled to within 0.03 K during the time of loading. As will become evident later from the results, a small change in temperature can be of major importance in influencing the time-to-break for polyethylene.

2) Time-to-Break Study

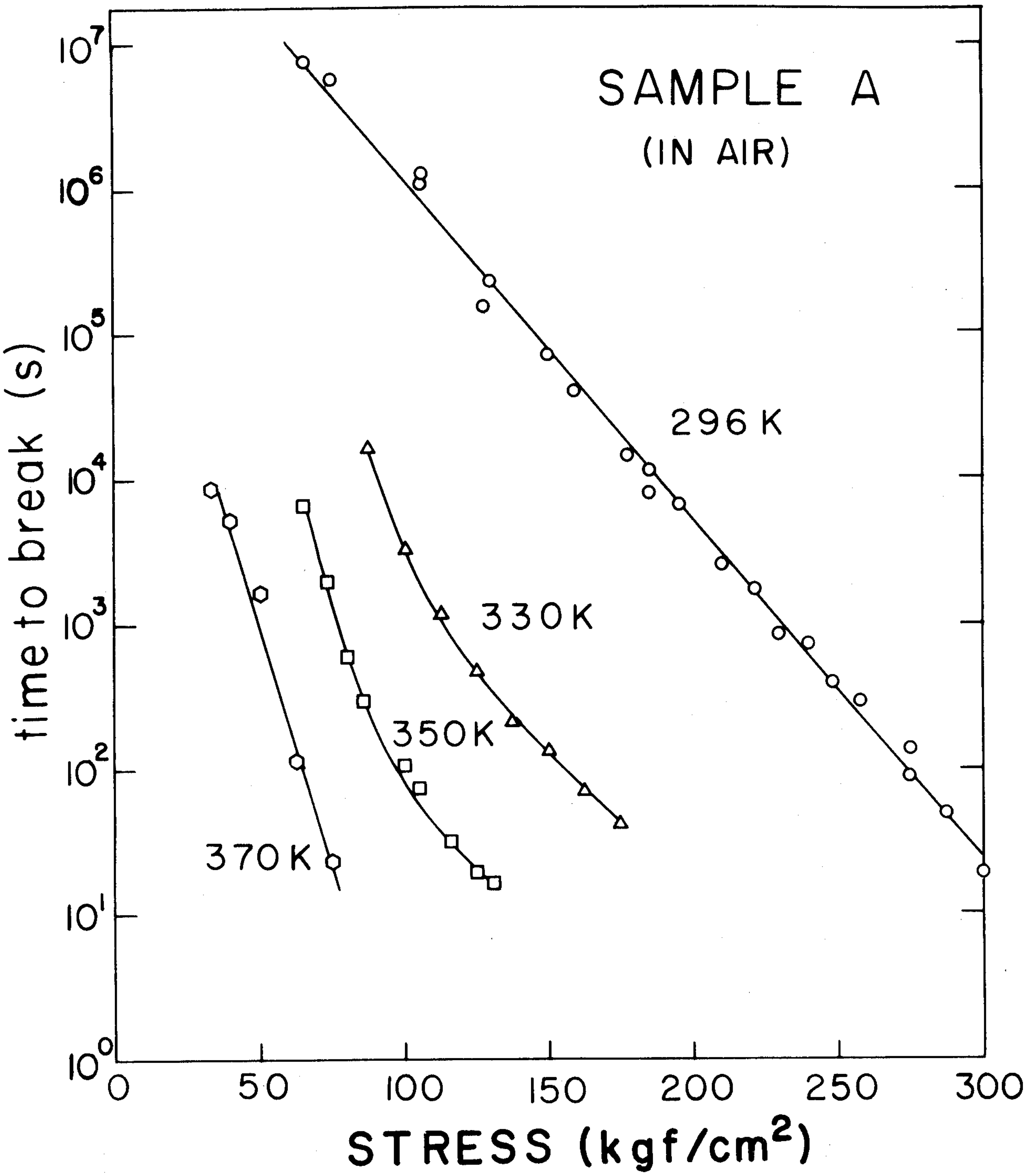
a) Time-to-break as a function of temperature for constant loads

Time-to-break data (t_B in seconds) as a function of stress (expressed as kgf/cm^2) are shown in figures 7.1, 7.2, and 7.3 for the three different molecular weight samples of polyethylene. Equivalent results for the two commercial containers are presented in figure 7.4.

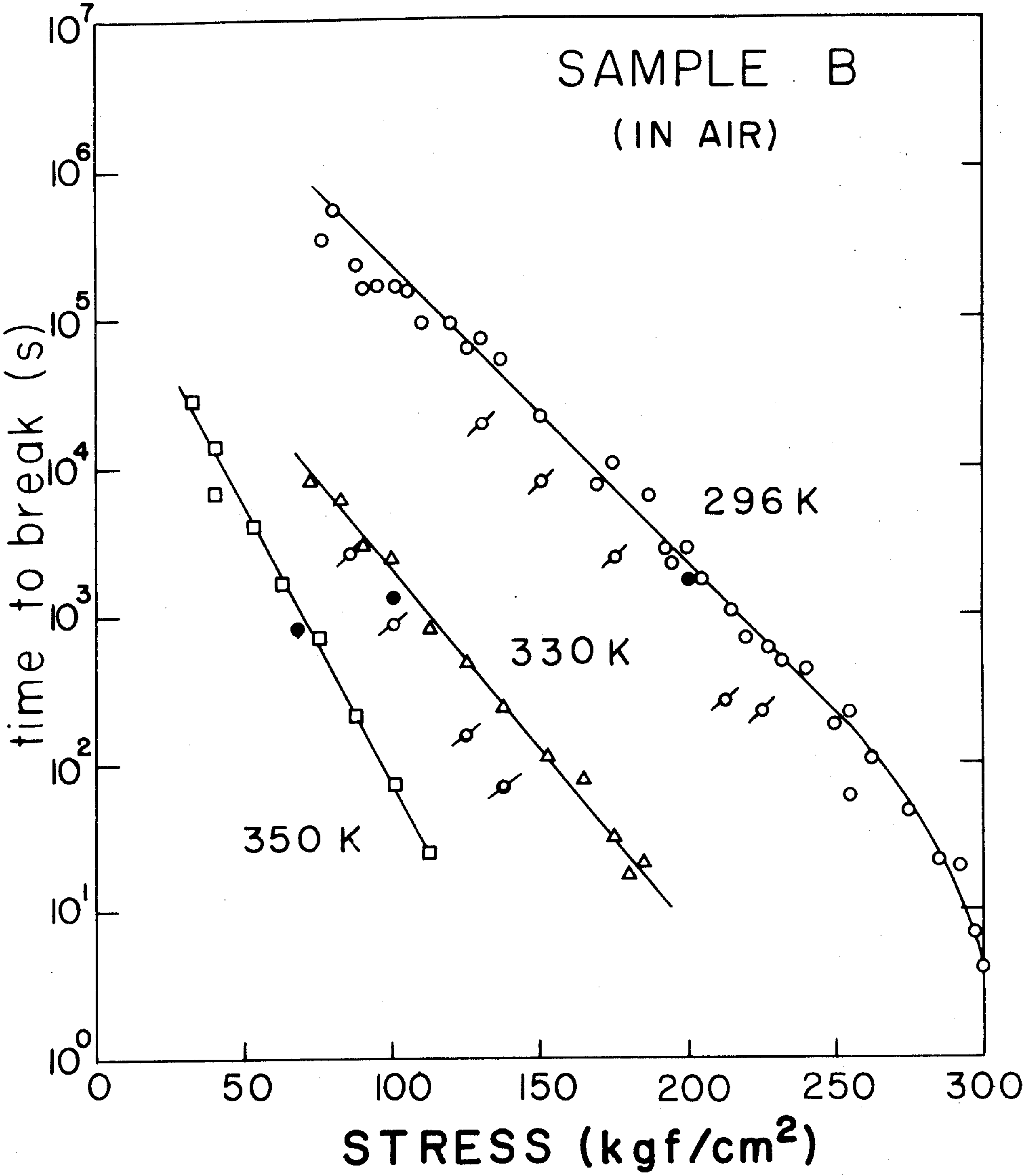
TABLE 7.1

SAMPLE CHARACTERISTICS PERTINENT TO TIME-TO-BREAK STUDY

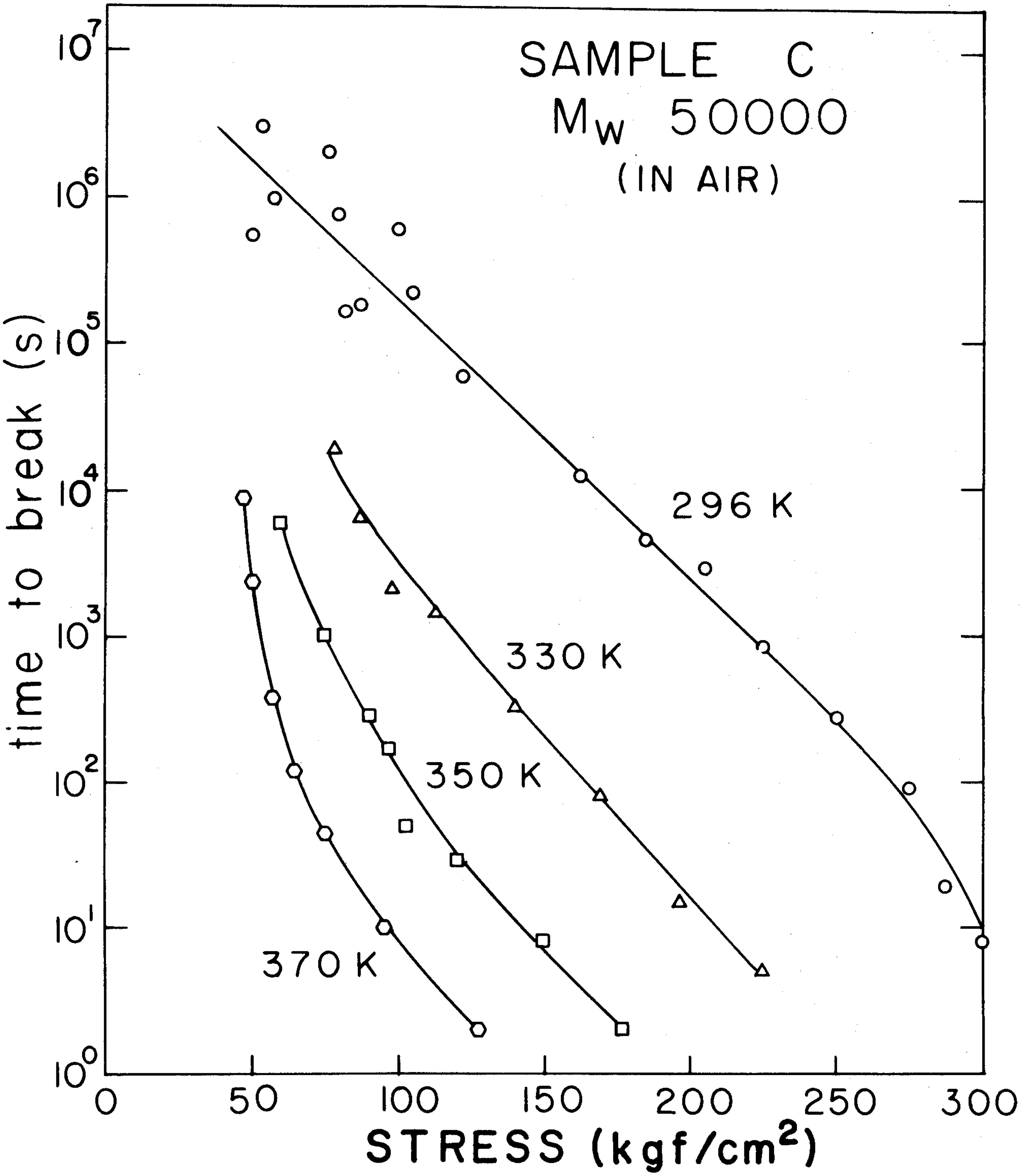
SAMPLE	APPROXIMATE MOLECULAR WEIGHT	MOLDING TEMPERATURE °C	ANNEALING TEMPERATURE °C	DENSITY AFTER ANNEALING G/CM^3
A	160,000	175	115	0.969
B	90,000	160	115	0.973
C	50,000	160	115	0.971
COMMERCIAL CIDER CONTAINER	UNKNOWN		UNTREATED	0.946
COMMERCIAL BLEACH CONTAINER	UNKNOWN		UNTREATED	0.957



7.1 Log. Time-to-Break Versus Static Load for Polyethylene Sample A (M_W = 160,000).



7.2 Log. Time-to-Break Versus Static Load for Polyethylene Sample B (M_W = 90,000). Open Symbols - in air, 0 - presoaked in motor oil at 60°C for 24 hours, 0 - presoaked in hexane at 23°C for 24 hours.



7.3 Log. Time-to-Break Versus Static Load for Polyethylene Sample C (M_W = 50,000).

For sample A (M_W = 160,000), it is to be observed from figure 7.1 that at room temperature (296 K) the log t_B is essentially a linear function of load over nearly six decades of time. Also, there is little scatter of the data points, particularly at the long times. In equation form the data can be expressed reasonably well by

$$\ln t_B = \ln t_o - \alpha\sigma_B \tag{1}$$

where t_o and α are material properties and σ is the applied stress expressed in kgf/cm^2. This equation is of the same form as that developed by Coleman [4] to describe the creep failure of nylon yarns. Interestingly enough, the linear line shown in figure 7.1 if extrapolated to zero load, yields a t_o from equation (1) of 2.4 x 10^8 seconds. It is known that at small loads, the curve will eventually turn upward since it is unlikely that a relaxed specimen would actually break under its own weight in a span of only 6.5 years. However, it must be recognized that it is possible for a polymeric container to fail in a finite time even if stored empty, due to the presence of internal stresses which require very long times to relax. It is also possible that at the very long times, environmental factors such as the presence of oxygen may become important contributions to early failure under stress.

For the two lower molecular weight samples B and C (figs. 7.2 and 7.3), similar remarks apply to the room temperature results. Note, however, that with decreased molecular weight the scatter becomes progressively worse at the long times.

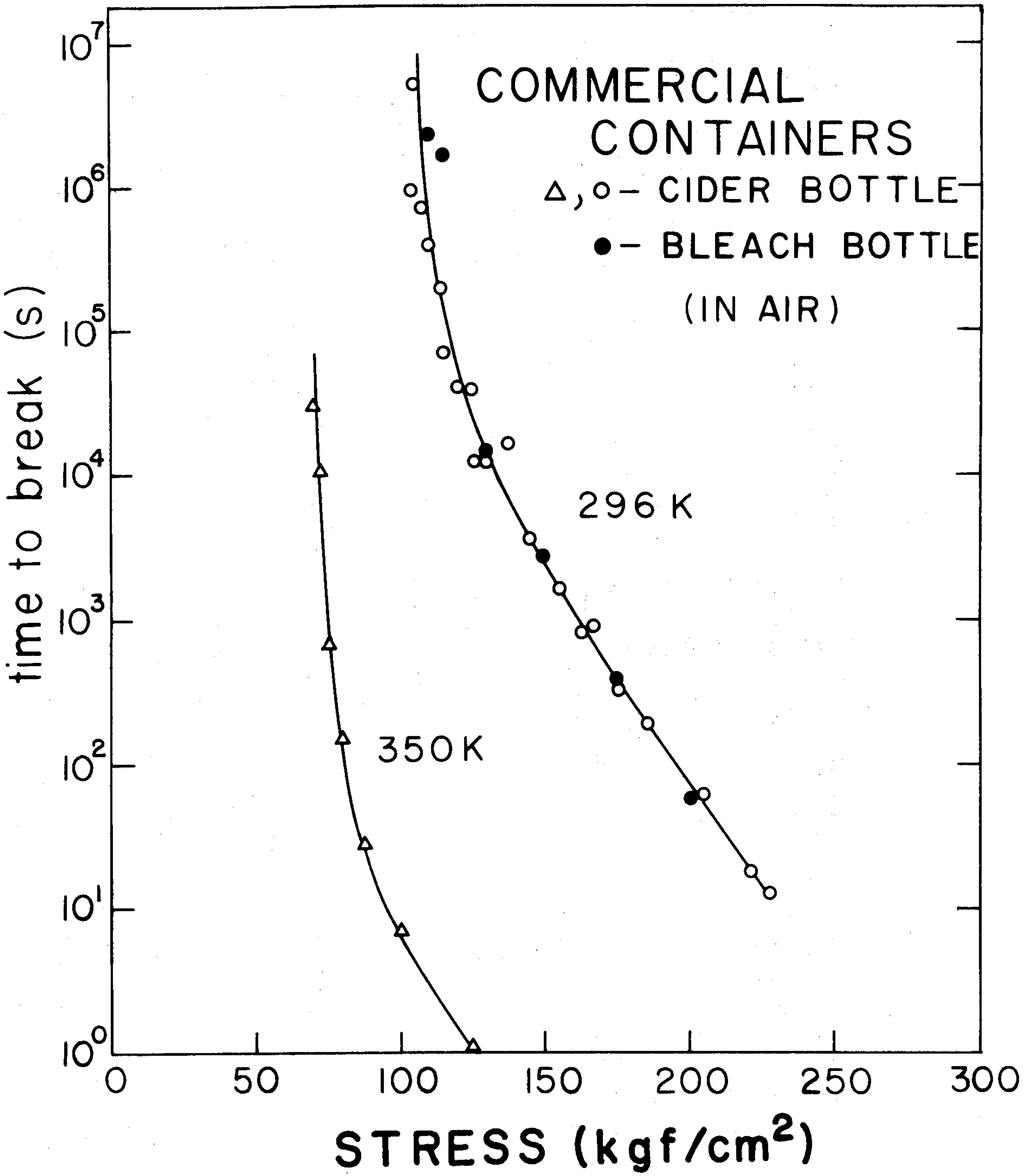
Since temperature is known to be an important factor in determining lifetime, all three PE resins were examined at several elevated temperatures. Just how dramatic the effect is can be seen from the results for sample A (fig. 7.1). For a stress of 75 kgf/cm^2, t_B dropped nearly 5.5 decades in time from 296 K to 370 K (97 °C). At 150 kgf/cm^2, an increase in temperature of only 34 °C decreased t_B by a factor of more than 600. Since plastic containers in actual use may be subjected to temperatures in this range, temperature must be considered of primary importance especially when hazardous materials are involved.

Another salient feature of the data is that, except for sample B, a pronounced curvature upward appears at the higher temperatures with decreased loading. It is interesting to find that at the higher temperatures the scatter in the data points becomes significantly less than is the case at room temperature. In the case of sample B, the slope of the log t_B vs load curve does increase with increased temperature, but there is little or no curvature of the line indicated.

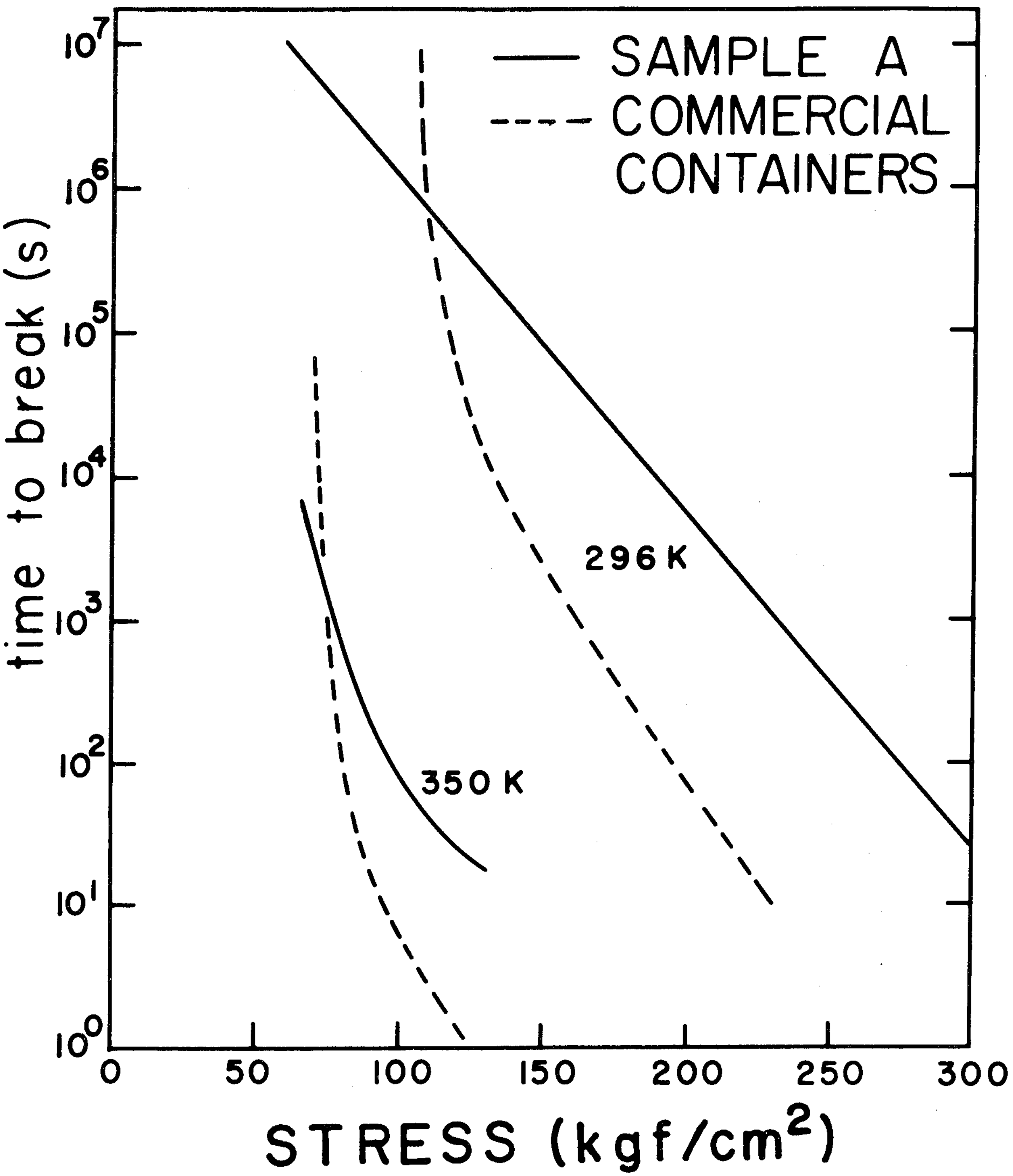
Several major features stand out when the results in figures 7.1 to 7.3 are compared overall. The first is that at large stress (>250 kgf/cm^2), the 296 K line is no longer linear but curves downward. This statement applies to sample A, but only at loads greater than those shown in figure 7.1. The second feature is that, while there does appear to be an effect of molecular weight, it is not especially important except at long times. That is, at room temperature the slope of the log t_B vs load time tends to decrease with decreased molecular weight, but only at long times (>10^5 seconds) does the effect become prominent. For example, at 75 kgf/cm^2 the t_B for sample C is about one decade less than that for sample A. However, it cannot be stated with certainty whether the observed behavior is a result of molecular weight, or is a manifestation of density or crystallinity differences, the possibility that more than one breaking mechanism is operative, or environmental factors.

Time-to-break data for specimens from the two commercial cider and bleach bottles are shown in figure 7.4. No substantive information is available concerning the polyethylene resin used to make either container. However, judging by their intended use it can be surmised that the molecular weight is likely to be high and that they contain some branched material. In addition, the bleach bottle contains white dye. Since both were blow-molded, some orientation may also be presented. In the present study, all of the specimens were cut vertically and it is not yet established whether or not specimens cut horizontally along a circumference, or diagonally, will have a measurably different time-to-break behavior.

The feature of primary interest is the much greater slope over the entire load range than is observed for the other three PE polymers. This feature has the interesting consequence that the curves cross over. Whereas the commercial containers fail much earlier at



7.4 Log. Time-to-Break Versus Static Load for Two Commercial Polyethylene Containers.



7.5 Comparison of Log. Time-to-Break Versus Static Load for Sample A and Two Commercial Polyethylene Containers.

large loads, they become superior in terms of time-to-break at the small loads. This behavior is demonstrated in figure 7.5 where the lines shown are those taken from figures 7.1 and 7.4. For example, at 296 K and a stress of 225 kgf/cm^2 the commercial bottle specimens broke in a time 100 times shorter than did sample A, yet at a stress of 100 kgf/cm^2 they are a decade or more longer in time-to-break. Based on the 350 K data, one would conclude that at stresses of less than about 60 kgf/cm^2, the commercial bottle would require an exceedingly long time-to-break in air.

Another interesting result is that both types of commercial bottles behave identically at room temperature. Whether this behavior is accidental or the two resins are basically the same is not known.

7.3 Environmental Factors

It is well known that environmental factors play an important role in deciding the ultimate properties of materials. Although environmental factors have not yet been examined in any depth, several possible stress-cracking agents have been examined in order to demonstrate the effect in this report. Specimens from sample B were soaked in motor oil at 60 °C for 24 hours and in hexane at 23 °C for 24 hours. The results are shown in figure 7.2. Only three specimens soaked in motor oil were tested, one at each of the temperatures used in the previous study. As is evident from figure 7.2, all three points essentially lie within the experimental scatter, and therefore the motor oil had little or no effect for the very limited range of test conditions carried out.

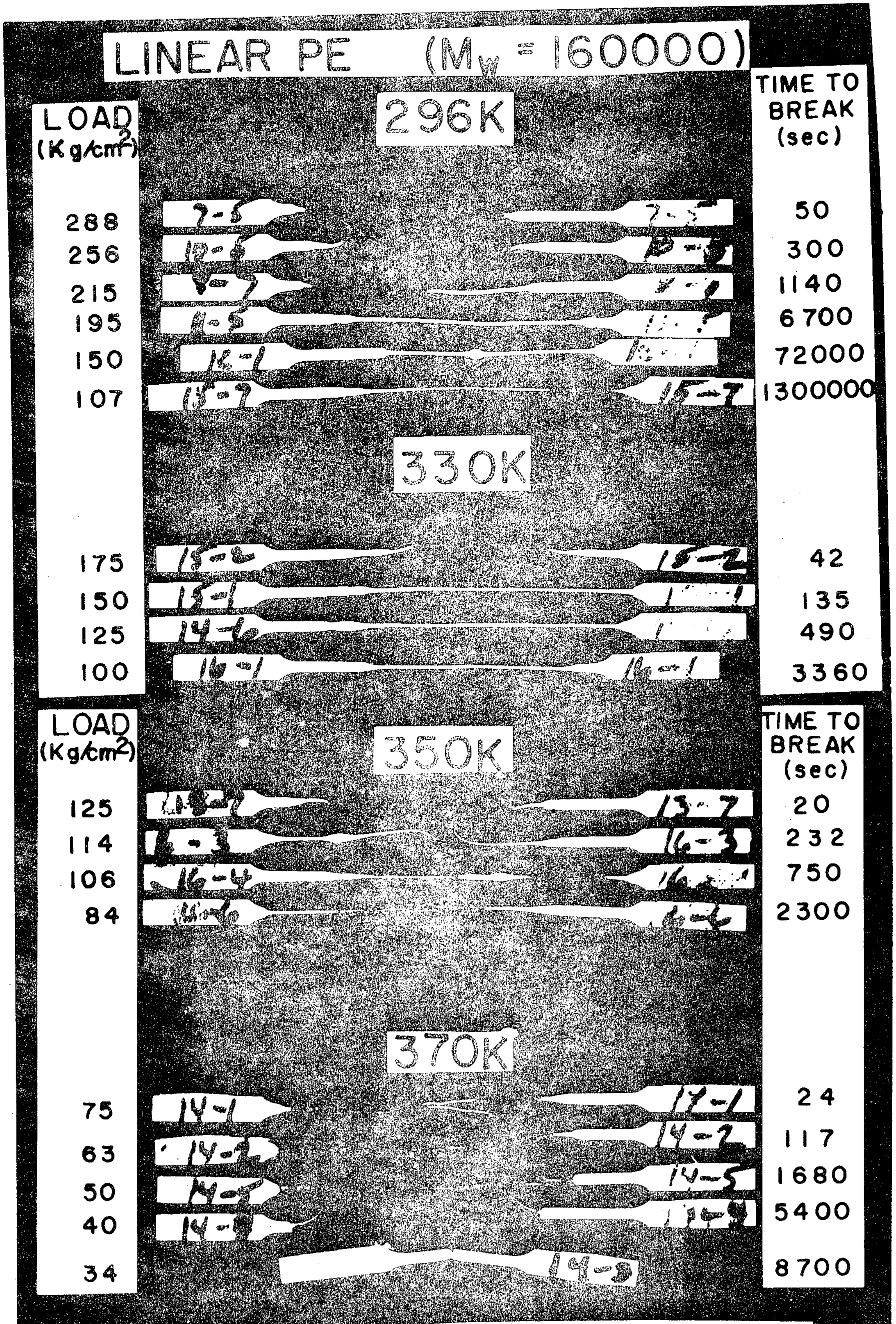
On the other hand, hexane, which is known to be a swelling agent for PE, has a profound influence on the time-to-break of this polyethylene even at room temperature. The time-to-break dropped by about a factor of two for specimens soaked in hexane for only one day. Note that for the specimens tested at 330 K (fig. 7.2), the effect appears to diminish as the load is decreased. This effect probably is a reflection that at elevated temperature, and since the specimen during the test was not submerged in hexane, the hexane was driven out of the specimen because of the increased length of the experiment.

It must be emphasized that all of the data shown here were obtained for specimens exposed to an environment prior to loading. Were the specimens to be in a stressed state during initial exposure, the effect no doubt will be far more dramatic.

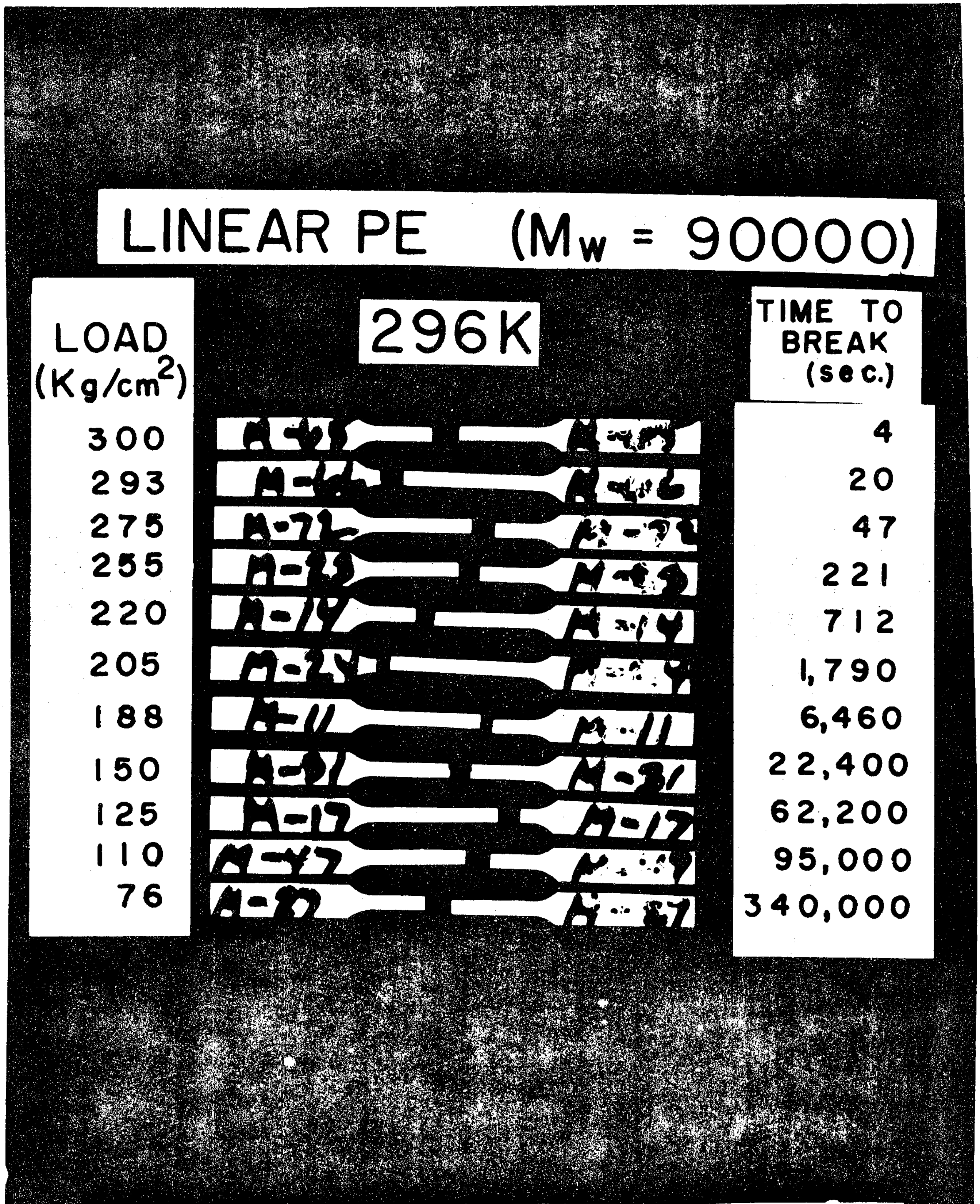
7.4 Specimen Appearance after Failure

Another aspect of the time-to-break study concerns the types of failure exhibited by the various samples of polyethylene. Included in figures 7.6 and 7.7 are photographs taken of a number of failed specimens which are representative of samples A and B. The behavior of sample C was essentially the same as that for sample B. Shown to the left of each specimen is the tensile load applied and to the right the time-to-break. Since several of the specimens did not actually break but cold-drew until the weight was stopped by the framework, the question arose as to what constituted breaking. As a criterion to determine the time-to-break, the rather simplistic definition was adopted in this study that failure occurred whenever a well defined neck appeared, or if no neck formed when the sample broke by crack growth. In cases where necking occurred, the specimen generally drew and/or broke in a time very short compared to the total time-to-break.

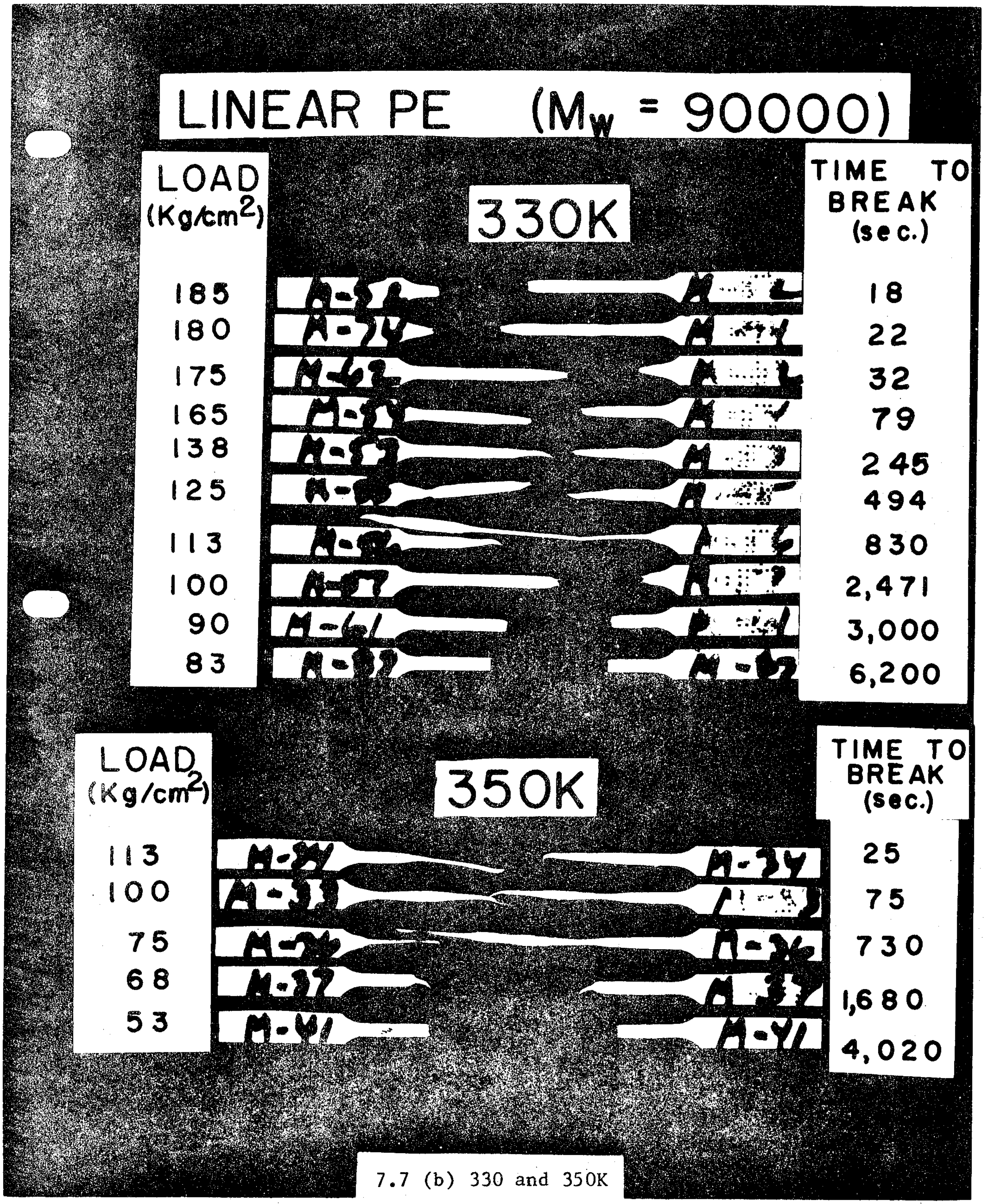
For sample A (MW = 160,000), it can be seen in figure 7.6 that at 296 K neck formation occurred over the entire tensile load range. Following neck formation at the very large loads, little, if any, cold-drawing occurred before the sample broke. As the applied load decreased, the tendency to cold-draw after necking increased until at intermediate times-to-break the specimens sometimes did not break but cold-draw to large extension ratios. Note that in some instances more than one neck formed. More recent data indicate that at even longer times the specimens show little or no tendency to neck and/or cold draw, but break cleanly. At the higher temperatures, the tendency to form a neck and then cold-draw becomes even more pronounced. However, at the highest temperature 370 K and for very small loads, the reverse was true as can be seen in figure 7.6 for the specimen stressed to 40 kgf/cm^2. Perhaps the most interesting specimen shown is the one at the bottom in figure 7.6 which purposely was unloaded before it could break. Long thin strands of polymer can be seen connecting the separated material, an indication that crazing occurred rather than simply crack growth.



7.6 Appearance of Specimens from Sample A after Failure.



7.7 Appearance of Specimens from Sample B after Failure: (a) 296K



7.7 (b) 330 and 350K

In marked contrast to sample A are the specimens from sample B (MW = 90,000) which at room temperature showed no sign of necking prior to breaking (see figure 7.7a). Over the entire load range, the fracture surfaces are relatively smooth as in brittle fracture. It is important to point out that prior to the actual breaking, in many instances severe damage in the form of a whitened appearance occurred throughout the interior of the entire gauge length. Such a result is usually indicative of massive internal and/or surface defects such as crazing and demonstrates that the failure represents a bulk phenomenon and does not arise simply from a single surface defect.

As for sample A, the tendency to neck and cold-draw becomes enhanced at the higher temperatures for sample B (see fig. 7.7b). The specimens tested at 330 K show most clearly the trend observed overall. At high loadings, necking occurred followed by little or no cold-drawing before fracture. As the load decreased, cold-drawing occurred more readily until finally at sufficiently small loads the trend was reversed. At very small loads, necking no longer occurred and the fracture was more of a brittle type. The effect of molecular weight appears to be primarily one of enhancing the extent of cold-drawing as the molecular weight increases. Sample C (MW = 50,000) showed even less tendency to cold-draw at the higher temperatures than did sample B. The results overall suggest that more than one failure mechanism is possible depending upon the load conditions and temperature.

7.5 Assumption of Additivity of Damage

One useful concept which relates directly to lifetime and lifetime prediction is the idea of additivity, or accumulation, of damage. That is to say, damage which a material experiences as a result of a particular stress history is not recovered, but accumulates in time to some point at which the material fails. In mathematical terms, this "criterion" can be expressed by an equation of the type

$$f(t) = \int_0^{t_B} \frac{d\xi}{\xi_B[\sigma(\xi)]}$$

where $\sigma(\xi)$ is the stress applied at time ξ and $\xi_B[\sigma(\xi)]$ is the time-to-break for a constant load σ. When $f(t)$ reaches unity ($f(t) = 1$), the material fails.

In simple form an example which will serve to demonstrate the idea is given in the figure 7.8 below.

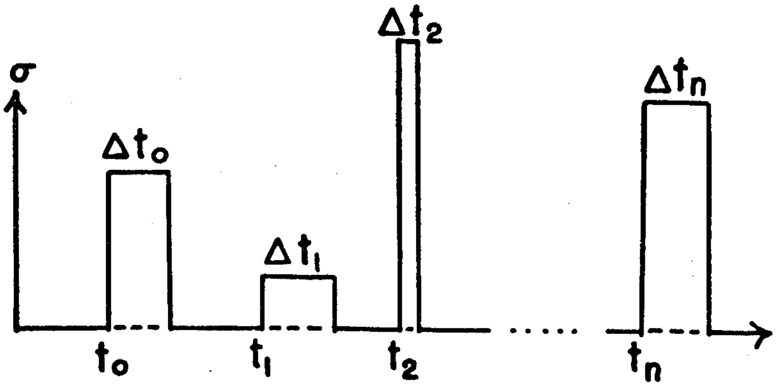


Figure 7.8 Schematic Representation of a Possible Stress History Applied to a Plastic Specimen.

Suppose a material up to a time t_0 has a history free of stresses. At time t_0, it is subjected to a stress σ_0 for a period Δt_0. At time t_1, it experiences a new stress σ_1 for a period Δt_1, and so on until at time t_n a stress σ_n is imposed for a period Δt_n. The cumulative time of damage or fraction time to failure, is then

$$f(t_n + \Delta t_n) = \frac{\Delta t_0}{\xi_B(\sigma_0)} + \frac{\Delta t_1}{\xi_B(\sigma_1)} + \ldots . + \frac{\Delta t_n}{\xi_B(\sigma_n)}$$

Note that in the time intervals where the stresses are zero there is no contribution to the damage. This means that in the interval from $t=0$ to $t=t_1$, the total damage $f(t_1)$ is simply

$$\frac{\Delta t_0}{\xi_B(\sigma_0)} .$$

However, the same damage would occur if a smaller stress σ was applied for the entire time interval from $t=0$ to $t=t_1$. This leads to the concept of equivalency of stress histories in which case the same total damage will result.

From experiments in our laboratory (see Section 7.2) carried out isothermally for several different temperatures, and the concept of time-temperature superposition, it is believed that the additivity of damage criterion will also work for stress histories where the temperature varies. If, in our previous example, the stress history depends on temperature as well as time so that at Δt_0 there is an associated θ_0 (temperature, then the general form of the expression from the fractional time to failure becomes

$$f(t_n + \Delta t_n) = \frac{\Delta t_0}{\xi_B(\sigma_0,\theta_0)} + \frac{\Delta t_1}{\xi_B(\sigma_1,\theta_1)} + \ldots + \frac{\Delta t_n}{\xi_B(\sigma_n,\theta_n)}$$

where now $\xi_B(\sigma_i,\theta_i)$ is then time-to-break at constant load σ_i at a temperature θ_i.

If $f(t_n + \Delta t_n)$ represents a typical stress and temperature history for one trip of a container, then for reuse

$$\frac{1}{f(t_n + \Delta t_n)} - 1 = N$$

represents the maximum number of additional trips that can be expected for the container. However, even for well-controlled samples the scatter in time-to-break can be a factor of two, so that the number of safe trips should be less than N/2. An additional safety factor may be desirable as well. If $f(t,\theta)$ for one trip is known, an equivalent stress and temperature for a short-duration test can be determined to give $2f(t,\theta)$. Then for reuse, several containers can be selected at random and subjected to the short-duration test. If they pass, the containers can be used for another trip. Naturally before the above test is applied sample containers will have to pass the drop test, or leak test, if necessary.

Now in order for the above test to be applicable, the times $\xi_B(\sigma_i,\theta_i)$, where i runs from 0 to n, for the container and the average damage per trip $f(t_n + \Delta t_n)$ must be known; that is to say, data of the type presented in Section 7.2. Fulmer [5] has shown that a scaling factor can be obtained between an actual container and laboratory specimens. Since the scaling depends on the shape, manufacturing conditions, and resin, the scaling factor must be determined not only when changes of design are involved, but also when a different resin is used. The average damage per trip, $f(t,\theta)$, can be estimated by modeling the various conditions of an average trip.

It must be remembered that an important assumption made above is that of a constant chemical environment, or to be more precise, under various stress and temperature histories in air. It remains to be determined whether the additivity of damage criterion remains valid in the presence of other chemical environments. Further research is currently underway in our laboratory to resolve this question.

With regard to the validity of the damage criterion itself, even in the absence of an adverse chemical environment, several experiments have been carried out involving relatively simple stress histories. The results of these experiments, which suggest that for the simple stress histories employed, the concept is valid, are summarized in Appendix A.

Finally in Appendix B are included comments pertinent to viscoelastic behavior in general. The comments are intended to show that it is possible from single- and multistep stress relaxation experiments to predict the stress for any other uniaxial strain history.

APPENDIX A

ADDITIVITY OF DAMAGE UNDER CONDITIONS OF A CONSTANT RATE OF LOADING

As pointed out in Section 7.3, a useful concept which relates directly to lifetime and lifetime prediction is the idea of additivity of damage. That is to say, damage which a material experiences as a result of a particular strain (or stress) history is not recovered, but accumulates in time to some point at which the material will fail. In equation form, this criterion can be expressed as

$$1 = \int_0^{t_B} \frac{d\xi}{\xi_B[\sigma(\xi)]} \tag{A-1}$$

where $\xi_B[\sigma(\xi)]$ is the time-to-break for stress $\sigma(\xi)$. Such a relationship will be valid only when the environmental conditions are held fixed. In principle, knowing the proper form of $\sigma(\xi)$, it should be possible to predict the time-to-break under a complex history of loading.

In the simple case under consideration here, that of static loading, it is known that the time-to-break (t_B) for sample A can be represented over most of the time scale covered in figure 7.1 by

$$t_B = t_o\, e^{-\alpha\sigma_B}$$

where t_o and α are material properties and σ_B is the applied load. Suppose now one wishes to predict from the static data the time-to-break for a similar specimen subjected to a constant rate of loading experiment. Then $\sigma(\xi) = \sigma_o + m\xi$ where m is the rate of loading expressed as kg/cm^2-s and σ_o is the preload, if any, in kg/cm^2. In the present case, σ_o represents a preload of the plastic bucket (15.7 kg/cm^2) applied at time t=0. Equation (A-1) then becomes

$$1 = \frac{1}{t_o} \int_0^{\hat{t}_B} e^{\alpha\,(\sigma_o + m\xi)} d\xi \quad ,$$

which integrates to yield

$$\hat{t}_B = \frac{1}{\alpha m} \ln \left(\frac{\alpha m t_o}{e^{\alpha\sigma_o}} + 1 \right). \tag{A-2}$$

Here $\hat{t}_B$ is the time-to-break at constant rate of loading. It is known from the data for sample A at 296 K (fig. 7.1) that $\alpha = 0.054$ cm^2 kgf^{-1} and $t_o = 2.4 \times 10^8$ seconds. For m values of 0.1 and 1.0 kgf/cm^2-s, equation (A-2) yields values for $\hat{t}_B$ of 2620 and 304 seconds, respectively. Constant rate of loading experiments have been done for a number of specimens from sample A at rates varying from 0.02 to 0.7 kgf/cm^2-s (room temperature). If plotted on log-log paper, the log $\hat{t}_B$ versus log m data yield a straight line. For rates of 0.1 and 1.0 kgf/cm^2-s, the experimental values for $\hat{t}_B$ are 2450 and 290 seconds, respectively. Therefore, the calculated values for $\hat{t}_B$ based upon static loading conditions are within 6 percent, or less of those determined from the constant rate of loading experiments. The agreement is remarkably good and is well within the experimental scatter.

It is also possible to go the other way, that is to be able to predict the time-to-break for static loading conditions (t_B) from constant rate of loading data ($\hat{t}_B$). In this latter case, the appropriate equation, as derived from equation (A-1), becomes

$$t_B = \hat{t}_B \left(1 + \frac{d\ln \hat{t}_B}{d\ln m}\right) \quad . \tag{A-3}$$

To be successful in this case requires evaluation of

$$\frac{d\ln \hat{t}_B}{d\ln m},$$

which for sample A at both room temperature and 350 K, represents the slope of straight lines, at least over the range of m covered. Values of t_B, as calculated from equation (A-3), are shown in figure A.2 for a number of specimens broken under a constant rate of loading. The solid lines represent the same lines shown in figure 7.1. Again, the agreement is remarkably good at both temperatures.

In principle, one might anticipate that this method can be extended to predict failure at long times based upon shorter time tests. For example, in the case where a preload σ_1 is applied for a time t_1 and a constant rate of loading history then superposed at time t_1, equation (A-1) takes the form

$$t_B = t_1 \left[1 - \frac{\hat{t}_B}{t_B}\left(1 + \frac{d\ln \hat{\hat{t}}_B}{d\ln m}\right)\right] \qquad \text{(A-4)}$$

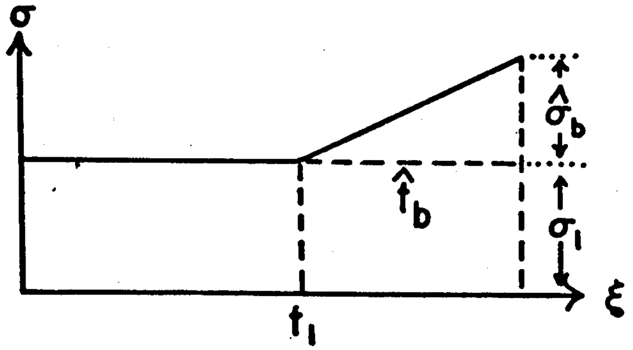
where now

t_B = time to break for a static stress of σ_1

$\hat{t}_B$ = time to break from application of a constant rate of loading

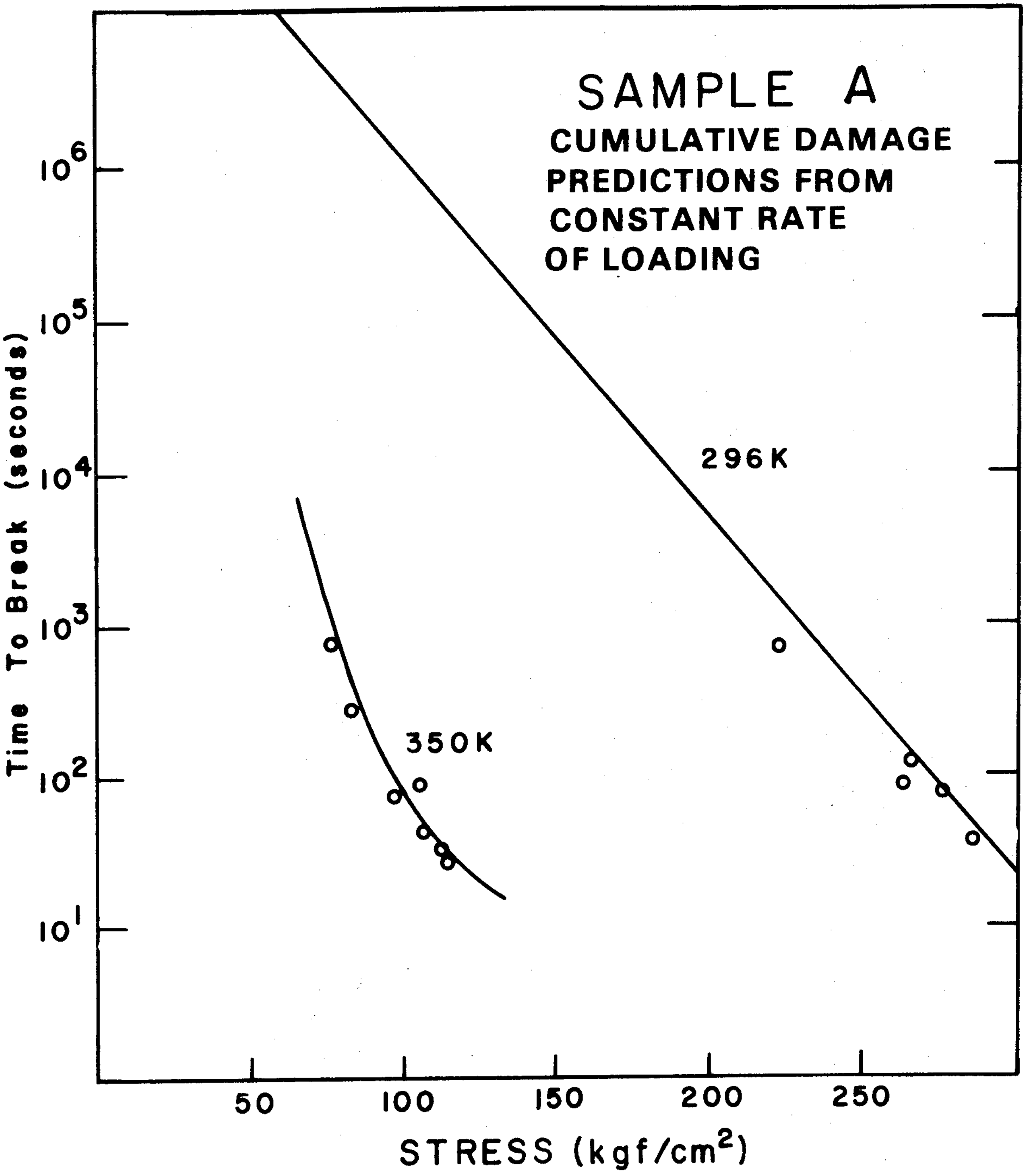
$\hat{\hat{t}}_B$ = time to break for a static load of $(\sigma_1 + \sigma_B)$

Schematically these quantities are shown in figure A-1 below.



A.1 Schematic Representation of a Constant Rate of Loading Experiment in which a Preload Has Been Applied for Time t_1.

An attempt has been made to check the validity of equation (A-4) by preloading specimens of sample A for specified times at stress in the 100 to 125 kgf/cm^2 range. The t_B's calculated from equation (A-4) tend to scatter over about one decade, falling generally on the low time side of the straight line shown in figure A-2. One problem with this method is that for preloaded samples the log-log plot t_B versus m does not necessarily yield a straight line so that the error in determining $d\ln t_B/d\ln m$ can be large.



A.2 Prediction of Time-to-Fail for a Static Load Based on Constant Rate of Loading Experiments. Solid Lines - Taken from Figure 7.1; Open Circles - Predicted Values for Time-to-Fail under Static Loading Conditions Based on Constant Rate of Loading Experiments.

In conclusion, it is found that for simple loading histories such as static loading or constant rate of loading (preloading for zero time), there is excellent agreement between the values of t_B calculated from static loading data and those determined experimentally from constant rate of loading results. Therefore, it would seem that the assumption of additivity of damage is a valid concept insofar as the simple histories investigated here are concerned.

APPENDIX B

A COMMENT ON VISCOELASTIC PROPERTIES

It was mentioned earlier that the mechanical properties of PE, and polymers in general, are time-dependent as well as strain and strain (or stress) history-dependent. Fracture mechanics as developed for metals cannot be used, especially for long time fatique cycling. Some years ago, a thermodynamic theory for describing the mechanical behavior of materials known as simple elastic fluids was developed in our laboratory. This theory derived by Bernstein, Kearsley and Zapas[4] and known as the BKZ theory, was later modified to describe the behavior of semicrystalline polymers.

In a simple version, one can translate the theory as follows: the stress at any time, t, is given as a summation of contributions from the configuration at time t and all past configurations at time τ, weighted with the elapsed time $t - \tau$. This type of mathematical formulation is known as a theory of materials with a fading memory. In the modified theory the elapsed time depends on the previous strain history.

As an example, consider simple extension. The tensile stress $\sigma(t)$ is given by the following equation

$$\sigma(t) = \int_{-\infty}^{t} H_{\star}\left(\frac{\lambda(t)}{\lambda(\tau)}\, ,\, \int_{\tau}^{t} \phi(\varepsilon(t),\, \varepsilon(\xi),\, t - \xi)\right) d\xi\, \frac{dII}{d\tau}\, d\tau \qquad \text{(B-1)}$$

where $\varepsilon(\tau)$ is the strain at time τ, $\lambda(\tau) = 1 + \varepsilon(\tau)$ and $H_{\star}(\circ, \circ)$ is the partial derivative of H with respect to the second argument. The function $\phi(\varepsilon(t), \varepsilon(\xi), t-\xi)$ is such that it equals unity when $\varepsilon(\xi)$ is equal to $\varepsilon(t)$. In a single step stress relaxation experiment where $\lambda(\tau) = 1$ for $-\infty<\tau<0$ and $\lambda(\tau)$ for $\tau>0$, equation (B-1) yields:

$$\sigma(t) = H(\lambda(t),t) \qquad \text{(B-2)}$$

where $H(1, t) = 0$, as derived from the BKZ theory.

From single step stress relaxation experiments, the behavior of H with respect to the first argument can be determined. Then from multi-step stress relaxation experiments, the dependence upon the second argument can be found. By making ϕ more specific, one can minimize the experiments needed. One can then predict the stress in any other uniaxial strain history.

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