

## Environmental Stress Cracking of Polyethylene\*

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### A. INTRODUCTION

In the presence of certain fluids, a polyethylene sample subject to a complex stress will break after an interval of time. The stress referred to is insufficient to break the material in the absence of these fluids (stress cracking agents). Examples of effective stress cracking agents are found among detergents of various types, alcohols and many other liquids. A great deal of information has been obtained in various places on this stress cracking problem, and its dependence on crystallinity, molecular weight of polymer, and other parameters have been examined before.<sup>1</sup> We have undertaken here to carry out an extensive study in the hope of throwing light on the mechanism of stress cracking in polyethylene.

The phenomenon of stress cracking is not limited to polyethylene and has been observed in other systems, notably glass, ceramics, and metals. For example, ordinary glasses which had been dried were found to be 20% stronger than wet ones, and 2 to 2.5 times stronger if dried and tested in vacuum.<sup>2</sup> Another example of a test on samples of porcelain subject to internal pressure showed that fracture occurred when water was used as the pressure fluid at a stress 80% of that obtained with oil as the pressure fluid.<sup>3</sup> Metals such as zinc, tin, and cadmium break at reduced stresses in the presence of fatty acids, mercury, or gallium,<sup>4</sup> and in a few experiments in our laboratories it was found that water was an effective stress cracking agent for films of nylon 66.<sup>5</sup>

### B. CRITERIA FOR A TESTING PROCEDURE

The first problem in setting up the experimental program was the selection of a suitable test. This is

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a crucial point, since different tests lead to different results. For the purpose of comparison with earlier data, the stress on the sample was to be complex, a condition which is fulfilled in the procedures to be discussed. In one popular test<sup>6</sup> the sample, a sheet 1½ by ½ by ⅛ in. is scratched along the length in a prescribed fashion, bent into a U shape, held in a fixed position, and submerged in a stress cracking agent. The time in which half of ten samples have broken is the stress cracking time. For our purpose, this test is not suitable. The stress on the sample varies enormously from one polymer to another; in soft polyethylene of low crystallinity, the stress is relatively small, and in some samples of highly crystalline polymer the sample is so brittle that it breaks before being inserted in the apparatus. The stiffness of crystalline polyethylene is very much increased when the polymer is allowed to cool slowly, the stress on the sample is a sensitive function of the technique of preparation, and fracture of the polyethylene sample occurs much sooner by this testing procedure when the sample is cooled slowly at the time of fabrication.

Another testing procedure by the "stress-raiser" technique was used by Carey.<sup>7</sup> A flat strip of polyethylene, 2 by ½ by 0.02 in. with a ⅛ in. diameter hole in the flat sheet is extended at a steady rate. The breaking time is recorded. An important advantage of this technique is that in so far as the polymer sample under test obeys the simple elasticity equations, the stresses in the sheet may be calculated from the known load on the sample.<sup>8</sup> The elastic limit was obviously exceeded in Carey's experiments, and also, in so far as the stress cracking phenomenon depends on time at a constant load, the technique of varying the load during a single experiment is a further complicating factor.

In another procedure, thin tubes are used as samples. The tubes are filled with compressed air.

which yields a biaxial stress, the hoop stress being twice as great as the stress along the length of the tube. This ratio could, of course, be modified by additional weights added on the tube. A shearing stress could be applied, if desired, by twisting the tube. A test of this sort is a very good one since the stress pattern is particularly simple and easily variable. The stress cracking agent could also be used to exert internal pressure, and this would represent an interesting change of conditions from the other experimental procedures, in which the liquid is in contact with the polymer but is not under pressure. A practical disadvantage of this test is that it is not easy to prepare samples such as these in quantity, with a closely controlled thermal history.

The following conditions were considered of primary importance in the experimental arrangement: (1) experiments carried out at a known stress, (2) quick and easy replication of experiments, (3) reproducible preparation of samples for testing, and (4) that stresses in the sample are known.

### C. EXPERIMENTAL PROCEDURE

The procedure followed in our stress cracking experiments was designed to satisfy the criteria set up in the previous section. The samples were geometrically identical with those of Carey, described earlier, but the experiments were carried out at a constant load. By working at constant load the macroscopic stress could be calculated, and would not change with time until the sample began to yield.

The preparation of the polyethylene samples was carried out in a controlled manner. Reproducing the conditions of preparation turned out to be a very important and, as shall be discussed later, much of the difficulty in the interpretation of many results already obtained by other workers and, indeed, of some of our own, arises from lack of sufficient control in sample preparation.

Several types of commercial polyethylene were used as basic material. These were Marlex<sup>9</sup>,\* Alathon 14,† Super Dylan 6200, 6600,‡ and a special low molecular weight sample of Super Dylan, henceforth referred to as Super Dylan LMW. These polymers were pressed into sheet form. The procedure followed was to melt a suitable amount of polymer and press the material

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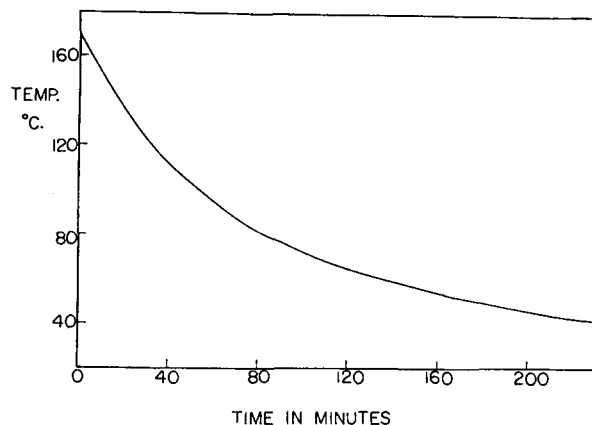


Fig. 1. The standard thermal history of polyethylene samples prepared for stress cracking; temperature in degrees centigrade versus time in minutes.

between two sheets of Teflon of 6 in.<sup>2</sup> backed by brass plates. The Teflon sheets were separated by brass spacers, so that the polyethylene sample would be relatively uniform in thickness. The total pressure was brought up to 70 psi; the polyethylene was brought to an equilibrium temperature of 170°C. and then allowed to cool slowly to room temperature under pressure. The standard cooling curve is shown in Figure 1. A number of experiments were carried out on samples cooled in a manner other than the standard one. Cases in which the standard procedure was not used in sample preparation will be indicated in the text.

The cooled polyethylene sheets were nominally 0.02 in. thick, sometimes varying slightly from this value. These sheets were cut into strips 1/2 in. wide.

The polyethylene strips mentioned were used for measurements of tensile strength, modulus, and stress cracking. In the center of each strip a round circular hole 1/16 in. in diameter was cut with a hardened steel punch. The cutting apparatus was designed to clamp the strip rigidly as the hole was cut. All stress cracking measurements were made on strips with the center hole cut out. Tensile measurements were made on strips with and without the center hole.

The stress cracking test was performed by suspending the strip in the stress cracking medium and by hanging a weight on the sample. The apparatus was so arranged that when the sample broke the weight hit a switch which actuated a pen on a rotating drum recorder. A schematic diagram is shown in Figure 2. As in almost all ultimate strength tests, reproducibility of the individual breaking

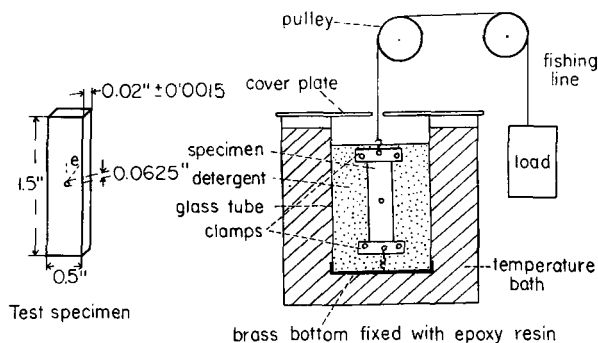


Fig. 2. Schematic diagram of stress cracking apparatus.

times was not good. In order to obtain a numerical value that represented the system fairly well, ten samples were run to obtain a single experimental point. The average of all experiments was taken as the stress cracking time,  $\bar{F}$ . Exceptions to this will be noted.

As was mentioned in a previous paragraph, the actual sample thickness varied slightly from the standard dimension. In all experiments the thickness of the individual samples was determined and the load adjusted so that all samples in a single experiment were at the same stress.

The stress cracking agent in most experiments was a nonionic detergent, Igepal Co-630.\* In some experiments other liquids were used, such as water, cyclohexanol, heptane, *tert*-butyl alcohol, and aqueous solutions of the Igepal. All experiments were conducted in a thermostat controlled to  $\pm 0.02^\circ\text{C}$ . Most experiments were done at  $50^\circ\text{C}$ ., a few at  $60^\circ\text{C}$ .

The tensile strength and modulus of polyethylene is to some extent a function of the rate at which the load is applied, particularly as the temperature is increased. The measurements reported here were done relatively slowly, small increments in the loading being added every five or ten minutes. In general, a complete tensile run took at least two hours. The results of the tensile tests do not change with small variations in the stress-time pattern.

Surface tension measurements on Igepal and Igepal solutions were performed with a Du Nuoy tensiometer. Osmotic pressure determinations were made at  $105^\circ\text{C}$ . with the use of carefully conditioned, regenerated cellulose membranes. The polymer was dissolved in xylene, and a trace of antioxidant was added to the solution, to prevent

\* General Aniline and Dyestuff Co., New York; described as a polyaryllalkyl glycol.

oxidation. The intrinsic viscosities were measured in xylene in a four-bulb Ubbelohde viscometer, and the results were extrapolated to zero shear rate. Kinetic energy corrections were included in the calculation.

Per cent crystallinities were determined by an x-ray method that followed the procedure of Kakudo and Ullman.<sup>9</sup> The densities were measured by mercury displacement, following the procedure recommended by Bekkedahl.<sup>10</sup>

Microscope investigations of stress cracking were made with thinner samples having smaller central holes, and at higher stresses than were used for the experiments in which the breaking times were measured. The polyethylene sheets were observed under crossed polaroids by means of transmitted light. After a number of preliminary trials, the satisfactory sample thickness was found to be 0.003 in. When these sheets were cooled slowly, as in the standard procedure, the spherulites intruded on one another and made observation difficult. Therefore the microscopic samples were cooled relatively rapidly. Higher stresses were applied on the microscope samples so that the stress cracking took place in about thirty minutes instead of several hours or several days. Igepal Co-630 was used as the stress cracking agent and the temperature was kept at about  $50^\circ\text{C}$ ., with variations of  $\pm 3^\circ\text{C}$ .

TABLE I  
Some Physical Properties of Polyethylene Used in This Research

	Alathon 14	Super Dylan 6600	Super Dylan 6200	Super Dylan LMW	Marlex 9
$[\eta]$ in xylene at $106^\circ\text{C}$ .	0.96	1.91		1.08	
Melt index*	2.35	0.97	3.44	7.2	0.82
Osmotic mol. wt.		24,800	17,500	20,800	50,100
Crystallinity, %	55	70			80
Density at $31^\circ\text{C}$ .	0.92		0.954	0.953	0.978
Tensile strength <sup>b</sup>					
* At $50^\circ\text{C}$ .	750	1670		1630	1620
* At $60^\circ\text{C}$ .	575	1420			1280
* At $50^\circ\text{C}$ . very slow cooling					
		1970			

\* Melt index is the grams of polymer flowing through a standard orifice at a standard temperature and pressure. A melt index of unity is supposed to correspond to a melt viscosity of 1,000,000 poises.

<sup>b</sup> Samples prepared with a thermal history shown in Figure 1.

#### D. CHARACTERIZATION OF THE POLYMERS

In Table I a variety of data are given which serve to characterize the samples examined here. In our view these are somewhat incomplete, since the distribution of molecular weights in any given sample is not known, although it may be roughly surmised in a few cases. Also, it should be pointed out that we have some reservations about the correctness of the osmometric results. Osmometry, as has been shown some years ago,<sup>11</sup> is a relatively difficult technique at best, and may give particularly misleading results, particularly when low molecular weight species diffuse through the membrane. There was no serious effort made to determine the extent of diffusion, and since the molecular weight distribution may have been wide, error was likely.

#### E. STRESS PATTERN IN THE POLYETHYLENE SAMPLE

Polyethylene to a first approximation may be treated as an elastic body. The stresses in a sheet under tension with a small circular hole are given by<sup>8</sup>

$$\begin{aligned}\sigma_r &= \frac{S}{2} \left( 1 - \frac{a^2}{r^2} \right) + \left( 1 + \frac{3a^4}{r^4} - \frac{4a^2}{r^2} \right) \cos 2\theta \\ \sigma_\theta &= \frac{S}{2} \left( 1 + \frac{a^2}{r^2} \right) - \frac{S}{2} \left( 1 + \frac{3a^4}{r^4} \right) \cos 2\theta \\ \tau_{r\theta} &= \frac{S}{2} \left( 1 - \frac{3a^4}{r^4} + \frac{2a^2}{r^2} \right) \sin 2\theta\end{aligned}\quad (1)$$

where  $S$  is the tensile stress on the specimen,  $\sigma_r$  the radial tensile stress in the sample,  $\sigma_\theta$  the tensile stress normal to the radius and in the plane of the sample, and  $\tau_{r\theta}$  the shearing stress. The origin of the coordinate system is at the center of the hole. The distance from the center of the hole is  $r$ ;  $\theta$  is measured clockwise from the vertical direction (see Fig. 2);  $a$  is the radius of the hole. At the edge of the hole,  $\sigma_r$  and  $\tau_{r\theta} = 0$  and  $\sigma_\theta = S(1 - 2 \cos 2\theta)$ . Therefore,  $\sigma_\theta = 3S$  at  $\theta = \pi/2$ , which is the maximum stress in the sample. The shearing stress is a maximum at  $\theta = \pi/4$  and  $r = 3a$ ,  $\tau_{r\theta}(3a, \pi/4) = 2/3S$ .

Equation (1) does not describe the real stresses in the sample in the interesting range. First of all, these equations are only valid for sheets of infinite width, although the errors arising from the finite width of the sample are less than 6%.<sup>2</sup> More important is the fact that the elastic limit is exceeded at the points of highest stress in all cases,

and also that the distortion of the circular hole is sufficient to change the stress pattern from the calculated values. The distortion is more pronounced for Alathon 14, and in long-time experiments in which a considerable amount of creep takes place.

The experimental graphs illustrating stress cracking have the stress  $\sigma_\theta(a, \pi/2)$  plotted as ordinate;  $\sigma_\theta(a, \pi/2)$  is the stress on the equator at the edge of the hole in the sample as calculated from eq. (1), and is of the order of the breaking strength of the polymer. The actual load on the sample far from the hole is  $1/3$  of this and, because of plastic flow of the sample at  $(a, \pi/2)$ ,  $\sigma_\theta(a, \pi/2)$  is only a *nominal value*.

The  $1/16$  in. hole is cut from the polyethylene sample to allow application of a complex stress when simply loaded. At the edge of this hole the birefringence is pronounced, since in the very process of cutting the hole some very strong shearing stresses permanently orient the polymer in the neighborhood of the hole. Most experiments were carried out on these cut samples without further annealing. Obviously, it is essential that the deformation of the polymer in the region surrounding this hole be roughly the same for comparable experiments. Every effort was made to insure this by repeatedly checking a standard experiment from time to time.

One of the ways of characterizing two materials in their stress cracking behavior is to compare the stress cracking times at a given stress. This is not entirely satisfactory from our point of view. If one sample, because of its molecular weight or crystalline content, for example, is stronger than another, it would be expected to last longer under the same stress conditions than the first sample. A more nearly appropriate procedure would be to compare the stress cracking times at loads which were equal when taken relative to the ultimate strength of the sample. For that reason tensile strengths and moduli were determined on several polymers (see Table I).

#### F. MICROSCOPIC EXAMINATION

Consider a 0.003 in. thick film of polyethylene with a circular hole 0.5 mm. in diameter, which is viewed under a microscope with crossed polaroids. This sample has been cooled rapidly in preparation so that the spherulites do not intrude on each other very extensively. If a tensile load is applied to the sample, the spherulites are disturbed mostly at an acute angle to the applied stress (see Figs.

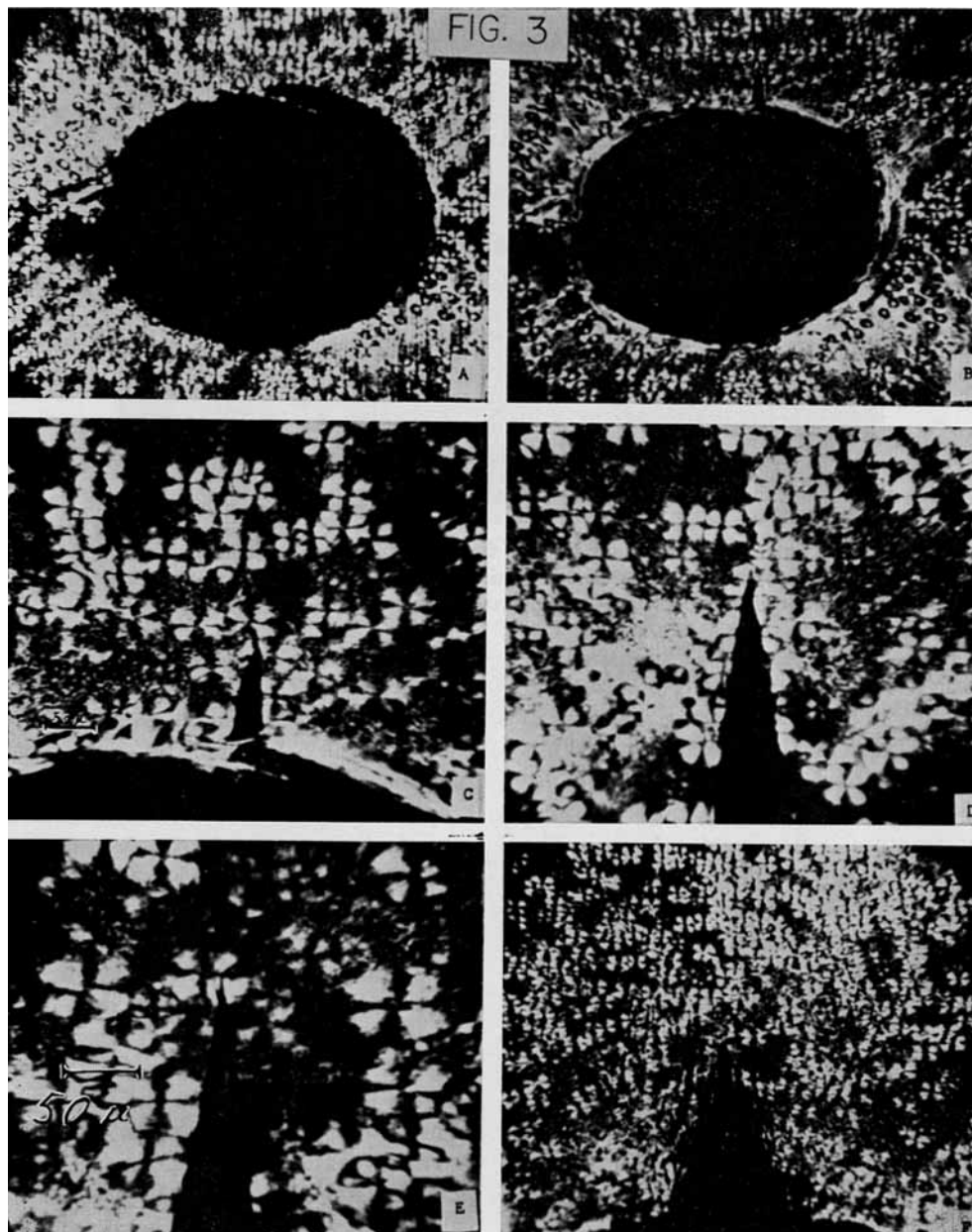


Fig. 3. Photomicrographs of a thin film undergoing fracture while stressed in the presence of Igepal detergent.

3a-f). We infer that this distortion of the spherulites arises from the shearing stress in the sheet. A series of photographs of a sample are shown in Figures 3a-f at various stages of the breaking process in the presence of the Igepal detergent. The crack is initiated at  $\theta = \pi/2$  at the edge of the hole near a flaw in the sample. The crack does not propagate in a perfectly straight line, but moves in an irregular though directed path. The spherulites in the path of the propagating crack are split, primarily along radial lines. The edges of the

crack are sharp, characteristic of brittle fracture. This is in contrast to what is observed when no Igepal is present. Breakage in the absence of Igepal occurs at higher stresses and is accompanied by cold drawing of the polymer. The broken edges have a very different appearance from that of the stress-cracked material.

#### G. GENERAL OBSERVATIONS

Three different types of cracking under stress are shown in Figure 4. The sample in 4b is in the



Fig. 4. Photograph of samples on the verge of fracture under stress cracking conditions: *left*, a linear polymer with *n*-heptane as the stress cracking agent, *middle*, a linear polymer, Super Dylan 6600, with Igepal; *right*, a branched polymer, Alathon 14, in Igepal.

process of being broken in the presence of a swelling agent, *n*-heptane. This is not stress cracking in the sense that the term has been used here. What has occurred is that the polyethylene is swollen by heptane, its mechanical strength falls off and, consequently, fracture is imminent. Note in the photograph that the imbibition of heptane covers a wide region. The effect on the strength is most prominent along the equatorial lines where the stresses are at a maximum.

In Figure 4a a picture of a sample of linear polyethylene which has begun to stress-crack is shown. The crack grows along the equator and extends until the circle separates into two approximately equal parts, the point of the crack moving toward the edges of the sample along the equatorial line. The area on which the load is supported continues to decrease as the crack grows, until the sample can no longer bear the stress and failure occurs.

Figure 4c shows an example of a highly branched polyethylene sample in the process of breaking. The characteristics of the breaking geometry are entirely different from those of the linear polymer. The break occurs along lines where the shearing stress is relatively large, and it would appear that failure occurs in a different way from that observed in linear polyethylene. It should be mentioned that while all samples of linear polymer exhibit the same features in stress cracking as those shown in Figure 4a, the branched polymer is somewhat erratic in this respect. The sample often tears

more irregularly than shown in Figure 4c, although these tears do occur at an angle of 45 to 60° from the vertical. Another difference between the branched (Alathon 14) and unbranched polyethylenes is that the branched material stretches to a markedly greater extent. As a consequence, the hole cut in the sample is appreciably deformed and the stress  $\sigma_{\theta}(a, \pi/2)$  is substantially reduced. The ratio of the tensile to shear stress in the branched polyethylene is much lower than calculated, and much lower than for the linear polymer. This may, in part, account for the fact that the branched polymer fails when the shear stresses are high whereas the linear polymer fails at or near the point of maximal normal tension.

The breaking patterns of branched and linear polyethylene, as seen in Figures 4a and 4c, are substantially different. The reason for this difference may be partly understood by examining Figure 3. Here it is seen that the spherulite structure is disturbed in regions in which the shearing stresses are high. This presumably weakens the material and creates a favorable path for the growth of cracks in the sample. Branched and linear pressure polymers differ in that the branched sample is more easily distorted. In the slowly cooled linear polyethylene, the intrusion of spherulites one on another does not permit the extensive disruption which occurs in the rapidly cooled material observed under the microscope or in the relatively low-crystalline branched polymer.

A very striking feature of Figure 4b is the whiten-

ing which shows up in the photograph of the region under greatest stress. The whitening shows where the polymer was more highly swollen with heptane. It is a characteristic property of many materials that tension tends to increase solubility, and this is shown very clearly here.

This broad white halo does not show up when Igepal is used as an environmental agent (see Figs. 4a and 4c), since Igepal is not an effective swelling agent for polyethylene. In one experiment a sample of linear polyethylene was heated well above the melting point and vigorously agitated in a container filled with Igepal. After cooling, the polyethylene was removed from the Igepal, the surface washed, and a small sample tested for Igepal, with the use of an infrared spectrometer (Perkin-Elmer Model 21). No Igepal was detected, indicating a maximum concentration of approximately 0.01% in the polyethylene. Some experiments on presoaking led to equivocal results, which did not show whether or not a significant quantity of Igepal dissolved in the polymer.

#### H. REPRODUCIBILITY OF RESULTS

The difficulty of reproducing an ultimate strength test is a common problem, and is dealt with, in general, by repeating the test on a number of samples, as was done here. Consider the results of two experiments yielding two different values of  $\bar{F}$  ( $\bar{F}$  is the mean time of breaking of a set of samples). The question that must be answered is, "Does the difference between the  $\bar{F}$ 's reflect a change in experimental conditions, or is this merely a statistical error?" This can be answered in two parts. First of all, let us assume that an experiment with one set of ten samples is identical in every respect with an experiment with a second set of ten samples. The probability of reproducibility can be easily calculated. The standard deviation of the mean,  $\sigma_m^2 = (\bar{F} - \bar{F})^2/[n(n-1)]$  has been found to vary with applied stress but is generally less than 5% of  $\bar{F}$  in these studies. The probability of a chance variation of 15% in  $\bar{F}$  is considerably less than one in a hundred. For any particular experiment,  $\sigma_m$  can be calculated and this can be precisely evaluated. See, for example, some results in Table II. However, other more serious difficulties arise in the preparation of the materials and in the control of the sample-cutting procedure and, consequently, a particular experiment is not always precisely reproduced. At one time a variation arose because the tool used for cutting the center

hole in the sample was dull. This was discovered by repeating a standard experiment and noticing that the value had changed from an earlier result. Replacing the cutting tool solved the problem. The difference in results, while substantial, was not indicated by visual inspection of the improperly cut polyethylene samples, which appeared to be the same as the standard material.

TABLE II

Expt. no.	Polymer	Expt. cond. <sup>b</sup>	$\bar{F}$	$\sigma_m$	100 ( $\sigma_m/\bar{F}$ )
83	SD 6600	10% Igepal	441	20	4.5
93	SD 6600	Cyclohexanol	743	66	8.9
99	SD 6600	Heptane	93	4	4.3
103	SD 6600	7 days presoak- ing, 100% Igepal	359	15	4.2
108	Al 14	0.3% Igepal	882	43	4.9
120	SD 6600	100% Igepal	390	25	6.4

<sup>a</sup> SD is Super Dylan; Al is Alathon.

<sup>b</sup> The load  $\sigma(a, \pi/2) = 2750$  psi, except in Expt. 108, where  $\sigma(a, \pi/2) = 1100$  psi.

A number of experiments were conducted which showed that the stress breaking times were very sensitive to the rate of cooling of the polymer sheets; see Table III. It is not certain that the control of the standard cooling procedure was made carefully enough to avoid introducing differences between batches of polymer. A serious aspect of this problem is that the need for very precise control only became apparent toward the end of the investigation. One standard experiment was repeated a number of times at intervals; results are listed in Table IV. Note that the discrepancy in  $\bar{F}$  between 120 and the others is too

TABLE III<sup>a</sup>

$T_i$ , °C.	$T_f$ , °C.	Rate of cooling	$\bar{F}$ , min.	Remarks
150	-80	Quenched, solid CO <sub>2</sub> and acetone	220	Polymer sheet, soft
"	20-25	Quenched, water	230	Polymer sheet, soft
"	"	Fig. 1 curve	390	
"	"	10°/hr.	550	
175	"	10°/hr.	650	
150	"	6°/hr.	580	Polymer sheet, brittle

<sup>a</sup>  $T_i$  is the temperature to which the sample was heated before cooling;  $T_f$  is the final temperature of the cooled sample; the applied stress was the same in all cases.

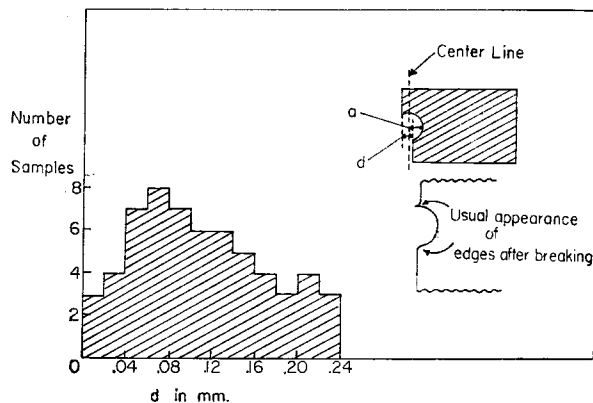


Fig. 5. A histogram showing the deviation of the point of fracture from the equatorial line of a series of stress-cracked samples of Super Dylan 6600.

large to be purely random. We attribute this to an accidental variation in sample preparation.

Superficially, it appeared from our results that the failure of the low-pressure polyethylene took place along the equatorial line. Careful observation of large numbers of broken samples shows that breakage generally occurs slightly off the line. The question arose whether this deviation is due to a random distribution of flaws or whether there is a tendency for the break to occur in a region in which some shearing effects weaken the structure. From eqs. (1) it can be seen that there is no shear along the equator ( $\tau_{r\theta}(r, \pi/2) = 0$ ). A histogram showing the deviations of the breaking point from the equator on a number of samples of Super Dylan 6600 is shown in Figure 5. If the shearing effect were negligible, the number of samples breaking at a given portion of the circumference of the circle would approach a maximum at the equator. This is not so, and the systematic deviations shown in Figure 5 may arise because of the small shearing stress required to initiate fractures.

#### I. MOLECULAR WEIGHT AND STRESS CRACKING

In Figure 6, the stress cracking times of three Ziegler-type polyethylene samples are shown as a function of stress. These results confirm the previously reported result that stress cracking is more severe the lower the molecular weight of the polyethylene. The general shape of the dependence of breaking time on load is about the same for these samples. The higher molecular weight polymer resists stress cracking for a longer time at a given load. Otherwise, there are no features which distinguish one curve from another.

One set of experiments was conducted on Super

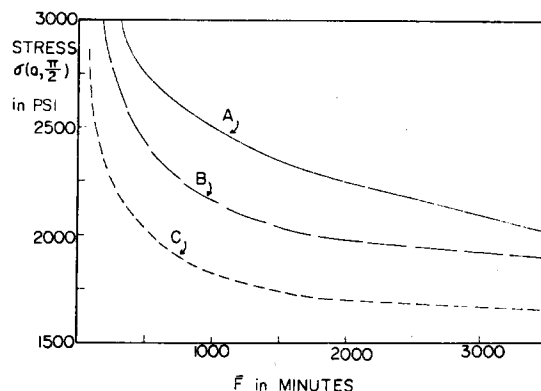


Fig. 6. Stress versus breaking time in Igepal of three linear Ziegler-type polyethylene samples: A, Super Dylan 6600; B, Super Dylan 6200; C, Super Dylan LMW.

Dylan 6600 from which much of the lowest molecular weight polymer had been removed. The procedure was the following. The polymer was dissolved in hot xylene and allowed to cool to room temperature. The solid polymer was washed with a little xylene and then dried in a vacuum oven at 40°C. for 4 days. No odor of xylene was present after drying. The polymer samples were fabricated in the usual way and tested under standard conditions.  $\bar{F}$  was found to be equal to 648 which may be compared with  $\bar{F} = 490$  obtained for the standard material.

#### J. TEMPERATURE AND STRESS CRACKING

A few stress cracking experiments were carried out at 60°C. instead of at 50°C. As the temperature was increased, the breaking time decreased at a given load, but otherwise the general appearance of the curves was unchanged. This is shown in Figure 7. If the stresses are normalized—that is, if the ordinate is the stress divided by the tensile strength at the temperature of measurement—the similarity between curves is much more striking. This also is shown in Figure 7. The difference between curves A and C, and D and F, respectively, probably arise from errors in the normalization procedure.

#### K. CRYSTALLINITY AND STRESS CRACKING

In Figure 8 the dependence of  $\bar{F}$  on stress is shown for three samples of polyethylene of varying crystallinity. The interesting thing in these graphs is not the magnitude of the stress at which stress cracking takes place at a given time, but rather the difference in the shape of the curves. The results



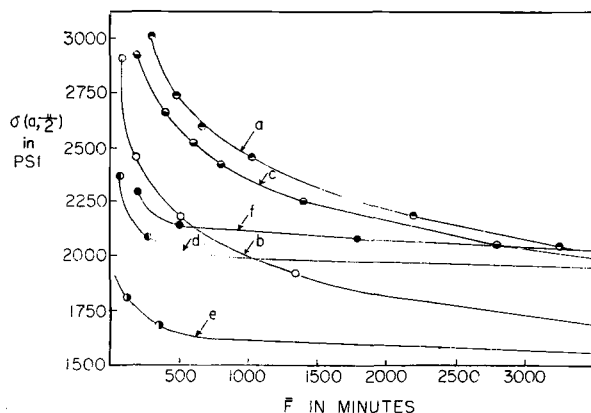


Fig. 7. Stress versus breaking time for a linear and branched polyethylene at 50 and 60°C. in Igepal. Curves *c* and *f* are curves calculated at 50°C. from the 60°C. data by correcting for the reduction in ultimate strength. The ultimate-strength data were taken from Table I. The calculated stress at 50°C. is obtained by multiplying the measured stress at 60°C. by the fraction, tensile strength at 50°C. divided by tensile strength at 60°C.: *a*, Super Dylan 6600 at 50°C.; *b*, Super Dylan 6600 at 60°C.; *c*, Super Dylan 6600 at 50°C. calculated; *d*, Alathon 14 at 50°C.; *e*, Alathon 14 at 60°C.; *f*, Alathon 14 at 50°C. calculated. The ordinate reads  $\sigma(a, \pi/2)$  for the linear polyethylene and  $\sigma(a, \pi/2) + 1000$  for Alathon.

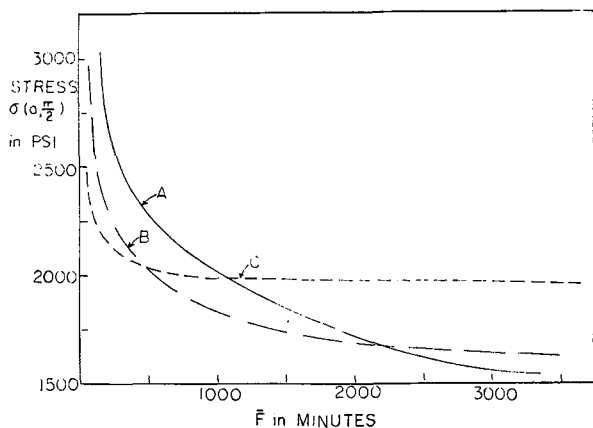


Fig. 8. Stress versus breaking time in Igepal of three different types of polyethylene: *A*, Marlex; *B*, Super Dylan LMW; *C*, Alathon 14. The ordinate reads  $\sigma(a, \pi/2)$  for the linear polyethylene and  $\sigma(a, \pi/2) + 1000$  for Alathon.

for Alathon 14 indicate that stress cracking stops suddenly below a certain load, while at the other extreme the Marlex 9 curve shows no such tendency to flatten out. In the latter case, as the stress is decreased, stress cracking still occurs, but at longer and longer times. The Super Dylan material which is intermediate in crystallinity but more nearly like Marlex 9 than Alathon 14, is intermediate as far as the stress-breaking time pattern is concerned.

## I. STRESS CRACKING AGENT AND BREAKING TIME

The effect of changes in the environment on stress cracking was studied under standard conditions. This experiment was motivated in part by the idea that a simple correlation between surface tension and stress cracking might be found. The results in Table V show quite clearly that no such correlation exists. The result for *n*-heptane arises from the fact that it swells polyethylene, as was shown in Figure 4b.

TABLE IV<sup>a</sup>

Expt. no.	$\bar{F}$
4	473
5	495
6	523
7	475
8	483
24	480
27	510
120	390

<sup>a</sup>  $\bar{F}_{av} = 491$ ;  $\sigma_m = 19$ ;  $\sigma(a, \pi/2) = 2750$  psi. The average quantity  $\bar{F}_{av}$  was obtained from the data in this table, experiment 120 being omitted. The standard deviation,  $\sigma_m$ , was obtained from the same data.

TABLE V

Effect of Various Environments on Super Dylan 6600<sup>a</sup>

Environment	$\gamma$ , dynes/cm.	$\bar{F}$ , min.
<i>tert</i> -Butanol	19.46	723
<i>n</i> -Heptane	20.60	93
Mineral oil	29.72	1093
Cyclohexanol	32.88	740
Igepal	34.03	480
Water	71.18	Did not break

<sup>a</sup>  $\sigma(a, \pi/2) = 2750$  psi.

If water is used as a stress cracking agent under standard conditions, no breaking takes place in a week or more. However, in some of our experiments with water as the environment, the polymer samples did break. In these cases the surface tension of the water was measured after breaking and found to be substantially lower than that of pure water. This lowering of the surface tension was due to the presence of Igepal Co-630, or small traces of soap, or perhaps droplets of oil from the oil thermostat in which the experiments were conducted. When the surface tension of the water was determined in cases in which no stress cracking took place, either it was unchanged or it was higher than in cases of stress cracking. Water seems not to be a stress cracking agent for polyethylene unless some impurity is present.

Once Igepal was used for stress cracking in a container it was never possible to remove all traces of it. The only way to obtain reproducible results in the water experiment was to make up a new set of tubes that had not been in contact with the detergent.

### M. IGEPAL SOLUTIONS AND STRESS CRACKING

An extended series of tests was conducted with the use of solutions of Igepal as the environmental agent. The results are a little difficult to interpret since the concentration of the detergent in solution changes with time because of the sorption of the detergent by the polymer and the container. For example, in Table VI the measured surface tensions of an Igepal solution at the beginning and end of an experiment are given. This was an experiment carried out in an Igepal solution of 1 part in 100,000. The data do not yield the amount of Igepal sorbed by the polymer, because the actual initial concentration of the solution was increased by initial desorption of Igepal from the surface of the container. Nevertheless, the Igepal solution does decrease in concentration during the experiment. While it follows that the polymer will sorb more Igepal from solutions of higher concentration, how much more and how this depends on time are not known.

TABLE VI

The Surface Tension of an Igepal Solution before Sorption by Polyethylene and after Sorption by Polyethylene

$\gamma$ (initial), dynes/cm.	$\gamma$ (final)
36.9	40.3
"	41.9
"	41.9
"	40.7
"	39.6
"	37.7
"	40.2
"	40.4
"	39.0
"	40.7

A plot of breaking time versus log per cent detergent for Super Dylan 6600 and Alathon 14 is shown in Figure 9. Stress cracking is more rapid in the high-concentration Igepal solutions and in the pure Igepal. However, the surface tension in solutions of low concentration is less than that of pure Igepal. This is further evidence that surface

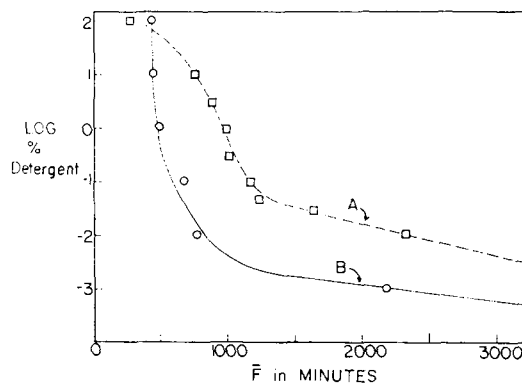


Fig. 9. Stress cracking time: (A) Alathon 14 and (B) Super Dylan 6600 in solutions of Igepal.

tension is not of itself an important factor in environmental stress cracking.

It had been expected that the break in the surface tension concentration curve of aqueous Igepal solutions would correspond to a sudden change in stress cracking time. This is not so for the Alathon samples, and is questionable for the Super Dylan 6600 material. The experiments suffer from the fact that the adsorption of Igepal on the surface is considerable; consequently, the concentration and therefore the surface tension change with time. To put this another way, the ordinate in Figure 9 represents the per cent detergent at the beginning of the stress cracking experiment, but what is really wanted is the per cent of detergent throughout the experiment. The decrease in detergent in the solution would correspond to a lowering of the ordinate in Figure 9. This tends to bring the results in correspondence with expectation, but the dependence of concentration (surface tension) on time hopelessly complicates the analysis. The interfacial tension between polymer and detergent solution would have been a better index than surface tension for this sort of comparison if, indeed, a correlation existed.

### N. THERMAL TREATMENT AND STRESS CRACKING

The stress cracking of polyethylene varies radically with the rate of cooling of the polyethylene during fabrication. Some results of experiments using Super Dylan 6600 are shown in Table VII. All these samples are highly crystalline, but the percentage crystallinity and, particularly, the size of the individual crystallites is smaller in the rapidly cooled sheets. Large spherulites are rigid bodies and if the sample is cooled slowly, these large spherulites are formed and the polymer sheet is

TABLE VII  
 Presoaking Experiments<sup>a</sup>

Expt. no.	Polymer <sup>b</sup>	Presoaking time	Presoaking conditions	$\bar{F}$	Remarks
120	SD 6600	None	—	390	
129	"	None	—	408	
131	"	None		405	
103	"	7 days at 50°C.	No hole, no load	360	
127	"	8 days at 50°C.	" "	440	
130	"	4 mos. at 50°C.	" "	568	
128	"	7 days at 50°C.	With hole, no load	280	
121	"	24 hrs. at 50°C.	" loaded, $\sigma(a, \pi/2) = 1370$ psi	328	
116	"	14 days at 50°C.	No hole, no load	No stress crack- ing	Full load applied in air; no stress cracking agent used.
133	"	None		275	Hole cut in center of sheet and kept in vacuum at 50°C. for 10 days before stress cracking was measured.
51	Marlex 9	None		218	
132	"	120 days at 50°C.	No hole, no load	301	

<sup>a</sup> The experiments were carried out using Igepal Co-360 as fluid in which sample was soaked and as stress cracking agents.

<sup>b</sup> SD is Super Dylan.

more brittle. The quenched samples are much softer. The results show that the slower the cooling rate, the longer is the stress cracking time.

In the standard procedure of sample preparation, the small hole in the center of the sheet was cut after the sample was annealed. The polyethylene at the boundary of the hole was sheared in cutting and oriented in part, as could be seen by viewing the sample under the microscope. In one experiment, the samples were annealed at 50°C. for 10 days under vacuum after the hole was cut. The annealing caused recrystallization at the surface, and introduced irregularities at the edge of the circular hole. These geometric irregularities obviously distort the calculated stress pattern, and in a way which is not reproducible from sample to sample. The lack of reproducibility in geometry was a primary reason for not using a postannealing procedure in sample preparation. The results on the annealed samples showed an  $\bar{F}$  of 275 as compared with 400 or higher for the unannealed material.

One experiment was carried out on some samples of Marlex 9 which had been strongly oriented in the direction of the applied stress. Stress cracking did not occur after several days. The stress was increased repeatedly until the sample began to creep, but no signs of a stress cracking phenomenon were observed at any time.

#### O. PRESOAK CONDITIONS

It had occurred to us that if the stress cracking liquid were allowed to permeate the polymer sample for a while before the stress was applied, the breaking conditions might be influenced. Accordingly, a number of experiments were conducted, the results of which are summarized in Table VII. The results are complex because several factors intervene simultaneously. In those cases in which the sample is soaked for a long time, an annealing takes place which, as was shown earlier (Table III), brings about an increase in stress cracking times. In cases in which a hole is cut in the sample before soaking, the exposure of the sample to the stress cracking agent is better. On the other hand, any annealing which takes place produces irregularities that concentrate the stress. These irregularities may also reduce the stress cracking time.

Because of these complications, we are reluctant to draw any conclusions about the effect of presoaking. It is not certain that the apparent changes are not artifacts.

#### DISCUSSION

Environmental stress cracking is a general phenomenon which takes place in amorphous and crystalline materials. Any explanation of our experiments must take this into account, although

it is not to be supposed that the unique properties of polymeric materials may be neglected.

Griffith's theory of fracture<sup>15</sup> is formulated in terms of the stress at the apex of a crack in a material. The work supplied by the applied force plus the decrease in the elastic energy in the stressed material upon fracture is converted into the surface energy of the fractured faces. The formula for the tensile stress required to propagate a crack of length  $c$  is given by

$$p \approx \sqrt{\frac{E\gamma}{c}} \quad (2)$$

$p$  being the stress,  $E$  Young's modulus, and  $\gamma$  the effective surface energy per unit area. The surface energy calculated by this formula is several orders of magnitude higher than the true surface energy, presumably because much of the energy is liberated as heat not specifically accounted for in this theory. However, before fracture occurs, the work goes into elastic energy plus surface separation and, at the point of breaking, the above relationship describes fracture of an elastic material. It should be noted that a reduction of the surface energy by an environmental agent would, according to the formula, reduce the stress required to rupture.

The mechanism proposed by Griffith does not take into account flow processes which occur in many materials. Some sort of plastic deformation is required before fracture occurs in most cases. Plastic deformation in crystalline solids usually follows certain lines of dislocation in the crystal lattice, and has been described elsewhere in considerable detail.<sup>16</sup> The fracture of crystalline solids takes place only after an accumulation of dislocations leads to the formation of micro cracks<sup>17-19</sup> which later propagate and cause rupture. These theories of fracture, which will not be enumerated here except as they apply to the particular problem, lead to formulae containing a term in the breaking stress proportional to the square root of the surface energy, as in eq. 2. Therefore, one should expect that, in so far as these theories explain fracture, an environmental agent which reduces the surface energy will reduce the load at which fracture takes place.

Environmental stress cracking takes place after a certain length of time: the lower the stress, the longer the time. The time factor arises from two sources. First, plastic deformation takes place over a period of time and, second, it may take some

time for the environmental agent to penetrate the micro cracks from which the ultimate fracture is initiated. Presumably, these factors could be separated by carrying through experiments at different loads, leading to fracture in the presence and absence of stress cracking agent. If the dependence on time were the same in both cases, one would assume that plastic deformation was the controlling factor. If the times were different because the accessibility of environmental agent to the micro cracks was rate determining, different time patterns would be found.

Polyethylene exhibits brittle fracture when broken in the presence of a stress cracking agent, while in the absence of the agent fracture takes place because of cold drawing (described as ductile). The ductile fracture is associated with substantial polymer orientation and a general breakdown of the secondary spherulitic structure in and near the neighborhood of the break. In brittle fracture, the secondary structure is substantially preserved. Both mechanisms can operate; brittle fracture of polyethylene in the absence of a surface-active liquid generally requires a higher stress than ductile fracture and therefore is not observed. The presence of a stress cracking agent lowers the threshold of the brittle mechanism sufficiently for it to become operative. The ductile mechanism is associated with a lower degree of crystallinity and with smaller crystallites. If linear polyethylene is annealed for a long time, larger crystallites are formed and brittle fracture takes place under stress even when no environmental agent is used.

It has been found in investigations of environmental stress cracking of metals that both normal and shear stresses are important in causing fracture.<sup>20,21</sup> The piling up of lattice dislocations at a grain boundary and their combining to form micro cracks occur upon application of shearing stresses, while the normal stresses exerted perpendicular to the plane of the micro crack cause the ultimate rupture.

The experiments on Alathon 14 led to fracture after much creep in the areas where shearing stresses were large. In this case, large plastic deformation led to rupture along the lines where one would expect plastic flow to be greatest. The crystalline formations of the Marlex and Super Dylan polyethylenes prohibit extensive plastic flow, and rupture takes place on application of the normal stresses. It is conceivable, but by no means certain, that the deviations of the fracture

surface from the equatorial line shown in Figure 5 are associated with shearing stresses required to initiate cracks in the sample.

The solutions of Igepal cause stress cracking, as does pure Igepal, because the concentration of Igepal at the polyethylene interface is in all probability very high except at very low Igepal solution concentration, the stress cracking time being relatively insensitive to concentration of the Igepal solution over a very wide range (Fig. 9).

The breaking time of a given polymer in different stress cracking agents is not dependent on surface tension alone but also is related to solubilization of the cracking agent (see Table V). This solubilization permits the migration of the stress cracking fluid to regions of incipient fracture, and is enhanced when the sample is under tension. The strength of the solid is obviously lower when partially swollen with a fluid.

The increased solubility of a material under tension can be shown by the following argument. The chemical potential of the stress cracking agent will be denoted by  $\mu_e$ . Consider a two-phase system in equilibrium the liquid stress cracking agent surrounding the polymer sample, and the polymer sample containing some quantity of the stress cracking fluid. The chemical potential is the same in both phases. If a force  $dF$  is applied to the polymer, the change in  $\mu_e$  may be written

$$\frac{d\mu_e}{dF} = \left(\frac{\partial\mu_e}{\partial F}\right)_{n_e} + \left(\frac{\partial\mu_e}{\partial n_e}\right)_F \frac{dn_e}{dF} = 0 \quad (3)$$

where  $\partial\mu$  is concentration of the stress cracking agent in the polymer;  $\mu_e$  does not change in the polymer because it must remain equal to  $\mu$ , in the surrounding fluid. If the force applied is small, the derivatives are essentially constant and by integration one obtains

$$\Delta n_e = - \left(\frac{\partial\mu_e}{\partial F}\right)_{n_e} / \left(\frac{\partial\mu_e}{\partial n_e}\right)_F \Delta F \quad (4)$$

An increment in free energy for the polymer sample may be written

$$dG = VdP - SdT + FdL + \mu_e dn_e + \mu_p dn_p \quad (5a)$$

$$\text{or} \quad d(G - FL) = VdP - SdT - LdF + \mu_e dn_e + \mu_p dn_p \quad (5b)$$

where the subscript  $p$  refers to polymer and  $L$  is length. From the cross derivatives in Equation 5b one can write

$$\left(\frac{\partial L}{\partial n_e}\right)_F = - \left(\frac{\partial\mu_e}{\partial F}\right)_{n_e} \quad (6)$$

Substituting eq. (6) into eq. (4) leads to the result:

$$\Delta n_e = \left(\frac{\partial L}{\partial\mu_e}\right)_F \Delta F \quad (7)$$

From swelling experiments on gels, it is known that  $\partial L/\partial\mu_e$  is positive, and therefore  $\Delta n_e$  is also positive. This demonstrates that application of an external stress increases the amount of stress cracking agent sorbed by the polymer.

The data obtained by us show that stress cracking is less severe for polyethylene of higher molecular weight. The single experiment on a polymer with the very low molecular weight fraction removed showed a slight improvement in stress cracking behavior, and on the basis of this we will assume provisionally that the molecular weight effect cannot be ascribed to the very low molecular weight material alone.

The molecular weight dependence of stress cracking might arise from the following factors.

1. A single polymer molecule may extend through several crystallites. The higher the molecular weight, the greater the number of carbon-carbon bonds to be broken before fracture. Breaking a carbon-carbon bond requires large quantities of energy, and therefore fracture, especially following plastic deformation along selected crystallographic directions, is less likely in materials of higher molecular weight.

2. The crystallite size for a high molecular weight polymer is smaller than for a low molecular weight material prepared according to the same time-temperature pattern. Brittle-type fracture, as a rule, is associated with larger crystallites, and this may be a supporting factor.

The authors regard the foregoing discussion as speculative. It has the virtue of being consistent with the data on the environmental stress cracking of polyethylene as well as general fracture processes and other examples of environmental stress cracking. Modifications and extensions depend, in part at least, on further experimentation.

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### Synopsis

The stress cracking of polyethylene was studied under various experimental conditions, and the importance of the effect of both crystallinity and molecular weight of the poly-

mer was established. Many of the variables were investigated, such as the thermal pretreatment of the sample, temperature of the sample, surface tension, and concentration of the stress-cracking agent, and the magnitude of the stress. The importance of this test procedure and the relationship that exists between the stress cracking of polymers and between similar problems affecting nonpolymeric systems have been analyzed. Some microscopic studies of stress cracking have also been made.

### Résumé

On a étudié la rupture sous tension du polyéthylène dans diverses conditions expérimentales. On a établi l'importance de la cristallinité et du poids moléculaire du polymère. On traite de plusieurs variables, telles que l'histoire thermique de l'échantillon, la température de mesure, la tension superficielle de l'agent de rupture sous tension, sa concentration et la grandeur de la force. L'importance de ce procédé d'analyse et la relation entre la rupture sous tension ont été généralisées pour les mêmes problèmes à des systèmes non-polymériques. On a également présenté des études microscopiques de la rupture sous tension.

### Zusammenfassung

Die milieubedingte Bildung von Spannungsrissen in Polyäthylen wurde unter verschiedenen experimentellen Bedingungen untersucht. Die Bedeutung des Einflusses der Kristallinität und des Molekulargewichts des Polymeren wurde sichergestellt. Viele der Variablen, wie die thermische Vorbehandlung der Probe, Messtemperatur, Oberflächenspannung und Konzentration des bei der Spannungsrissbildung einwirkenden Stoffes und die Gross der Spannung wurden behandelt. Die Bedeutung des Testvorganges und die Beziehung der Spannungsrissbildung bei Polymeren zu den gleichen Problemen bei nichtpolymeren Systemen werden diskutiert. Einige mikroskopische Untersuchungen der Spannungsrissbildung wurden ebenfalls durchgeführt.

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